The German Contribution to the WMO GAW Programme:
Upon the 225th Anniversary of GAW Hohenpeissenberg Observatory
No. 167

Monitoring and Research of Climate, Weather & Environmental Change

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Edited by Wolfgang Fricke, Leonard A. Barrie and Ruprecht Schleyer
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1. Introduction

The atmosphere, like the other components of the Earth system, is affected by the continuous increase in human population and activity, which have resulted in a variety of remarkable changes since the industrial revolution of the 19th century (IGACO, 1994). Among these are:

- The increase in greenhouse gases and aerosols in the atmosphere and associated weather and climate change.
- The global decrease in stratospheric ozone and the attendant increase in surface ultraviolet radiation affecting human health and ecosystems.
- The occurrence of summer smog over most cities in the world, including the developing countries, and the increased ozone background in the northern troposphere.
- The increase in fine particles in regions of industrial development and population growth with an attendant reduction in visibility and an increase in human health effects.
- Acid rain and the eutrophication of surface waters and other natural ecosystems by enhanced atmospheric deposition of nutrients.
- Enhanced aerosol and photo-oxidant levels due to biomass burning and other agricultural activity.
- The long range transport of air pollution to regions far from the industrial activity.

Many of these changes in atmospheric composition have socio-economic consequences affecting weather, climate, human and ecosystem health, water supply and quality, and agricultural production. A variety of abatement measures have been introduced or are being considered under international conventions coordinating actions at the regional and national level. However, continued growth in human activities to expand economies and to alleviate poverty, will ensure that these effects continue to be important for the foreseeable future and will require information for sound policy making.

The Members of the World Meteorological Organization (WMO) have long recognized the importance of atmospheric chemistry in weather and climate processes. In 1989, it was given particular emphasis when the Global Atmosphere Watch (GAW) Programme was established by the Executive Council (EC XLI, 1989) merging two long-term monitoring programmes that dated back to the 1970s or earlier: the Global Ozone Observing System (GOOS) and the Background Air Pollution Monitoring Network (BAPMoN). The Commission for Atmospheric Science (CAS X, 1990) supported this decision emphasizing that “a fundamental concept of GAW was that atmospheric composition observations must be given the same importance as that given to the classical meteorological parameters such as temperature, wind and precipitation”. WMO Congress subsequently endorsed GAW in 1991(CG XI, 1991) and GAW Technical Regulations were developed and approved in 1992 (EC XLIV, 1992). Since that time GAW has evolved into a leading programme in the WMO integrated global observing system.

The current GAW programme is described in detail in the Strategic Implementation Plan: 2001-2007 (Strategic Plan, 2001; Strategic Plan Addendum, 2004). Supported by facilities and a partnership of managers, scientists and technical expertise from 80 countries, it is coordinated by
the WMO Secretariat in Geneva and the Open Programme Area Group of experts on Environmental Pollution and Atmospheric Chemistry (OPAG-EPAC) of the WMO Commission for Atmospheric Science (CAS). This Strategic Implementation Plan: 2001-2007 notes that the rationale of GAW is driven by the need to:

- Understand the complex mechanisms with respect to natural and anthropogenic atmospheric change.
- Improve the understanding of interactions between the atmosphere, ocean and biosphere.
- Provide reliable scientific data and information for national and international policy makers.

and hence, its mission is to:

1. Make reliable, comprehensive observations of the chemical composition and selected physical characteristics of the atmosphere on global and regional scales.
2. Provide the scientific community with the means to predict future atmospheric states.
3. Organize assessments in support of formulating environmental policy.

Since 1989, GAW has become a leader in quality assurance of global atmospheric composition observations, a key player in major international science assessments, a steward of co-ordinated global air chemistry monitoring networks and a developer of enhanced intellectual and technological capabilities related to air pollution observations and modelling in developing parts of the world.

The WMO/GAW office and leaders of its Scientific Advisory Groups (SAGs) have been actively involved in supporting the United Nations Framework Convention on Climate Change (UNFCCC) through contributions to the Strategic Implementation Plan of the Second Report on the Adequacy of the Global Observing Systems for Climate by the Global Climate Observing Strategy (GCOS). Essential Climate Variables (ECVs) that need to be systematically measured globally in order to address major issues are officially recognized and include greenhouse gases, ozone and aerosols. GAW is designated as the lead international programme in furthering the observational requirements.

In addition to addressing climate applications, the GAW community is responding to the increasing demand by numerical weather prediction research and operations for support in adding aerosols, ozone and their gaseous precursors to research and operational forecasting. It is recognized that the inclusion of chemical variables not only adds air quality forecasts and climate-forcing analyses to the products and services of meteorological services but also, through feedback on direct and indirect radiative forcing and precipitation formation, influence the accuracy and usefulness of a traditional weather forecast.

The next generation GAW (2008-2015) will follow the mandate from WMO Members and lead the coordination of an international integrated global atmospheric chemistry observing system. It will also respond to the needs and clearly link to the plans of international observing projects/systems/strategies (e.g. GCOS, IGOS, GEO) and of atmospheric process research (i.e. national, regional and international such as the IGAC, SOLAS and ILEAPS projects of IGBP and the regional projects (GEMS, ACCENT, EUSAAR, SCOUT and GEOMON of the European Commission). The Strategic Implementation Plan: 2008-2015 will build on the successes of past activities while recognizing changes afforded by technological advances and the shifting capabilities of WMO members and partners.

The GAW programme has a framework strategy upon which to build, namely, the Theme Report of the International Global Observing Strategy (IGOS) on Integrated Global Atmospheric Chemistry Observations (IGACO, 1994). IGOS is a partnership of international organizations concerned with global environmental issues and ways to better harness observations in addressing them. An international panel of experts and reviewers led by WMO and the European Space Agency produced IGACO. The Theme Report IGACO confirms the importance of GAW and contains guidance/recommendations on how to proceed to deliver services and products through
integration of global air chemistry observations. IGACO provides a blueprint for the next generation GAW activities and WMO is the designated lead in the implementation.

Taking into account the IGACO strategy, the next generation GAW will promote the application of atmospheric chemistry to:

- Reduce societal environmental risk and meet the requirements of environmental Conventions.
- Strengthen capabilities to predict climate, weather and air quality.
- To contribute to scientific assessments in support of environmental policy.

through

1. Maintaining and applying global, long-term observations of the chemical composition and selected physical characteristics of the atmosphere.
2. Emphasising quality assurance and quality control.
3. Delivering integrated products and services of relevance to user needs.

The changes in the rationale and thrust between the current GAW programme and the next generation programme (2008-2015) are subtle but nonetheless significant. While continuing to deliver excellent surface-based observations and support of scientific assessments and conventions, there will be more emphasis on integration of all types of observations from surface-based, airborne and satellites platforms through the use of data assimilation, atmospheric models and analysis to yield services and products attuned to users needs. More than ever, support by National Meteorological and Hydrological Services is needed to fill gaps in the eroding resources for surface-based observations as well as building partnerships to bridge institutional gaps and barriers to cooperation needed for an integrated observation system. The GAW programme provides the core upon which to build.

2. IGACO: A Strategy For the Next Generation GAW Programme

Within the framework of the IGACO strategy, the next generation GAW programme will evolve to meet the observational needs and challenges of climate change, ozone depletion, air quality and long range transport of air pollution. The merging of ground-based in situ and remote sensing observations with routine aircraft and satellite measurements through the use of “smart interpolators” that are under development by the research and modelling community is at once a daunting and exciting challenge.

The IGACO Report essentially confirms that the decision of WMO in 1989 (see Section 1 above) to create GAW was far sighted. It defines 14 target variables groups in the atmosphere that are ripe for integration using atmospheric models that assimilate not only meteorological observations but also chemical constituents. The components of an integrated observing system to be addressed by GAW are summarized in Figure 1. It is important that the groundwork laid by GAW in the past 17 years for global surface-based and aircraft monitoring systems is maintained and strengthened. Technological advances in measurement methodology and data exchange will shape the next generation GAW monitoring programme.
3. Components of the Global Atmospheric Watch Programme

The components of GAW are summarized in Figure 2. The focus is on six target variable groups: greenhouse gases, UV radiation, ozone, aerosols, major reactive gases (CO, VOCs, NO, and SO$_2$), and precipitation chemistry. GAW Scientific Advisory Groups (SAGs) for each of the six target variable groups have the task of establishing measurement standards and requirements.
while calibration and quality assurance facilities help to ensure valid observations. The emphasis on standardization, calibration, quality assurance, data archiving/analysis and building the air chemistry monitoring networks has resulted in major advances. Over 80% of the facilities related to quality assurance and archiving in GAW have been established since 1989 while the rest that preceded GAW have been strengthened through membership in the programme. In addition to these facilities, 7 regional calibration centres for total ozone are in operation.

The GAW Station Information System (GAWSIS) is a web-based network-tracking tool that hosts all GAW metadata on observatory managers, location and measurement activities. It can answer the question: “What do we have for a global long term network measuring the variable X?” Global or Regional GAW stations are operated by WMO Members while Contributing stations are operated by partner networks that agree to contribute data of known quality to a GAW World Data Centre. In 2006, there were 24 Global stations, 200 Regional stations and approximately 90 Contributing stations delivering data to GAW World Data Centres. Five GAW World Data Centres collect, document and archive data and quality assurance information and make them freely available to the scientific community for analysis and assessments. Note the linkages of GAW to contributing partner networks, aircraft and satellite observations that contribute to integrated global atmospheric chemistry observations. Implementation of recommendations in Chapter 5 of the IGACO strategy (IGACO, 1994) will be done through four Theme Foci on: Ozone, Greenhouse Gases, Air Quality and Aerosol-Climate Interactions. Secretariats supported by WMO institutions will host the development of implementation plans for the IGACO strategy and as shown in Figure 2 are advised by the Scientific Advisory Groups of GAW. The aim is to develop better synthesis and analysis products (see Section 4) for their user communities. The Finnish Meteorological Institute is the first to establish a secretariat for IGACO-ozone in October 2005.

There are GAW Global, Regional and Contributing stations that support the monitoring of GAW target variables in each of the six groups. Global and Regional stations are operated by a WMO Member and are defined by Technical Regulations adopted by the WMO Executive Council in 1992 (EC XLIV; 1992) as well as the GAW Strategic Implementation Plan (Strategic Plan, 2001; Strategic Plan Addendum, 2004). Contributing stations are those that conform to GAW measurement guidelines, quality assurance standards and submit data to GAW data centres. They are mostly in partner networks that fill major gaps in the global monitoring network. The difference between a Global and a Regional GAW station lies in the facilities available for long-term measurements, the number of GAW target variables measured, the scientific activity at the site and the commitment of the host country. The location of the 24 GAW Global stations is shown in Figure 3.

To monitor global distributions and trends of a particular variable with sufficient resolution to answer outstanding gaps in understanding of environmental issues related to global issues requires not only Global but also Regional and Contributing stations. As an example, the GAW Global Monitoring Network for CO$_2$ and CH$_4$ is shown in Figure 4. In October 2005, it was recognized as a comprehensive network of the Global Climate Observing System (GCOS) co-sponsored by WMO and other international organizations. It is thereby formally a network under the UN Framework Convention on Climate Change.
Figure 3: Global stations in the Global Atmosphere Watch network. Note that the Hohenpeissenberg observatory is the oldest in the network and in the top ten percentile for breadth and quality of programme.

Figure 4: The GAW Global Monitoring Network for CO₂ and CH₄, a comprehensive network of the Global Climate Observing System under the UNFCCC. It has strong support from German researchers and facilities.
In Figure 5, the GAW Global Networks for balloon sonde ozone and total column ozone are shown. They play an essential role in monitoring the success of the Vienna Convention on Protection of the Ozone Layer and the controls on ozone depleting substances enacted under the associated Montreal Protocol. There are also global networks for other variables such as methane, nitrous oxide, aerosol variables, surface ozone, reactive gases and precipitation chemistry that involve different combinations of the three types of stations and network configurations.

Figure 5: The GAW global network delivering data from 2001-2004 for total column (a) and balloon sonde (b) ozone observations. The ozone research group at Hohenpeissenberg is a major contributor (courtesy of the WMO-GAW World Ozone and UV Data Centre, WOUDC/Environment Canada).

GAW activities, in Germany and internationally, result in a broad spectrum of services and products that could not be described adequately within the scope of this paper. They are pertinent to a wide range of geographical scales from local (station specific) to regional to hemispheric to global. German Global GAW observatories at Zugspitze, Hohenpeissenberg, and Neumayer in Antarctica as well as a number of Regional stations have long term records of atmospheric composition dating back 40 years or more. Some of these are described in more detail in other sections of this report. Collectively, they represent a unique national global change detection resource as well as a satellite ground truthing network. Examples of global GAW products to which Germany contributes significantly are: the quadrennial WMO/UNEP Scientific Assessment of Ozone Depletion, the WMO Antarctic Ozone Bulletin and the WMO Greenhouse Gas Bulletin. Future services include the coordination of near real time delivery of GAW observations for numerical weather and air quality prediction through the WMO Information System.
The GAW Urban Research Meteorology and Environment (GURME) project focusing on urban air quality was developed in response to the requests from WMO Members that play an important role in the study and management of urban environments. National Meteorological and Hydrological Services throughout the world are broadening their traditional focus on observing classical meteorological variables and weather forecasting to also include air quality variables. GURME fosters collaboration with environmental agencies responsible for air quality measurements and management. It addresses the end-to-end aspects of air quality that link observation issues, to data assimilation techniques, to numerical models, to the diverse array of dissemination methods, and to the capacity building required for developing countries to reap the full benefits of air quality management tools. Application of high resolution meteorological models on an urban scale by the German Weather Service will lead to better air quality management.

Conclusion

Atmospheric chemistry monitoring and research activities in Germany conducted by a variety of agencies have long been a major cornerstone of the WMO Global Atmosphere Watch programme. GAW is based on the contribution of national programmes that are committed to international cooperation. These nations realize that because greenhouse gases, ozone, aerosols and other constituents often have atmospheric lifetimes longer than the time for winds to cross their country that a regional to global perspective is necessary. Through solid commitments and activities, they acknowledge the fact that developed countries need to lend support to less-developed countries in the form of quality assurance advice and assistance, training, auditing and infrastructure maintenance. This report highlights the services and products resulting from a cooperative effort involving many departments and institutions in Germany that make GAW a unique international global atmospheric chemistry observing system.

References


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A. GAW RESEARCH FACILITIES AND PROGRAMMES IN GERMANY: FOREWORD

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Germany has contributed to WMO coordinated global atmospheric chemistry research and monitoring of greenhouse gases, ozone, UV, aerosols, reactive gases precipitation chemistry and radiation monitoring networks under the Global Ozone Observing System (GO3OS) and the Background Air Pollution Monitoring Network (BAPMoN) before they were merged into GAW in 1989. A major objective of GAW was to emphasize data quality and to develop a network of about 30 Global observatories that, when complemented by Regional station observations, would serve to better understand weather, climate and air quality.

In support of GAW, Germany operates the following nine facilities that are also shown in a map in Figure 1 and described in detail in this section of the report:

![Figure 1: Location of GAW quality assurance facilities and global or regional stations in Germany.](image-url)
1. The Global Station Zugspitze/Hohenpeissenberg.
2. The Global Station Neumayer in the Antarctic.
3. The Regional Stations Schauinsland and Neuglobsow.
4. The World Calibration Centre for Aerosol Physics.
5. The World Calibration Centre for VOC and N\textsubscript{2}O.
6. The World Calibration Centre for Ozone Sondes.
7. The QA/SAC Germany.
8. The Regional Calibration Centre for Dobson Total Ozone Instruments.
9. The GAW Training and Education Centre (GAWTEC).

Further German activities related to GAW are the DACH co-operation between the alpine observatories Jungfraujoch, Sonnblick, Zugspitze and Hohenpeissenberg, and contributions to the GAW Urban Research Meteorology and Environment Project (GURME).

These facilities and programmes support all components of the GAW programme described in the first section of this report (Barrie and Fricke). They serve to detect trends in air pollution related to legislated emissions controls, increasing population and industrial growth, to assure the quality and comparability of observations globally, to build capacity in developing countries and to better understand problems related to air pollution and changing climate.

The future of the GAW programme in Germany will include:

- Generally improved international engagement.
- Improved co-operation within the GAW international programme.
- Enhanced contribution to the future development of GAW, especially with regard to the envisaged Earth observation programmes.
- Improved co-operation with the regional networks EMEP and EIONET in Europe.
- Continuing offer for research campaigns at the GAW platforms.
- Contribution to improved (chemical) weather forecast.
- Accelerated data delivery.
- Public dissemination of trajectories calculated for all GAW Global Stations.

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The GAW Global Observatory Zugspitze/Hohenpeissenberg

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Introduction

The GAW Global Station Zugspitze/Hohenpeissenberg is one of the few Global Stations with two stations located on mountain tops not far from each other and supported by two departments.

The Zugspitze station is situated at 2650 m a.s.l. at the northern rim of the Alps in the Environmental Research Station "Schneefernerhaus", on the southern slope of Zugspitze summit, which is 2960 m a.s.l. and has a weather station since more than 100 years.

The Hohenpeissenberg station is situated in an observatory in the pre-alpine area about 40 km north of Zugspitze, on a mountain top at 985 m a.s.l. Here, meteorological observations date back to the late 18th century.

While the Hohenpeissenberg observatory is operated by the Deutscher Wetterdienst (German Weather Service, DWD) only, the monitoring programme at the Environmental Research Station "Schneefernerhaus" is shared with Umweltbundesamt (Federal Environment Agency, UBA). The benefit of two institutions working closely together to run a common Global observatory of two stations is obvious: The monitoring strategy can be optimised, the costs be shared, and the interpretation of data from different viewpoints adds to the value and improves the mutual understanding.

Zugspitze

Starting in 1999, the German 'Umweltbundesamt' (UBA, Federal Environment Agency) built up the platform Zugspitze at the site Schneefernerhaus, situated at 2965 m asl, approximately 300 m below the Zugspitze summit. The Zugspitze is Germany's highest mountain, and is located on the Austrian/German border.

The measurement programme of the GAW Global Station - Platform Zugspitze consists of:

- Climate forcing atmospheric gases: CO₂, CH₄, N₂O, SF₆, halogenated carbons.
- Reactive atmospheric trace gases: Ozone, CO, NO, NO₂, NOₓ, NOy, PAN, VOCs, carbonyl samples.
- Aerosols with size distributions of fine and ultrafine particles in the range from 10 - 800 nm.

The GAW global station Zugspitze/Hohenpeissenberg is operated in cooperation with the Hohenpeissenberg observatory of the 'Deutsche Wetterdienst' (DWD, German Weather Service). The platform Zugspitze also is an integrated station in the UBA air quality network which contributes to EMEP (European Monitoring and Evaluation Programme) and thus Zugspitze also delivers data to EMEP.
In addition, the GAW platform Zugspitze provides data for research activities of other scientific projects in the Environmental Research Station Schneefernerhaus. Presently, own research activities concentrate on the determination of the northern hemispheric background of fine and ultrafine aerosol particles at the Zugspitze site. By quantifying the size distribution and source regions of mid and long range transported fine dust an important task for the requirements of the German environmental protection politics can be fulfilled. In that way the imported amount of fine dust can be quantified. Air mass transport and source regions are determined by retroplume modelling including turbulent diffusion and convection using the flexpart model of A. Stohl. The project also promises to give a reliable and differentiated information about the spatial representativity of the measurement site Schneefernerhaus.

In the close future measurement data will be provided to support ground truthing for the calibration of satellite measurements.

In order to ensure state of the art measurements a number of technical and scientific cooperations exists, for example with the University of Heidelberg for the measurement of radiation forcing gases, with the Institut für Troposphärenforschung Leipzig (IFT) for the measurement of ultrafine aerosol distributions and with the Meteorological observatory for the measurement of nitrogen oxides.

**Hohenpeissenberg**

The Hohenpeissenberg Observatory was founded in 1781 (Figure 1). Since that year, meteorological data have been continuously recorded. The observations were extended to more parameters in 1879 (Figure 2), radiation measurements commenced in 1948. First tests with an X-band precipitation radar began in 1967, leading to the development of today's German precipitation radar network with Hohenpeissenberg still hosting the research radar for this network. The comprehensive ozone monitoring programme has been started in 1966 with the ozone sonde and Dobson total ozone measurements. The ozone lidar, extending the profiles up to 50 km, has become operational in 1987.
Figure 1: The Hohenpeissenberg Meteorological Observatory.

Figure 2: History of measurements and observations at Hohenpeissenberg Meteorological Observatory.
Building upon this long-term experience, the monitoring activities at Hohenpeissenberg were substantially extended in 1995 for participation in the GAW programme. Table 1 lists all components that are being measured for GAW. In addition to the well-established ozone monitoring programme, a substantial amount of trace gases is now being monitored. It allows insight into processes that, e.g., lead to the formation of photochemical smog or acidic precipitation.

The only long term observations of OH and sulfuric acid in the world have been made at Hohenpeissenberg since 1998 to characterize the oxidizing capacity, photo-chemistry and secondary aerosol formation.

The aerosol measurements are especially important for assessing the impact of particulate matter in air on climate. The combination of continuous information on physical, chemical and optical properties is unique to GAW Global Stations, which emphasizes their importance for improving the understanding of how the aerosol influences climate. In addition, such a comprehensive aerosol programme allows to distinguish between anthropogenic and natural contributions to climate effects, which is a pre-requisite for optimized mitigation strategies.

Table 1: GAW monitoring programme at Hohenpeissenberg.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reactive trace gases</th>
<th>SO₂, CO, NO, NO₂, NOₓ, NO₃, PAN, H₂O₂, VOCs, OH, H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>Ambient, Vertical profile with ozonesonde and Lidar (troposphere and stratosphere), Total ozone (Dobson and Brewer)</td>
<td></td>
</tr>
<tr>
<td>Aerosol: Physical characteristics</td>
<td>Mass, Number (&gt; 3 nm, &gt; 11 nm, &gt; 100 nm), Size distribution (0.1 to 7.5 µm)</td>
<td></td>
</tr>
<tr>
<td>Aerosol: Chemical characteristics</td>
<td>Impactor (4 size classes), IC analysis for anions and cations as in precipitation</td>
<td></td>
</tr>
<tr>
<td>Aerosol: Optical characteristics</td>
<td>Scattering, absorption (BC), turbidity</td>
<td></td>
</tr>
<tr>
<td>Precipitation chemistry</td>
<td>pH, electr. conductivity, sulfate, nitrate, chloride, ammonium, sodium, potassium, calcium, magnesium, heavy metals</td>
<td></td>
</tr>
<tr>
<td>Solar Radiation</td>
<td>Global, diffuse, IR, UV-B, Photolysis frequencies j-NO₂ and j-(O₁D)</td>
<td></td>
</tr>
<tr>
<td>Meteorology</td>
<td>Full set of WMO class I station data</td>
<td></td>
</tr>
</tbody>
</table>

Special emphasis is put on high data quality within the GAW programme. This is indispensable for comparable and consistent data. The Hohenpeissenberg observatory therefore participates in routine external audits, round robins and laboratory intercomparisons whenever and for whatever component they are offered. The quality management at Hohenpeissenberg in particular and at DWD in general is certified to DIN EN ISO 9001.

In 2006 a flask sampling programme was started to link the online observations of CO and VOC within GAW at Hohenpeissenberg to the global flask sampling network of NOAA GMD (formerly CMDL).

Back trajectories for interpretation of the data measured have been calculated as a matter of routine for Hohenpeissenberg and Zugspitze since the early 1990s. They are used for improving the understanding of transport and chemical transformation processes of all kinds of locally observed trace substances as well as the spatial allocation of trends. Since 2003 they are available for all GAW Global Stations.
The Hohenpeissenberg observatory also serves as a platform for process studies that use the comprehensive routine monitoring programme as a base and for generalizing the results from their special investigations. A substantial amount of projects has therefore been carried out at this research platform during the last 10 years. They are listed at the end of this report.

Ozone Bulletins and GAW Letters are being alternately published every month, accentuating ongoing results from data interpretation or dealing with current topics in air chemistry and climate. Both are also available on the Internet, the GAW letter also in English (see www.dwd.de/gaw).

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Station description

The ‘Alfred Wegener Institut für Polar- und Meeresforschung’ (AWI, Alfred Wegener Institute for Polar and Marine Research) in Bremerhaven, one of the 15 major research institutions of the Helmholtz Society of German Research Centres, is carrying out research projects in Antarctica since 1978. In 1981, AWI started to run the permanently manned Georg-von-Neumayer-Station (70°37´S, 8°22´W) next to the Atka Iceport on the Ekstöm Ice Shelf at the northwest edge of the Weddell Sea in Antarctica, see Figure 1.

![Figure 1: Mean location of the sea ice edge for February (minimum) and September (maximum).](image)

Ice movements and heavy snow deposits necessitated the construction of a new station building in the early 1990s. The new station - just called Neumayer - took over the observatory programmes without interruption. It is situated about 6 km southeast from the former one, see Figure 2.

A third succession station (Neumayer III) will be erected within the following years. The designated lifetime of Neumayer III is about 25 years. An uninterruptible continuation of all relevant observatory programmes is planned.

Neumayer Station - as well as its predecessor - consists mainly out of two parallel steel tubes each 90 meters long and 8 meters in diameter. Originally, the tubes have been constructed on top of the snow surface. Due to snow accumulation the whole construction gets deeper and deeper covered by snow. Only the top of the entrance towers – which have to be elongated every other year - as well as some antennas and scientific equipment are kept above the snow surface.
First of all, Neumayer serves as research station. Research is focused on meteorology, air chemistry and geophysics. The meteorological observatory programme started in 1981. One year later, a permanent air chemistry observatory as well as a geophysical observatory was installed. Most of these observatory programmes are of importance for climate research performed within international networks like the Global Telecommunication System (GTS), Global Atmospheric Watch (GAW), Network for the Detection of Stratospheric Change (NDSC), Baseline Surface Radiation Network (BSRN).

**Surrounding of the station**

The Ekvstom Ice Shelf has a homogenous, flat surface, sloping gently upward to the south. Except for some insignificant nunataks about 100 km south of Neumayer, no ice-free land surface exists. The ice shelf is 230 m thick at Neumayer and moves with a velocity of 170 m per year towards the breaking edge about 16 km farther north.

Atka Iceport is mostly covered with fast ice. The ice is safe enough to stand on to visit the emperor penguin colony and to watch the Weddell seals. Only during January and February the Atka Iceport becomes mainly ice free.

North of the station, at a distance of about 15 km, pack ice is predominant. In some years pack ice vanish during a few summer weeks completely, while in other years some ice floes remain. In any season strong westerly winds can open up a coastal polynia north of Neumayer.
At Neumayer the maximum solar incidence angle is 42.8°. The Sun stays permanently above the horizon from November 19 to January 24 and permanently below the horizon from May 19 to July 27.

**Meteorological observatory**

The meteorological observatory of Neumayer is an integral part of many international networks, mostly associated with the World Meteorological Organization. The data from Neumayer help to close significant gaps in the global weather and climate observing networks. The observatory programme contains the following parts:

**3-hourly routine synoptic observations:** Synoptic observations are carried out routinely every 3 hours. They include measurements of air temperature (at 2m and 10m height), air pressure (values are reduced to mean sea level), wind vector (at 2m and 10m height), dew point temperature (at 2m height), clouds (cloud amount, type and height), horizontal visibility, present and past weather snowdrift and whiteout. The full programme is carried out at 0, 9, 12, 15, 18, 21 UTC. During night time at 3 and 6 UTC the visual observations are omitted (http://www.awi.de/MET/Neumayer/latest_obse.html)

**Daily upper air soundings:** Routinely once daily (about 10:45 UTC) a radiosonde is launched to measure vertical profiles of air pressure, temperature, relative humidity and the wind vector (http://www.awi.de/MET/Neumayer/nrt_temp). Upper air soundings are carried out with VAISALA radiosondes which directly measure air pressure, air temperature and relative humidity. The wind vector is determined with the aid of the GPS navigation system, the height information is calculated using the hydrostatic approximation. Helium filled balloons (TOTEX 600g, 800g) are used to obtain an ascent velocity of about 5m/s. Typically the balloons burst at heights between 25 and 35 km.

**Weekly ozone soundings:** Normally, one ozonesonde is launched every week to measure the vertical ozone profile through the troposphere and the lower stratosphere. For the ozone soundings a VAISALA radiosonde is connected via an interface to a VAISALA ECC sonde. A 1500g TOTEX balloon is used for these ascents.

**Surface radiation measurements:** The surface radiation measurements are performed within the framework of the Baseline Surface Radiation Network (BSRN). The following radiation quantities are measured every other second and stored in form of 1 minute averages:

- global (solar) radiation with glas-filter (305 - 2800nm)
- global radiation with OG1-filter (530 - 2800nm)
- global radiation with RG8-filter (695 - 2800nm)
- UV radiation (300 - 370nm)
- diffuse sky radiation (305 - 2800nm)
- direct solar radiation (305 - 2800nm)
- reflected solar radiation (305 - 2800nm)
- downward long-wave radiation (4 – 50µm)
- upward long-wave radiation (4 – 50µm)
- sunshine duration. (yes/no)

**Air chemistry observatory**

Due to the fact that continental Antarctica is largely free of trace compound sources, aerosols and trace gases measured at Neumayer mainly originate from the marine boundary layer of the southern Atlantic or are advected by long range transport via the free troposphere. Hence, the measured trace compounds are representative for the local marine boundary layer as well as for the remote southern hemisphere. Given that the impact of local pollution is negligible, trend measurements document the global impact of civilization on the atmospheric burden of long lived trace compounds like greenhouse gases. Thus, in very close cooperation with the meteorological observatory, the air-chemistry observatory from Neumayer became a significant part of the Global
Atmospheric Watch (GAW) Network. Neumayer covers a wide range of GAW type measurements (aerosol, greenhouse gas, meteo, ozone, radio nuclide, solar radiation). Many of these measurements started 20 years ago and are ongoing (http://www.empa.ch/gaw/gawsis/default.asp).

The established research programme opens new potentialities to assess atmospheric circulation in the southern hemisphere, source regions and variability of bio-geochemical source strengths like the bioproductivity of the southern Atlantic. In addition, photochemical and deposition processes within the polar atmospheric boundary layer as well as the physico-chemical interaction of the firn-atmosphere interface are addressed. Finally, in combination with the meteorological observatory the research programme is particularly dedicated to contribute to the interpretation of trace compound profiles retrieved from Antarctic ice cores.

The first air chemistry observatory at Neumayer was initiated and constructed by the Institut für Umweltphysik, University of Heidelberg (UHEI-IUP) in 1982. Following almost 13 years of operation, the technical equipment and the data acquisition facilities had to be renewed. The present observatory was designed in collaboration between AWI and UHEI-IUP as a container building placed on a platform some metres above the snow surface, see Figure 3.

![Figure 3: The GAW Global Air Chemistry Observatory Neumayer.](image)

All experiments installed in the air chemistry observatory are under daily control and daily performance protocols are available. A ventilated stainless steel inlet stack (total height about 8 m above the snow surface) supplies the experiments with ambient air.

Concerning anthropogenic pollutants, the Antarctic atmosphere is "ultra clean". Local pollution by vehicles and the base itself is, thus, a potential problem for many measurements aimed at representing the background status of the Antarctic troposphere. Consequently, a central aspect of the technical concept concerns the ability of contamination-free sampling of aerosols and trace gases. This is realized by several means:

- The air chemistry observatory is situated in a clean air area about 1500 m south of Neumayer. Due to the fact that northern wind directions are very rare, contamination from the base can be excluded for most of the time.
- The power supply (20 kW) is provided by a cable from the main station, thus no fuel-driven generator is operated in the very vicinity.
Contamination-free sampling is controlled by the permanently recorded wind velocity, wind direction and by condensation particle concentration.

In the meanwhile, the convincing research concept of the air chemistry observatory from Neumayer and the strict realization of contamination free sampling have been frequently adopted. As a consequence, several comparable observatories are now set up in Antarctica enabling the documentation of the changing composition of the atmosphere on a continental or even global scale. Obviously, the importance of the data retrieved from the air chemistry observatory will be significantly enhanced in the future and a continuing operation is of fundamental interest (http://www.awi-bremerhaven.de/GPH/SPUSO.html).

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The GAW Regional Station at Schauinsland

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The GAW-regional station Schauinsland is located on the Schauinsland mountain (1285 m asl) in the southwestern part of the black forest. It lies approximately 1000 m above the near Rhine valley and the city of Freiburg (horizontal distance of about 15 kilometer). The station is situated in the east of the top on a flat ridge and is surrounded by meadows and forests (Figure 1).

![Figure 1: The GAW-Regional Station Schauinsland.](image)

**Geographical information:**

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</table>

A special aspect of the Schauinsland site is the fact, that it often lies above the boundary layer at night and in winter (stationary temperature inversion). At these times well mixed tropospheric background air surrounds the station. After decomposition of the inversion air enriched with trace constituents reaches the station. Depending on these meteorological conditions tropospheric background as well as locally influenced air can be measured.

The air quality measuring site exists since the middle of the sixties. It was founded by the 'Deutsche Forschungsgemeinschaft' (DFG, German Science Foundation) as part of a German monitoring network to investigate the composition of unpolluted air and background air pollution. In 1974 the network was integrated in the newly established 'Umweltbundesamt' (UBA, Federal Environment Agency). In the 1960s and early 1970s a lot of pioneering work concerning the development of methods to measure trace substances in air was necessary. Some measuring systems were developed by the station personal themselves.
Today, the site is one of seven stations of the German air monitoring network operated by the UBA. It serves for long-term monitoring of long-range transboundary air pollution within the scope of international programmes. Besides GAW, the data contribute to the European Monitoring and Evaluation Programme (EMEP). In addition, the station serves as platform for research projects (e.g. CarboEurope-IP funded by EU) and is responsible for quality assurance of the greenhouse gases measurements within the total UBA-air monitoring network.

Over the years, the observational programme has changed according to new and emerging questions. While at the beginning sulphur dioxide was a main concern, its concentration in Germany today is very low. At the beginning of the nineties the tropospheric ozone became more important and a national ozone early warning system was installed. Recently one focus is on components with global effects such as greenhouse gases.

The measurement programme contains the following parameters (measuring period at Figure 2):

**gases:** sulphur dioxide ($SO_2$), ozone ($O_3$), nitrogen oxides ($NO_x$, NO, NO$_2$), carbon monoxide (CO), carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), sulphur hexafluoride (SF$_6$), hydrocarbons, peroxyacetyl nitrate (PAN), ammonia (NH$_3$), C$_{13}$, C$_{14}$, O$_{18}$

**aerosols:** concentration and ingredients: PM$_{10}$, PM$_{2.5}$, heavy metals: As, Cd, Cu, Fe, Mn, Ni, Pb
ions: $SO_4^{2-}$, $\Sigma NH_3^+$, $NH_4^+$, $\Sigma HNO_3^+$, NO$_3^-$
particle number and size distribution

**precipitation:** amount, pH-value, conductivity, ions: $SO_4^{2-}$, NO$_3^-$, Cl$^-$, K$^+$, Na$^+$, NH$_4^+$, Mg$^{2+}$, Ca$^{2+}$

**meteorology:** air temperature, wind direction and speed, relative humidity, air-pressure

**radiation:** solar radiation, uv-spectrum

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**Figure 2:** Number of measured years for several components at GAW Regional Station Schauinsland. ****
The GAW Regional Station at Neuglobsow

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The GAW regional station Neuglobsow is situated directly at the southeast edge of the 'Großer Stechlin See' (Great Lake Stechlin), at the southeast border of the 'Mecklenburger Seenplatte' (Mecklenburgia Lake District). The station is surrounded by a big forest of a National Park without industry or agriculture. The distance to the next village, Neuglobsow, is 1.5 km, which is located 6 km southwest of Fürstenberg. The sparsely populated surroundings are plain with small hills. The coordinates are 53° 09' N and 13° 02’ E, elevation is 62 m a.s.l.

Figure 1: The GAW Regional Station Neuglobsow.

From 1979 to 1991 the Stechlin Lake District was operated as a background site to monitor pollutants in air and precipitation as well as their effects on ecosystems. In 1991 the monitoring site Neuglobsow was integrated into the German air monitoring network operated by the 'Umweltbundesamt' (UBA, Federal Environment Agency).

The monitoring site Neuglobsow now serves as a regional GAW station as well as an EMEP site (European Monitoring and Evaluation Programme). In addition, Neuglobsow is one of two German Integrated Monitoring sites, the international cooperative programme of the Convention on Long-range Transboundary Air Pollution which investigates the effects of air pollutants on ecosystems.

Monitoring Programme

Gases
Sulphur dioxide (SO₂), ozone (O₃), nitrate monoxide/-dioxide (NO/NO₂), carbon dioxide (CO₂), methane (CH₄), carbon monoxide (CO), volatile organic compounds (VOC), carbonyls, NH₄.

Aerosols
PM₁₀ and ingredients: heavy metals (As, Cd, Cu, Fe, Mn, Ni, Pb), Ions (SO₄²⁻, ∑ NH₃+ NH₄⁺, ∑ HNO₃+ NO₃⁻)
Precipitation (open land and forest)
Precipitation amount, pH, conductivity, major ions (SO$_4^{2-}$, NO$_3^-$, Cl$,^-$, K$^+$, Na$^+$, NH$_4^+$, Mg$^{2+}$, Ca$^{2+}$).

Meteorology
Temperature, air pressure, relative humidity, wind speed and direction, precipitation amount, global radiation, reflex radiation, sunshine duration.

Integrated Monitoring
Precipitation throughfall, soil water chemistry, ground water chemistry, lake water chemistry, phenology, litter fall and chemistry, vegetation structure and species cover.

Water balance
Monitoring and survey of the water balance within the Stechlin Lake District.
There are four more stations in Germany which contribute to GAW: Westerland, Zingst, Waldhof and Schmücke (Figure 1). They are part of the German air monitoring network operated by the 'Umweltbundesamt' (UBA, Federal Environment Agency). Above all, they are operated as EMEP stations, however, they contribute to other international programmes, i.e. the convention on the protection of the marine environment of the North-East Atlantic (OSPAR), the convention on the protection of the marine environment of the Baltic Sea area (HELCOM), and GAW.

The contributions to GAW are carbon dioxide, methane, ozone and meteorological data. For more information see http://www.umweltbundesamt.de/luft/luftmessnetze/ubamessnetz.htm.

Figure 1: Location of GAW stations in Germany. One GAW global station: Zugspitze/Hohenpeissenberg with its two platforms Zugspitze and Hohenpeissenberg. Two regional stations: Schauinsland and Neuglobsow. Four contributing stations: Westerland, Zingst, Waldhof and Schmücke.

Geographical information:

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Introduction

The global network of ozone sounding stations provides the longest time series of the vertical ozone distribution between surface and 30-35 km altitude. Up to an altitude of about 20 km ozone sondes constitute the most important data source with long term data coverage for the derivation of ozone trends with sufficient vertical resolution, particularly in the important, climate sensitive, altitude region around the tropopause [SPARC-IoC-GAW Assessment of Trends in the Vertical Distribution of Ozone: 1998]. Furthermore, ozone sondes are widely used to study photochemical and dynamical processes in the atmosphere or to validate and evaluate satellite observations for long term stability assessments. Ozone trend assessments have shown that there is an urgent need to improve the homogeneity and quality of ozone sounding data to ensure more confidence in observed trends [WMO Scientific Assessment of Ozone Depletion: 1994, 1998, 2002]. This must be achieved by intercalibration and intercomparison of existing ozone sonde types and different operating procedures (e.g. preparation, data processing etc.) used.

The sonde simulation facility (http://www.fz-juelich.de/icg(icg-ii/esf/) at the 'Forschungszentrum Jülich' is established as World Calibration Centre for Ozone Sondes (WCCOS) as part of the quality assurance plan for ozone sondes that are in routine use in the GAW programme with following three major tasks:

- QA-Procedures: Establishment and up-date of Standard Operating Procedures (SOP's) of different sonde types
- QA-Manufacturers: Performance check of sondes from different manufacturers
- QA-Operation: Test of sonde profiling capabilities of sounding laboratories

JOSIE 1996-2000

Since 1996 several JOSIE (= Juelich Ozone Sonde Intercomparison Experiment: http://www.fz-juelich.de/icg(icg-ii/josie) activities to assess the performance of ECC-ozone sondes have been conducted at WCCOS [see GAW Reports No. 130, 157, 158]. In order to determine precision, accuracy and response of the ozone sondes as a function of sonde type, altitude, and ozone level, the different ozone sonde types were tested under a variety of conditions and compared with an accurate UV-photometer. Special attention was paid to outstanding issues with a strong focus on the influence of operating procedures on in-flight performance, particularly for the ECC-sonde [Smit et al., 2006]. The experiments have shown that the performance characteristics of the two different ECC-sonde types can be significant different, even when operated under the same conditions. Particularly above 20 km the ENSCI-Z sonde tends to measure 5-10 % more ozone than the SPC-6A sonde.

Below 20 km the differences are 5 % or less, but appear to show some differences with year of manufacture. There is a significant difference in the ozone readings when sondes of the same type are operated with different cathode sensing solutions. For each ECC-manufacturer type the use of 1.0% KI (full buffer) gives 5% larger ozone values compared with the use of 0.5% KI (half buffer), and as much as 10% larger values compared with 2.0% KI (no buffer).

For ozone sounding stations performing long term measurements this means that changing the sensing solution type or ECC-sonde type can easily introduce a change of ±5% or more in their records, affecting determination of ozone trends. Standardization of operating procedures for ECC-
sondes yields a precision better than ± (3-5) % and an accuracy of about ± (5-10) % up to 30 km altitude.

**JOSIE-BESOS-ASOPOS (2001-2005)**

Under the auspices of WMO/GAW, in 2001 the Assessment of Standard Operating Procedures for Ozone Sondes (ASOPOS) has been initiated. Major goal of ASOPOS is to establish a set of standard operating procedures (SOPs) that will be recommended and documented by the WMO for each of the three major types of ozone sondes (ECC, BM+hybrids and KC79/96) used in the GAW ozone sounding network. After a critical evaluation of the entire series of JOSIE-experiments preliminary SOP’s (Standard Operating Procedures) were unanimously agreed by a panel of ozone sonde experts.

In April 2004 the WMO/BESOS (Balloon Experiment on Standards for Ozone Sondes) field campaign at the University of Wyoming at Laramie, USA, was conducted to test the provisional SOP’s for ECC-ozonesondes in the real atmosphere. The BESOS balloon gondola contained 18 ozonesondes, which were individually prepared according the preliminary SOP’s. As ozone reference served the same UV-photometer as used in JOSIE at WCCOS in Juelich. BESOS focused exclusively on the influence of the use of different sensing solutions on the performance of ECC-sondes from two different manufacturers.

At 20-23 September 2004 a WMO/ASOPOS meeting of ozone sonde experts had been held at Jüllich, Germany to evaluate the BESOS-results in combination with the results from JOSIE- and other laboratory and field studies in order finally to establish WMO-recommended SOP’s, for the different major types of ozone sondes used in the GAW-ozone sounding network. Unanimous agreement on SOP’s was achieved by the ASOPOS-panel. Also it was concluded that the sonde to sonde differences observed in JOSIE are borne out in BESOS such that the JOSIE-simulation chamber experiments are representative for the real atmosphere, sonde to sonde and in comparison with UV-photometer as ozone reference instrument. Standardization of the operating procedures (SOP’s) leads to the best precision.

The ASOPOS-panel is preparing a detailed document describing the SOPs for ECC-sondes with a strong emphasis to explain the recommended methodologies. Similar documents about SOPs for Brewer-Mast and KC96 sondes are in preparation. It is expected that these documents will be published in 2007 as GAW-reports and established at WMO as recommended SOPs for the three major ozone sonde types used nowadays in GAW.

**Mid-term perspectives WCCOS**

Further, the ASOPOS-panel of ozone sonde experts strongly recommend for future (5-10 year) activities of the WCCOS to focus on:

- Implementation of SOP’s in global network: deriving transfer functions for non-SOP using sounding stations to homogenize sonde data through intercomparison experiments in the simulation chamber at the WCCOS and in the field.
- QA-Manufacturing on regular base (every 1-2 year).
- QA-SOP by regular evaluation and eventual update (every 5 year).
- Scientific research on outstanding issues (e.g. pump flow efficiency, background).

**References**


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Atmospheric aerosols play an important role in regional and global climate as well as in air quality. Aerosol particles scatter and absorb light and thus influence the radiation balance of the earth. Furthermore, they act as cloud condensation nuclei and determine the microphysical and subsequently also the optical properties of clouds. Depending on the chemical composition, aerosol particles can also harm human’s health as well as the biosphere.

Coordinated Quality Assurance and Quality Control (QA/QC) are thus required to ensure a comparable world-wide aerosol monitoring programme to observe long-term trends of aerosol properties. The GAW-Scientific Advisory Group for Aerosols established a World Calibration Centre for Aerosol Physics hosted by the 'Leibniz-Institut für Troposphärenforschung e.V.' (IFT, Leibniz Institute for Tropospheric Research) in Leipzig, Germany. The duties of the WCCAP for the QA/QC programme are listed in the following.

**Tasks of the WCCAP**
- Site audits of WMO-GAW stations on request or due to priorities given by the Scientific Advisory Groups for Aerosols.
- Calibration and intercomparison workshops for physical aerosol instrumentation at the WCCAP facilities.
- Aerosol training courses for station personnel and young scientists.
- Advice in the implementation of new sampling sites, inlet configuration, aerosol instrumentation.
- Twinning partnership to build up new aerosol programmes.
- Development of Standard Operation Procedures for physical aerosol instrumentation.

The WCCAP is funded by the German 'Umweltbundesamt' (UBA, Federal Environment Agency) since 2002. The IFT as host institute dedicated a separate laboratory for the WCCAP activities including several types of aerosol generators and instrumentation for aerosol characterization. Since then, the WCCAP organized several calibration and intercomparison workshops, held aerosol training courses, performed audits of GAW-stations, and established twinning partnerships.

**Activities since 2002**

**Audits and site visits**
- Tamanrasset/Assekrem, Algeria, February 2003.
- Hohenpeissenberg, Germany, October 2003.
- Anmyeon, South Korea, April 2004.
- Pallas, Finland, August 2004.
- Danum Valley, Malaysia, October 2004.
- Mace Head, Ireland, October 2004.
- Danum Valley, Malaysia, November 2004.
- Waliguan-Beijing, China, June 2005.
- Danum Valley, Malaysia, November 2005.
- Danum Valley, Malaysia, March/April 2006.
- Cape Point, South Africa, May 2006.
- Ny Alesund, Norway, July 2006.
Intercomparison and calibration workshops
- Condensation Particle Counters, Leipzig, Germany, November 2002.
- Integrating Nephelometers, Leipzig, Germany, November 2003 (Heintzenberg et al., 2006).
- Absorption photometers, Leipzig; Germany, November 2005.

Aerosol training courses
- Schneefernerhaus, Zugspitze, Germany, October 2002, in cooperation with GAWTEC.
- Schneefernerhaus, Zugspitze, Germany, October 2003, in cooperation with GAWTEC.
- Hyytiälä, Finland, May 2004, in cooperation with the Nordic Centre of Excellence and the EC-project CREATE.
- Schneefernerhaus, Zugspitze, Germany, September 2004, in cooperation with GAWTEC.
- Beijing, China, December 2004, in cooperation with CAMS and Peking University.
- Schneefernerhaus, Zugspitze, Germany, Sept./Oct. 2005, in cooperation with GAWTEC.
- Beijing, China, December 2005, in cooperation with CAMS and Peking University.
- Hyytiälä, Finland, May 2006, in cooperation the EU-projects EUSAAR and ACCENT.

Twinning partnership
- Malaysian Meteorological Service (Danum Valley)
- Bulgarian Academy of Science (BEO Moussala)

The WCCAP will continue its programme in future. Emphasis will be given to audits of the remaining global GAW station with an aerosol programme and in repeating calibration and intercomparison workshops for core physical aerosol parameters such as the scattering and absorption coefficient. However, a major task will be capacity building including further aerosol training courses, twinning partnerships, and individual training at the WCC facilities in Leipzig.

Furthermore, the WCCAP cooperates with EMEP to establish a common aerosol programme, and with the EU-projects ACCENT and EUSSAR for QA/QS.

For information, a WCCAP home page was set up under following address:
http://gaw.tropos.de/WCCPAP/index.html

The home page of the GAW-Scientific Advisory Group for Aerosols can be found under
http://gaw.tropos.de/

References

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Nitrous oxide (N\textsubscript{2}O) in the atmosphere has both natural and anthropogenic sources, such as oceans, fossil fuel, biomass burning and agricultural fertilisers. It contributes about 6% to the enhanced greenhouse effect. N\textsubscript{2}O is increasing at a rate of about 0.7 - 0.8 ppb per year. While it is inert in the troposphere, its major sink is photochemical transformation in the stratosphere. Because of its long atmospheric lifetime (about 120 years), background levels of nitrous oxide can be representatively determined at GAW global stations. Moreover, regional stations may give useful insights into the global N\textsubscript{2}O budget. N\textsubscript{2}O concentration trends are used in climate models and for describing the nitrogen cycle in the atmosphere.

Co-ordinated Quality Assurance and Quality Control (QA/QC) are required when wanting to combine N\textsubscript{2}O measurements from different sites and different monitoring programmes in order to increase the global data coverage. The ultimate goal will be traceability to a single scale. Therefore, the GAW Strategic Implementation Plan (WMO/GAW Report No. 142) has requested the establishment of a World Calibration Centre for N\textsubscript{2}O (WCC-N\textsubscript{2}O) as a central GAW facility in order to take over QA/QC responsibility. However, in spite of its name, the WCC is not supposed to maintain its own calibration scale, but is linked to the GAW N\textsubscript{2}O scale, which is maintained by the Central Calibration Laboratory (operated by NOAA in Boulder, USA).

Major tasks of the WCC-N\textsubscript{2}O are:

- Development of quality control procedures.
- Maintaining N\textsubscript{2}O standards for QA/QC purposes.
- Conducting performance and system audits at stations.
- Conducting round-robin experiments and participating in intercomparisons organised by other institutions.
- Providing training and long-term technical help for station scientists and technicians.

The implementation of the WCC-N\textsubscript{2}O began at the Fraunhofer Institute IFU in 2001. Since 2002 the WCC-N\textsubscript{2}O is hosted by the 'Institut für Meteorologie und Klimaforschung - Bereich Atmosphärische Umweltforschung' of the 'Forschungszentrum Karlsruhe' (IMK-IFU, Institute for Meteorology and Climate Research - Atmospheric Environmental Research Division), located in Garmisch-Partenkirchen, Germany. Formal approval by WMO/GAW was received in November 2002. The activities of the WCC-N\textsubscript{2}O are conducted under supervision and through funding of the Quality Assurance/Science Activity Centre (QA/SAC) Germany, operated by the 'Umweltbundesamt' (UBA, Federal Environment Agency).

In order to introduce this new GAW facility and to discuss major issues related to its activities, the WCC-N\textsubscript{2}O has participated in several GAW-related meetings and workshops. Presentations given there have covered its concept and structure, general aspects and challenges of global N\textsubscript{2}O monitoring as well as specific points, such as Data Quality Objectives (DQO) and Measurement Guidelines (MG). The WCC-N\textsubscript{2}O maintains close relationships with the Scientific Advisory Group for Greenhouse Gases (SAG GG), where it is represented by its manager, who took part in two regular meetings of the SAG GG (2003 and 2005). In this way the WCC-N\textsubscript{2}O has been directly involved in decisions related to the current work of GAW as well as future concepts.

The WCC-N\textsubscript{2}O operates a laboratory equipped with a gas chromatographic system that mainly serves for comparisons of standards of different rank (cf. Figure 1). The high-pressure cylinders kept at the WCC-N\textsubscript{2}O comprise a suite of laboratory standards directly calibrated by the
CCL, which cover the range of 250 to 350 ppb, and a larger number of N₂O gas mixtures in air, forming the pool of travelling standards for quality control audits and intercomparison experiments.

Three full performance and system audits for N₂O were conducted until mid-2006. These comprised the GAW regional station Schauinsland (Germany) in November 2002 as well as at the two GAW global stations Cape Point (South Africa) in February 2003 and Zugspitze/Hohenpeissenberg (Germany) in December 2005. The WCC-N₂O was selected as a participant in the international NOAA, NASA and WMO round-robin experiment IHALACE (International HALocarbon in Air Comparison Experiment). Three IHALACE gas tanks were analysed in July 2005. In addition, the WCC-N₂O took part in a small-scale round-robin organised by UBA Schauinsland.

Figure 1: Schematic of the traceability of calibrations, round-robin experiments and audits. The left part shows the relationships in terms of institutions involved, the right part explains the hierarchy of standards.

Work on Measurement Guidelines (MGs) including DQOs has been central to the activities of the WCC-N₂O during recent years. The MGs are intended to appear as part of a WMO/GAW report dealing with both CH₄ and N₂O. The report also contains a chapter on ISO terminology and definitions of terms relevant to trace gas measurements. Contributions and valuable advice from a number of colleagues within GAW, but also from metrological institutions are gratefully acknowledged. In response to a GAW request, this terminology section will also form a stand-alone document, with the aim of input from other GAW communities. Moreover, guidelines for audits are being prepared. For these future GAW documents, the WCC-N₂O has taken over coordinating functions.

The WCC-N₂O has contributed to most of the courses organised by the GAW Training and Education Centre since its inception. Because an urgent need of improving the general skills of data visualisation was identified, the lectures primarily addressed this issue. In line with the task of the WCC-N₂O to provide technical assistance to stations, exchange of expertise took place with two global stations. At one of them an upgrade of its N₂O instrumentation has been planned, while at the other N₂O measurements have just started.

In the near future activities of the WCC-N₂O will include finalisation of the individual guidelines for N₂O measurements, audits and terminology, respectively. Moreover, closer links to major networks using calibration scales other than the GAW scale need to be established with the aim of improving the comparability of N₂O results worldwide.
For brief information of a wider community, a WCC-N$_2$O home page has been set up: http://imk.fzk.de/wcc-n2o/. Further information on WCC-N$_2$O activities can be accessed via (i) http://www.wmo.ch/index-en.html, under GAW homepage/GAW 2005 Presentations, as well as (ii) http://www.cmdl.noaa.gov/ccgg/co2experts/ (Presentations, Abstracts).

Furthermore, the WCC-N$_2$O has contributed to recent WMO/GAW Reports:


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The GAW World Calibration Centre for Volatile Organic Compounds (WCC-VOC)
IMK-IFU, Garmisch-Partenkirchen

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Introduction
Volatil organic compounds (VOC) (often also referred to as non-methane hydrocarbons, NMHC) are recognized to be important precursors of tropospheric ozone as well as other oxidants and organic aerosols. The production of ozone and other photooxidants in the troposphere by reactions of volatile organic compounds (VOC), nitrogen oxides and sunlight is recognised as a serious global environmental problem becoming even more important considering Global Environmental Change. In consequence, monitoring of key VOC in a global network is of paramount importance for understanding the oxidative power including self-cleansing capacity of the lower atmosphere and changes induced by anthropogenic activities.

VOC and GAW
Tropospheric VOCs are one of the recommended measurements to be made at global sites under the Global Atmospheric Watch (GAW) programme of the World Meteorological Organization (WMO). They are an Integrated Global Atmospheric Chemistry Observations (IGACO) component of IGOS (Integrated Global Observing Strategy) and are considered to play major roles in (1) tropospheric air quality, (2) the oxidation capacity of the atmosphere, and in (3) chemistry-climate interactions.

For VOC data of adequate and known quality coordinated Quality Assurance and Quality Control (QA/QC) measures are required. A prerequisite is the establishment of a single VOC scale for tracing back standards used in calibration procedures. Therefore, the GAW Strategic Implementation Plan (WMO/GAW Report No. 111) has requested the establishment of a World Calibration Centre for VOC (WCC-VOC) as a central GAW facility. WCC-VOC is supposed to have the QA/QC responsibility. However, it will not maintain its own calibration scale, but will be linked to the GAW VOC scale to be established by a Central Calibration Laboratory (CCL) in analogy to other GAW trace gases (see Figure (WCC-N₂O)).

In order to achieve long-term good quality of the data reported from the GAW-VOC network, the WCC-VOC contributes by:

- Developing quality control procedures together with VOC experts.
- Ensuring traceability of standards to the GAW-VOC reference standard (scale).
- Conducting performance and system audits at stations.
- Performing round-robin experiments (intercomparisons).
- Supporting network-wide quality review.
- Providing training and long-term technical consulting to station scientists and technicians (e.g. through the GAW Training and Education Centre (GAWTEC)).

The GAW QA/QC procedures adhere to the following principles: (1) to use internationally accepted methods and vocabulary to describe uncertainty in measurements and (2) to harmonise measurement methodology at the stations by using approved measurement guidelines and standard operating procedures (SOPs). A “Performance Audit” is defined as a voluntary check for conformity of a measurement where the audit criteria are the Data Quality Objectives (DQOs) for a specific compound (see WMO-GAW Report No. 142). In the absence of DQOs, an audit should ensure a traceability of the reported values back to the scale. A “System Audit” is more generally...
defined as a check of the overall performance of a station related to QA/QC procedures of the GAW system.

The WCC-VOC is embedded in the GAW network as shown in Figure 1.

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**The WCC VOC within GAW**

*Global Atmosphere Watch (GAW)*

**GAW Central Facilities:**

- Scientific Advisory Groups (SAGs)
- Quality Assurance/Science Activity Centres (QA/SACs)
- World Calibration Centres (WCCs)
- World Data Centres (WDCs)

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**Figure 1:** The role of the WCC-VOC in the organisation chart of the GAW system.

The WCC-VOC was implemented at the Fraunhofer Institute IFU in Garmisch-Partenkirchen, Germany, in 2001. From 2002 onwards, the further activities of the WCC-VOC, being now hosted by the Forschungszentrum Karlsruhe, IMK-IFU (Garmisch-Partenkirchen), have been conducted under supervision and through funding of the Quality Assurance/Science Activity Centre (QA/SAC) Germany, operated by the German Environmental Agency (UBA) in Langen. The WCC-VOC was not officially operational as a new GAW facility within the GAW network before the formal approval by WMO GAW in November 2002. The internet homepage of the WCC-VOC ([http://imk-ifu.fzk.de/wcc-voc/](http://imk-ifu.fzk.de/wcc-voc/)) provides more information.

**The WCC-VOC Data Quality Objectives**

The WCC-VOC has suggested Data Quality Objectives (DQOs; WMO Report 111, WMO-GAW, 1995) and Standard Operating Procedures (SOP) for canister sampling (see GAW-WCC-VOC Final Report 2002-2004, UBA, Germany) which are still awaiting official approval by the Scientific Advisory Group for Reactive Gases (SAG RG).

Currently, the WCC applies the DQOs suggested in WMO Report (1995). In Table 1 the DQOs are listed according to the specific VOC class. For the non-methane hydrocarbons (NMHCs) listed in the table standards which are traceable to the National Institute of Standards and Technology (NIST) are available for ethane, propane, acetylene, isoprene, benzene, toluene, n-butane, iso-butane, n-pentane, iso-pentane, and α-pinene. With the improvement of analytical
techniques and sampling methods (flask sampling, continuous) DQOs will be adjusted, e.g. for some VOCs analysed by the proton transfer-reaction-mass-spectrometry precision levels of 5% can be achieved.

**Table 1:** Data quality objectives for VOC to be achieved by GAW stations as suggested in the WMO Report 111 (1995).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Accuracy</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>Alkenes</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>Alkynes</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>Aromatics</td>
<td>15%</td>
<td>10%</td>
</tr>
<tr>
<td>Alcohols</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>Ethers</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>20%</td>
<td>10%</td>
</tr>
<tr>
<td>Ketones</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>Organic Acids</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>Esters</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>mixing ratio &lt; 0.1 ppb</td>
<td>50%</td>
<td>50%</td>
</tr>
</tbody>
</table>

Currently, the facilities at WCC-VOC for grab sample VOC analysis consist of a sample preparation unit including sample injection, water removal, and pre-concentration, and an analytical system. To ensure uninterrupted analysis, two systems are in operation.

**The WCC-VOC Reference Method and Standard**

Basically, the WCC-VOC reference method follows a GC method as proposed by Habram et al. (1998). The detection limit is between 10-15 pptv for most compounds for sample volume of 400 ml.

The current mode of operation of the WCC-VOC addresses the stage 1 and some stage 2 compounds as outlined by the WMO-Report No. 111, 1995. The WCC-VOC standard now contains 73 species in N₂ (prepared and certified by E. Apel, NCAR) in the mixing ratio range from 170 pptv (i-propylbenzene and 3-ethyltoluene) to 11.30 ppbv (ethane). 21 VOCs are traceable to NIST. This calibration gas mixture also includes those VOCs recommended in the WMO-GAW Report 111 (Table 2).

**Table 2:** Minimum set of VOCs in the WCC-VOC-Standard as suggested in WMO-GAW Report 111.

<table>
<thead>
<tr>
<th>Ethane</th>
<th>Trans 2 Pentene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>Cis 2 Pentene</td>
</tr>
<tr>
<td>Ethyne</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>Propane</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>Propene</td>
<td>2 Methylpentane</td>
</tr>
<tr>
<td>Propyne</td>
<td>3 Methylpentane</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Isoprene</td>
</tr>
<tr>
<td>2 Methylpropane</td>
<td>n-Heptane</td>
</tr>
<tr>
<td>Compound</td>
<td>Compound</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>2 Methylpropene</td>
<td>Benzene</td>
</tr>
<tr>
<td>Trans 2 Butene</td>
<td>Toluene</td>
</tr>
<tr>
<td>Cis 2 Butene</td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>1 Butene</td>
<td>1, 2 Xylene</td>
</tr>
<tr>
<td>1, 3 Butadiene</td>
<td>1,3 Xylene</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>1,3,5 Trimethylbenzene</td>
</tr>
</tbody>
</table>

**WCC-VOC Intercomparisons and Audits**

In 2003 the WCC-VOC conducted a first intercomparison for VOC among 9 different stations/laboratories (10 instruments) from 7 countries (Brazil, Canada (2 labs), Czech Republic, Finland, Germany (2 labs; 3 instruments), Ireland, and Slovakia), representing 4 measurement programmes (GAW, EMEP, CAPMoN, LBA). These sites either run canister or online measurements. Contrary to previous studies (Apel et al., 1994, 1999, 2003; Romero, 1995; Solberg et al., 1995; Slemr et al., 2002) it is the first worldwide experiment considering both systems.

From the results of the intercomparison it appears imperative to strengthen harmonization procedures. The intercomparison also confirmed that only two separate gas chromatographic systems, one focusing on low volatile species and one focusing on high volatile compounds, are capable to cover the entire suite of C₂-C₁₄ VOCs. Future activities should include frequent intercomparisons with less VOC (5-10) on a more rigorous time schedule basis. Also the exchange of canisters for concurrent air sampling and subsequent mutual analysis among different laboratories is strongly recommended.

For elucidating and solving possible problems in VOC-analysis and reporting, systems and performance audits were conducted at the GAW stations Arembepe (Brazil) and Pallas (Finland), and the regional station Starina (Slovakia).

**WCC-VOC Training and Consulting**

The WCC-VOC has given specific VOC training courses focusing on lectures and practical exercises related to techniques and problems of VOC analysis in air samples, QA/QC procedures, data analysis and reporting organised by GAWTEC. As GAW is further extending its network, WCC-VOC has been in the process of advising Mexican scientists on GAW procedures for VOC analysis and suggested recommendations for improvements which will help to establish a future operation centre in Mexico.

**WCC-VOC and other QA/QC Programmes**

Within the scope of the ACCENT (Atmospheric Composition Change: European Network of Excellence) programme an intercomparison focusing on oxygen containing VOC was performed in the SAPHIR-Chamber of the Research Centre of Jülich. 12 groups including the WCC-VOC participated in this intercomparison with a variety of different instruments covering the whole range from standard techniques to newly developed methods. The aim of the WCC-VOC participation was (1) to learn about different methods used for analysing oxygenated VOC in ambient air, (2) to evaluate the performance of those different methods, and (3) to learn how oxygenated VOCs can be properly quality assured. First results demonstrate that the HANTZSCH-Method of the WCC-VOC is excellently suited to quantify down to sub-ppb levels of formaldehyde in ambient air samples.
**GAW-Meetings**

At the GAW 2005 workshop in Geneva in March 2005 a VOC Expert Group embedded in the SAG RG was founded with the head of the WCC-VOC as a founding member.


A WMO-GAW-VOC Expert Workshop was performed in Geneva in order to discuss the current and future GAW-VOC programme aiming at setting up a revised GAW-VOC Activity plan for 2008 to 2014. The upcoming GAW-VOC network will focus on two air sampling techniques; (1) off-line grab sampling with subsequent analysis in central laboratories and (2) on-line analysis of VOC at selected stations. Further the VOC compound list to be reported by the GAW-VOC stations was adjusted and now also includes heterogeneous hydrocarbons containing oxygen, nitrogen as well as sulphur atoms (Table 3).

### Table 3: Recommended VOC list to be reported from GAW-Stations in the future.

<table>
<thead>
<tr>
<th>Compound</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>Acetone</td>
</tr>
<tr>
<td>Propane</td>
<td>DMS</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Benzene</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Toluene</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Iso-Butane</td>
</tr>
<tr>
<td>Selected Monoterpenes</td>
<td>n-Butane</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>Iso-Pentane</td>
</tr>
<tr>
<td>Methanol</td>
<td>n-Pentane</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
</tr>
</tbody>
</table>

**Future**

The upcoming activities will include: (1) continuous operation of the WCC-VOC, (2) maintaining standards of different rank linked to the scale (3) performing round robin exercises and station audits, (4) training station personnel in the frame of GAWTEC courses and on-site visits, (5) cooperation with the RG-VOC group, the SAG RG and the World Data Centres (WDCs) and other VOC programmes.

**References**


****
80 years ago the Dobson Spectrophotometer was developed by the British Prof. G.M.B. Dobson in Oxford. In the course of the following decades the first small network of 6 Dobsons in 1926 expands to a global network of temporarily more than 100 instruments. This network formed the basis of the currently existing WMO Global Ozone Observing System within the GAW programme. The demand for high quality data (reliable trend analyses and validation of satellite borne instruments) lead to the development of a well organized calibration system of one World and several Regional Dobson Calibration Centre (WDCC and RDCC) (Figure 1).

This system of Regional Dobson Calibration Centres (RDCC) is a GAW infrastructure that has been created after two decades of the successful implementation of regular Dobson calibration campaigns carried out by the World Dobson Calibration Centre (WDCC) acting at the NOAA/GMD, Boulder, CO.

Main purposes of the system are:

- To transfer the calibration scale defined by the World Primary Dobson Spectrophotometer D083 (WPDS) into the Dobson part of the GAW ozone monitoring network through regional intercomparisons of spectrophotometers.
- To assist in maintenance of Dobson instruments in the regions by technical services, spare parts or expert missions.
- To implement new technologies and GAW rules, e.g. QA procedures, software and IT tools for processing of observations and data transfer.

The RDCC for Europe was established in 1999 and has been run in the past seven years by the Meteorological Observatory Hohenpeissenberg (Germany) in close partnership with the experts from the Solar and Ozone Observatory Hradec Kralove (SOO-HK), Czech Republic. In the meanwhile 39 Dobsons (10 twice) out of 18 countries have successfully been calibrated in 12
campaigns (11 at MOHp (Figure 2), 1 at Arosa). Approximately 10 of these instruments were completely refurbished too, among them three Dobsons of the British Antarctic Survey being normally located at the South Pole. Unfortunately the supply with spare parts got into stagnation after the manufacturer of the Dobson, Beck-Ealing in London stopped the production in the nineties. In the last years, however, several suppliers for important optical, mechanical and electronical parts like mirrors, shutter motors and microamperemeters could be found to solve this problem. In addition new electronics, mechanical parts of the optical wedge or the sun director are developed and/or produced in the workshops of Boulder, Hohenpeissenberg or Hradec Kralove. New test and calibration tools like the Hohenpeissenberg semi-automated wedge calibrator were designed and constructed, which relieve the calibration work significantly.

The success of the Dobson calibration system can be seen in Figure 3. All instruments coming to an intercomparison have to undergo an initial calibration to determine the state of their calibration before any work is done. Since the mid eighties, when regular intercomparisons with a 4- to 5-years cycle were started, the relative difference of the Dobsons to the reference instruments dropped significantly. For the majority of the instruments it is now close or even below the ±1%-quality limit.

**Figure 2:** Dobson experts at calibration work on the platform at Hohenpeissenberg.

**Figure 3:** Evolution of the relative differences of the Dobson instruments to the reference Dobson at the initial calibration, i.e. before any instrumental change has been applied.
These efforts enabled the creation of a large number of long, homogeneous and reliable Dobson data records all over the world, some of them now longer than 30 or 40 years. Thus the Dobson instruments still form a major backbone of the global ozone monitoring network in the WMO/GAW observation programme. Despite of the introduction of modern instruments like the Brewer Spectrophotometer trend analyses and satellite validation are unimaginable without this seasoned instrument.
The GAW Quality Assurance/Science Activity Centre (QA/SAC) Germany

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\texttt{k.mannschreck@schneefernerhaus.de}

The primary goal of the GAW quality assurance (QA) activities is the delivery of scientifically sound data sets that can be used for assessing the contribution of the changing atmosphere to climate change and related environmental issues, and finally for making public policy decisions. In order to facilitate this the data must be consistent, meet the GAW data quality objectives and be supported by meta data.

The great challenge for the GAW QA system is that the GAW programme integrates the contributions from a number of national meteorological and hydrological services and research institutes. The QA system is built around Quality Assurance/Science Activity Centres (QA/SACs) which usually have global scope as defined in the most recent edition of the GAW Strategic Plan (Strategic Plan 2000-2007, GAW report No. 142) and are responsible for specific atmospheric parameters.

Based on the commitment of Germany to the World Meteorological Organisation to establish and run a QA/SAC, the ‘Umweltbundesamt’ (UBA, Federal Environment Agency) of Germany has assumed responsibility for QA/SAC Germany on a long-term basis in June 2000. UBA had temporarily contracted its operation to the ‘Forschungszentrum Karlsruhe GmbH, Institut für Meteorologie und Klimaforschung - Bereich Atmosphärische Umweltforschung’ (IMK-IFU, Research Centre Karlsruhe, Atmospheric Environmental Research Division, formerly Fraunhofer Institute for Atmospheric Environmental Research, IFU) during the implementation and starting phase. Since December 2001 UBA has continued the operation of QA/SAC Germany under own management.

QA/SAC Germany has the worldwide responsibility for the quality assurance of physical properties of aerosols, volatile organic compounds and nitrous oxide. For each of these compounds World Calibration Centres (WCCs) were established and are funded by QA/SAC Germany. The main tasks of QA/SAC Germany are to

- Develop Standard Operating Procedures (SOPs) for the compounds indicated above together with the respective WCCs and to help to implement them at GAW sites.
- Co-ordinate data quality assessments of these parameters by means of regular system and performance audits, laboratory intercomparisons and data reviews.
- Provide training and long-term support for station personnel, especially in countries with limited national funding resources.
- Co-ordinate these activities with other QA/SACs.

An integral part of QA/SAC Germany is the GAW Training and Education Centre (GAWTEC) run at the Umweltforschungsstation Schneefernerhaus (UFS, Environmental Research Station) on the Zugspitze, the highest mountain of Germany. Since 2004 GAWTEC is funded by UBA (60%) and the State of Bavaria (40%).

Information on QA/SAC Germany, the three associated WCCs and GAWTEC as well as the German contributions to GAW and the GAW programme can be found on the homepage of QA/SAC Germany: http://www.umweltbundesamt.de/uba-info-daten/daten/gaw.
GAWTEC, the GAW Training and Education Centre, has been established in 2001 to support the QA/SAC Germany in its quality assurance and capacity building tasks. GAWTEC is located at the 'Umweltforschungsstation Schneefernerhaus' (UFS, Environmental Research Station Schneefernerhaus), which among other research activities hosts the high-alpine branch of the GAW-Global Station Zugspitze-Hohenpeissenberg, and is managed by the UFS Ltd.

GAWTEC offers twice a year courses on measurement techniques, analytical analysis, and data handling to GAW station personnel from all over the world. Courses take two weeks, focus on practical work with instruments, and are limited to 10-12 participants for maximum benefit. Training lessons are given mainly by experts from the 'Deutsche Wetterdienst' (DWD, German Weather Service), especially the meteorological observatory Hohenpeissenberg, the 'Umweltbundesamt' (UBA, Federal Environment Agency) and the UBA-financed WCC-N₂O, WCC-VOC (both at FZK-IFU, Garmisch-Partenkirchen) and WCC-AP (Institut für Troposphärenforschung, Leipzig), and the Swiss WCC for Surface Ozone, CO and CH₄, hosted by EMPA and funded by MeteoSwiss. For coverage of special topics GAWTEC can rely on additional teachers from inside and outside the GAW community; almost regular support comes from QA/SAC Americas, WORCC Davos and German universities, while just recently NOAA's CMDL provided training in greenhouse gases.

The specific objectives for each course are determined in agreement with the WMO/GAW secretary and depend on actual station needs that are reported from WCC audits and known from personal questionnaires. Major topics are measurement techniques for aerosols, carbon monoxide, surface ozone, precipitation (including chemical analysis), radiation (including UV broadband instruments), VOCs, and greenhouse gases. Data handling and data quality assurance are essential parts of all courses.

Courses generally cover two main topics and focus on the improvement of personal skills in measurement techniques, data handling and data evaluation, the demonstration and application of methods for error and malfunction detection, identification and solution, and the enhancement of personal ability for data interpretation by expanding the understanding of atmospheric processes. Most of the time trainees and teachers stay together at the UFS allowing for open-end exercises and discussions, special lessons are given at the nearby WCCs or the observatory Hohenpeissenberg.

The participation is free of charge. Flight costs for trainees are covered by WMO, full board and local travels provided by GAWTEC, which until 2004 was funded exclusively by the Bavarian Ministry for the Environment. Since then GAWTEC is part of the QA/SAC Germany and therefore operates now mainly through funds from UBA, but is still assisted by grants from the State of Bavaria.

Courses are offered primarily to GAW station staff (technicians and junior scientists) working at Global and Regional stations. Experience however has shown that also staff from central facilities may need and require specific GAW QA training. Quite often there is no clear distinction between station and laboratory staff, and in many countries central or regional GAW-
associated laboratories are in charge of on-site calibration and even in-situ measurements. Moreover, personnel from central facilities often oversee several stations and therefore are ideal multipliers for QA measures.

Figure 2: Origin of trainees (courses I-XI) by affiliation (left) and WMO regions (right).

Including the training session in May 2006, 11 courses were held, in which 121 trainees from 47 countries (Table 1) participated. Major topics were surface ozone (in 6 courses), physical aerosol properties (4), precipitation chemistry (4), carbon monoxide (3), VOCs (2), radiation inclusive UV-B-broadband instruments (3), and greenhouse gases (1).

Table 1: Countries involved in GAWTEC courses I-XI.

<table>
<thead>
<tr>
<th>Algeria</th>
<th>France</th>
<th>Morocco</th>
<th>Slovenia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argentina</td>
<td>Hungary</td>
<td>Nigeria</td>
<td>South Africa</td>
</tr>
<tr>
<td>Australia</td>
<td>Indonesia</td>
<td>Pakistan</td>
<td>Spain</td>
</tr>
<tr>
<td>Belarus</td>
<td>Jordan</td>
<td>Paraguay</td>
<td>Thailand</td>
</tr>
<tr>
<td>Brasil</td>
<td>Kazakhstan</td>
<td>Philippines</td>
<td>Tunisia</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>Kenya</td>
<td>Poland</td>
<td>Turkey</td>
</tr>
<tr>
<td>Chile</td>
<td>Latvia</td>
<td>Portugal</td>
<td>Ukraine</td>
</tr>
<tr>
<td>China</td>
<td>Lithuania</td>
<td>Republic of Korea</td>
<td>United Arab Emirates</td>
</tr>
<tr>
<td>Croatia</td>
<td>Macedonia</td>
<td>Romania</td>
<td>Uruguay</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>Malaysia</td>
<td>Russian Federation</td>
<td>Uzbekistan</td>
</tr>
<tr>
<td>Estonia</td>
<td>Moldova</td>
<td>Serbia &amp; Montenegro</td>
<td>Yugoslavia</td>
</tr>
<tr>
<td>Finland</td>
<td>Mongolia</td>
<td>Slovakia</td>
<td></td>
</tr>
</tbody>
</table>

GAWTEC also provides technical help to stations. In two courses portable instruments were intercompared at the UFS and then, if needed, checked and re-calibrated at no costs for participants: UV broadband sensors at NOAA's Central UV Calibration Facility, particle counters at the WCC-AP. On request, however to limited extent, also an emergency on-site assistance is available. By sending experts direct support was provided to the Air Chemistry Lab at the Federal Hydrometeorological Institute in Belgrade and the Global Station Ushuaia, the latter one combined with short training courses at the RCC for Surface Ozone at Buenos Aires (attended also by staff from GAW stations in Chile, Paraguay, and Uruguay) and the Regional Station La Quiaca.

Besides the training aspect GAWTEC considers itself an ideal platform to strengthen corporate identity, where especially station staff experience that without their devoted work GAW's global approach would not work.

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GAW DACH is a joint co-operation between the German ("D"), Austrian ("A") and Swiss ("CH") Meteorological Agencies DWD, ZAMG and MeteoSwiss. Further project partners are the German Umweltbundesamt (Federal Environment Agency), the Austrian Umweltbundesamt, the Institute for Analytical Chemistry (University Vienna), the Institute for Meteorology and Physics (Agricultural University Vienna), and the Swiss Federal Laboratory for Materials Testing and Research (EMPA). DWD is hosting this co-operation. The DACH project aims at co-ordinating the national monitoring activities within the GAW programme among the GAW Global Stations Zugspitze/Hohenpeissenberg, Jungfraujoch (Switzerland) and the Regional Station Sonnblick (Austria). These alpine observatories have a long history of measuring physical and chemical parameters in the atmosphere and are situated at distances and elevations that allow for comparing the concentrations of trace substances in the air within a wide range of lifetimes (Figure 1).

The main objectives of this co-operation are

- To guarantee comparability of the data through quality control and use of common standards.
- To build a common data base.
- To investigate the spatial representativeness of the data.
- To develop filters for extracting data with extended spatial representativeness from the dataset.

An important goal of GAW is the early detection of large scale changes in atmospheric chemistry that have a potential for affecting weather and climate. Filter functions taking into account meteorological and chemical processes have turned out to be an important tool for detecting those trends earlier and more reliably. By combining data from the four stations, such trend analyses can be improved and made more representative in space. Continental monitoring sites in complex terrain affected by relatively close highly populated and industrialized regions should therefore co-operate for a representative picture of the area.
Results from the DACH co-operation have been published in Fricke et al. (2000). They show that there is still room for further development and improvement of the filters. Their elaboration has led to new findings, but also revealed some shortcomings that need further clarification. Most promising at the alpine stations are filters that consider meteorological processes, especially if not only local stability criteria are used but also trajectory information for detection of periods with influence from the boundary layer is applied.

The DACH co-operation is a promising model of cooperation with and among other GAW stations. It serves for data quality, which is an inevitable prerequisite for data evaluation and interpretation. On the long run, the continuous exchange of experience associated with this cooperation leads to a harmonization of monitoring techniques and programmes, since unnecessary measurements can be pointed out and additional measurements necessary for the aims of GAW are identified. The way of co-operation within the DACH project can therefore serve as a general model of linking stations with the aim of characterizing a whole region with respect to atmospheric chemistry.

Beyond the production of high quality data the development of filters for extended representativeness of data has contributed to a deeper understanding of the specific conditions at the participating stations and to the identification of processes influencing the observed concentration profiles and thus having a potential for affecting climate (see Section B, Fricke and Gilge).

References

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More than 40 million people in 115 major European urban areas are estimated by the European Environment Agency to be exposed to pollutant levels exceeding WHO standards, often during severe short-term pollution episodes. The EU FP5 project FUMAPEX (Integrated Systems for Forecasting Urban Meteorology, Air Pollution and Population Exposure, 2002-2005) thus aimed at improving the meteorological forecasts for urban areas, the connection of numerical weather prediction (NWP) models to urban air pollution and exposure models, the building of improved urban air quality and information systems and their application to cities in various European climates. The 'Deutsche Wetterdienst' (DWD, German Weather Service) participated in improving and evaluating high-resolution NWP and dispersion models employed in emergency systems and for various public and private end users.

The quality of the meteorological data is expected to improve through using downscaled data from advanced ‘urbanised’ NWP models. Thus in step one, the operational DWD non-hydrostatic NWP model Lokalmodell (LM, and its Italian version LAMI of the Bologna ARPA-SMR partners) was downscaled from the operational 7km to about 1km by multiple model nesting and validated for 10 pollution episodes in Helsinki, Oslo, Valencia and Bologna.

Like in the other models evaluated during a model inter-comparison led by DWD (several HIRLAM versions, RAMS, MM5, LM), only increasing model resolution to about 1 km in the LM usually shows little effect, with some progress for coastal and near-mountain stations mainly due to the improved land-sea mask, corresponding soil parameters (Figure 1 left) and model topography. The LM (as other models) apparently performs better in predicting the meteorologically frequent conditions of summer ozone episodes than the sometimes extreme winter / spring inversion episodes in Scandinavia, but also in the Po valley. As for all models involved, the poorest model performance is confirmed for LM for the winter inversion episodes due to well-known model deficiencies in forecasting extreme temperature inversions and (very) stable conditions (Figure 1 right).

**Figure 1:** Left: LM 48h forecast of 2m temperature for 7,2,8,1.1km resolution, and observations, for 23 Mar 1998, 00UTC, Helsinki coastal station Kaisaniemi. Right: Heat island effect drifted downwind from city, 1.1km LM MH forecast for 10 Apr 2002 +36h, Helsinki area (4 black dots = city obs stations), in m above model orography. Left: non-urbanised operational version, right: urbanised physiograph. parameters and anthrop. heat source of 60W/m².
For Bologna, deficiencies in temperature and wind forecasts are also due to an inherently complex location at a highly variable border between Apennine mountain wind regime and larger-scale Po valley circulation. When large temperature gradients prevail (also for Scandinavian winter episodes with cold land/warm sea), false wind speed and direction forecasting may cause erroneous temperature advection and deteriorate the forecast performance (Fay and Neunhäuserer, 2005b). The results of the other models often resemble the LM ones (Fay et al., 2005a, 2006). The LM/LAMI was the only model tested in all above target cities covering climates as different as Scandinavian and Mediterranean. Its performance was medium to best for the various parameters and criteria considered in the model inter-comparison.

First urbanisation steps were applied to LM by introducing urbanised physiographic parameters and an anthropogenic heat source (Neunhäuserer et al., 2005, 2006). The definition of a soil type ‘city’ along with corresponding changes of hydrothermic properties and an added anthropogenic heat source influence the surface heat and water budgets and the dynamics. A sensitivity study for a Helsinki spring dust episode showed a distinct heat island effect (up to 7°C in surface temperature), improved urban fluxes and general model results compared to measurements even through these simple urbanisation measures.

The DWD mixing height (MH) scheme (based on the LM turbulence scheme and run operationally for MH dissemination to end users) was tested for the above air pollution episodes. The results (Fay and Neunhäuserer, 2005a) show a very distinct improvement due to the highly resolved topography. The non-urbanised scheme generally performs well for daytime mixing heights for the FUMAPEX episodes in different climates and seasons. It does, however, fail (like other schemes) for very strong stability and extreme and shallow inversions persisting even during daytime as in the Helsinki Dec 1995 episode, confirming the need of improvements. The urbanised LM input data led to realistically increased mixing heights above the city and even many kilometres downwind for the Helsinki spring episode (Figure 1 right) without actually adapting or urbanising the LM turbulence scheme or the MH module themselves, but just by incorporating the urbanised LM results into the MH scheme.

The DWD trajectory model (TM) and the Lagrangian particle dispersion model (LPDM) were tested for the above pollution episodes. In mountainous Valencia and Oslo, dispersion simulations are very sensitive to grid resolution, the 1.1 km simulations generally showing improved topographic influence (channelling, blocking, improved mesoscale circulations) compared to the 7 km forecasts. Increased turbulence and vertical velocity enlarge the general dimensions of the LPDM plume, show the effect of the increased land-sea circulation (Figure 2) and partially large local impacts of urbanisation measures on the concentration distribution.

Figure 2: Vertical cross-sections of LPDM plume above Helsinki (coast at right margin), 10 Apr 2002, UTC, left: original, right: urbanised physiographic parameters plus 60W/m² anthropogenic heat source above city: increased sea breeze effect.
In conclusion, FUMAPEX successfully advanced the introduction, evaluation and urbanisation of high-resolution versions of the NWP Lokalmodell and dispersion models at the DWD. Episode and sensitivity studies show that these models are consistently formulated without the need of intermediate interface modules so that even simple urbanisation steps in the LM lead to distinctly urban results including the urban heat island effect in all models. The comprehensive model evaluation and inter-comparison co-ordinated by the DWD highlights the already existing potential of mesoscale models in forecasting pollution episodes, the deficiencies especially in stable inversion situations and recommended improvements in scale-adapted and urbanised parameterisations.

References


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CARIBIC: Routine Atmospheric Chemistry Observations from a Lufthansa Commercial Aircraft

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CARIBIC i.e. Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrumented Container (www.caribic.de) is a long term project designed to carry out atmospheric chemistry research using an airfreight container (1.5 ton gross weight) packed with analysers and air sample collection equipment that operate automatically during intercontinental flights onboard of a Lufthansa Airbus A340-600. A forerunner of CARIBIC has been in operation using a LTU Airways Boeing between 1997-2002. With the new extended CARIBIC-LUFTHANSA system (in operation since December 1994) a time horizon of 10 years is projected. Essential is that each monthly flight occasion provides an extensive data set for research purposes, and that over the years systematic, coherent monitoring can be conducted.

The analytical capabilities of CARIBIC are listed in Table 1. From this table it can be gleaned that CARIBIC constitutes a fully fledged flying observatory indeed. Gas phase and particle measurements are carried out with considerable detail. Even remote sensing using a miniature DOAS system is incorporated. Thus, in addition to land based observatories where in situ measurements are carried out, and/or remote sensing is done, CARIBIC offers a flying observatory. The great benefit is that regions of the atmosphere from which traditionally little information is gathered systematically, or none at all, can now be probed regularly. The fact that the UTLS can be regularly investigated, including the effects of convection on mixing and chemistry is a major advantage of CARIBIC.

Table 1: Instrumentation of the new CARIBIC container onboard a Lufthansa A340-600.

<table>
<thead>
<tr>
<th>Trace Constituent</th>
<th>Equipment/Analyser</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. O₃ fast</td>
<td>Chemiluminescence on an organic dye</td>
</tr>
<tr>
<td>2. O₃ precise</td>
<td>UV absorption</td>
</tr>
<tr>
<td>3. CO</td>
<td>VUV fluorescence</td>
</tr>
<tr>
<td>4. H₂O gaseous</td>
<td>Diode laser photo acoustic</td>
</tr>
<tr>
<td>5. H₂O total</td>
<td>Diode laser photo acoustic and chilled mirror</td>
</tr>
<tr>
<td>6. NO</td>
<td>Chemiluminescence with O₃</td>
</tr>
<tr>
<td>7. NOy</td>
<td>Chemiluminescence after conversion to NO</td>
</tr>
<tr>
<td>8. Hg</td>
<td>Enrichment and atomic fluorescence</td>
</tr>
<tr>
<td>9. CO₂</td>
<td>Non-Dispersive Infrared Absorption (NDIR)</td>
</tr>
<tr>
<td>10. O₂ ultra high precision</td>
<td>Electrochemical Cells</td>
</tr>
<tr>
<td>11. Methanol, acetone, acetaldehyde</td>
<td>Proton transfer mass spectrometer (PTR-MS)</td>
</tr>
<tr>
<td>12. Aerosol particles with diameter &gt;4 nm</td>
<td>Condensation particle counter (CPC)</td>
</tr>
<tr>
<td>13. Aerosol particles with diameter &gt;12 nm</td>
<td>Condensation particle counter (CPC)</td>
</tr>
<tr>
<td>14. Aerosol particles with diameter &gt;18 nm</td>
<td>Condensation particle counter (CPC)</td>
</tr>
<tr>
<td>15. Aerosol size distribution 150 - 5000 nm</td>
<td>Optical particle counter (OPC)</td>
</tr>
<tr>
<td>16. Aerosol elemental composition</td>
<td>Impactor collection, analysis by PIXE</td>
</tr>
<tr>
<td>17. Particle morphology</td>
<td>Impactor collection, analysis by electron microscope</td>
</tr>
<tr>
<td>18. Samples for VOC</td>
<td>Enrichment and analysis by GC-MS</td>
</tr>
<tr>
<td>19. Hydrocarbons, halocarbons, GHGs</td>
<td>Whole air sampler and analysis by GC</td>
</tr>
<tr>
<td>20. BrO, HCHO, OCIO, O₃</td>
<td>Differential optical absorption spectroscopy (DOAS)</td>
</tr>
<tr>
<td>21. Cirrus (under certain conditions)</td>
<td>Camera</td>
</tr>
</tbody>
</table>
It is well known that good advances are made in tropospheric measurements using satellite based remote sensing. Several important species can thus be gauged on a truly global scale. This way of atmosphere observation will no doubt become a major pillar of atmospheric monitoring, even though satellite equipment does have a limited lifetime, and not all wishes of atmospheric chemists can be fulfilled in this respect.

IGACO is an approach that is designed to construct a rational system for global scale atmospheric chemistry and composition monitoring. It embraces land based station, regular aircraft flight (MOZAIC, CARIBIC), and satellites. In the future GAW will use the IGACO approach more explicitly, which will lead to a system better tuned for future requirements. Based on this development it is clear that CARIBIC can play a regular significant role in the IGACO approach. Basically, as stated above, a flying observatory has been developed, that fills the gap between surface and space measurements.

CARIBIC has 11 science partners from 6 European countries. Contributions from these partners, supplemented with funding from the Max Planck Society, the European Union and Industry for a sufficiently firm basis for the routine operation of CARIBIC over the years to come. The photographs show the inlet system and the measurement container.

**Figure 1:** The new CARIBIC inlet mounted on Airbus 340-600 of Lufthansa.

**Figure 2:** The new CARIBIC container in the cargo bay of A340-600 (3.2 x 1.6 x 1.5 m, 1450 kg).
B. SELECTED RESEARCH RESULTS:  
FOREWORD

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This section of the report comprises selected research and monitoring results from WMO-GAW atmospheric chemistry observatories in Germany. They include long term trends going as far back as 40 years but mostly dealing with the last decade and a half since GAW was created and a more extensive programme was established. All of the atmospheric constituents measured are directly or indirectly affecting our living conditions through air quality, weather and climate.

While most of the temperature records commonly used in climate research do not date back further than about 1860, the Hohenpeissenberg record started in 1781 (Figure 1), making it the oldest meteorological mountain observatory in the world with continuous mercury thermometer measurements to date. The record shows a period of high annual average temperatures around 1800. This anomaly is only found at stations within a radius of some hundred kilometres south and east of Hohenpeissenberg, e.g. Innsbruck and Vienna. It is neither apparent in other areas of Central Europe nor in the average for the northern hemisphere. After 1880 the Hohenpeissenberg temperature record closely follows the global temperature trend.

For a better understanding of the physical and chemical interrelations resulting in the temperature increase, many contributing factors - natural and anthropogenic - must be taken into account. Knowledge of the long-term records of many components is therefore essential. It can only be hoped that selected atmospheric chemistry observations begun at Hohenpeissenberg in the last half of the 20th century will enjoy the continuity of support that has produced this temperature record spanning over two centuries.

Figure 1: Time series of annual average temperature at Hohenpeissenberg since 1781 (thin red line). The thick red line is a low-pass filter.

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Measurement of Reactive Trace Gases at Hohenpeissenberg as Part of GAW

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Besides the Greenhouse Gases the Reactive Gases are of enormous importance for tropospheric chemistry and climate change. The "Strategy for the Implementation of the Atmosphere Watch Programme (2001-2007)", GAW-Report No. 142, highly recommends the measurement of reactive trace gases, especially surface ozone, carbon monoxide, volatile organic compounds and nitrogen oxides.

On basis of these recommendations the German weather service at the Meteorological Observatory Hohenpeissenberg developed an appropriate measuring programme since 1995 (ground based ozone since 1972); extended by distinct parameters, which are important for some fields of atmospheric research like acid rain, summer smog episodes or oxidation capacity of the atmosphere.

The measuring programme of the reactive trace gases, with exception of the volatile organic compounds and the measurement of the OH radical, which are described separately in this issue (see Ch. Plass-Duelmer and H. Berresheim) is summarized in Table 1.

Table 1: Monitoring techniques, time resolution and calibration techniques of reactive trace gases at Meteorological Observatory Hohenpeissenberg.

<table>
<thead>
<tr>
<th>Component</th>
<th>Monitoring technique</th>
<th>Company</th>
<th>Time res.</th>
<th>Status</th>
<th>Calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>ozone (O$_3$), surface (2x)</td>
<td>UV-absorption</td>
<td>TECO 49 C</td>
<td>10 min</td>
<td>operational</td>
<td>1/month with transfer standard Teco 49PS (U.S. O$_3$reference standard)</td>
</tr>
<tr>
<td>ozone (O$_3$), surface</td>
<td>Chemiluminescence</td>
<td>UPK (Bendix)</td>
<td>10 min</td>
<td>operational</td>
<td></td>
</tr>
<tr>
<td>ozone (O$_3$), surface</td>
<td>Electro chem. / KI</td>
<td>self built</td>
<td>10 min</td>
<td>operational</td>
<td></td>
</tr>
<tr>
<td>Sulphur dioxide (SO$_2$)</td>
<td>Fluorescence</td>
<td>TE 43 S</td>
<td>10 min</td>
<td>operational</td>
<td>1/week with calib. gas (Messer Griesheim), dynamical dilution with MFC</td>
</tr>
<tr>
<td>carbon monoxide (CO)</td>
<td>Gasfiltercorr. / cat. Zero air</td>
<td>TE 48 S /self built</td>
<td>10 min</td>
<td>operational</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Res.-fluorescence</td>
<td>Aero Laser</td>
<td>10 min</td>
<td>operational</td>
<td>2/day with calib. Gas</td>
</tr>
<tr>
<td>Nitrogen oxide (NO)</td>
<td>Chemiluminescence with O$_3$</td>
<td>ECO-Physics CLD 770AL ppt</td>
<td>10 min</td>
<td>operational</td>
<td>every 2$^{nd}$ day with calib. gas (MG) / MFC</td>
</tr>
<tr>
<td>Nitrogen oxide (NO)</td>
<td>Chemiluminescence with O$_3$</td>
<td>ECO-Physics CLD 770AL ppt</td>
<td>10 min</td>
<td>operational (backup)</td>
<td>every 2$^{nd}$ day with calib. gas (MG) / MFC</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO$_2$)</td>
<td>Photolysis converter/chemiluminescence</td>
<td>ECO-Physics PLC/CLD</td>
<td>10 min</td>
<td>operational</td>
<td>every 2$^{nd}$ day with gas phase titration (GPT)</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO$_2$)</td>
<td>Blue light converter/chemiluminescence</td>
<td>Droplet Meas. / TE 42 C TL</td>
<td>10 min</td>
<td>operational (backup)</td>
<td>1/week with GPT</td>
</tr>
<tr>
<td>Nitrogen oxides (NO$_x$)</td>
<td>Molybdenum conv. / chemiluminescence</td>
<td>TE 42 C TL</td>
<td>10 min</td>
<td>Operational</td>
<td>1/week with GPT</td>
</tr>
<tr>
<td>sum reactive nitrogen oxides (NOy)</td>
<td>Gold converter / chemiluminescence</td>
<td>self built</td>
<td>10 min</td>
<td>operational</td>
<td>every 2$^{nd}$ day with GPT</td>
</tr>
<tr>
<td>Peroxyacetylnitrile (PAN)</td>
<td>GC / ECD</td>
<td>Meteorologieconsult</td>
<td>6 / hour</td>
<td>operational</td>
<td>1/week with acetone photolysis, GPT &amp; dilution with MFC</td>
</tr>
<tr>
<td>H$_2$O$_2$ &amp; ROOH</td>
<td>Enzyme catalysed fluorescence</td>
<td>Aero-Laser / self built</td>
<td>10 min</td>
<td>operational</td>
<td>2/week liquid calib. (gas phase calib.)</td>
</tr>
<tr>
<td>Radon – 222</td>
<td>Aerosol beta activity</td>
<td>Tracerlab</td>
<td>10 min</td>
<td>operational</td>
<td>Manufacturer</td>
</tr>
</tbody>
</table>
Time series of selected trace gases are shown in the following:

**Carbon Monoxide (CO):**

The main sources are the oxidation of methane (CH\(_4\)) and biomass burning. In the northern hemisphere, due to the use of fossil fuels, carbon monoxide emission constitutes a source of almost equal importance as compared to methane oxidation. The main sink for carbon monoxide is the oxidation to carbon dioxide (CO\(_2\)) by the hydroxyl (OH) radical. As CO is the most important sink for the OH radical, an increase of the carbon monoxide mixing ratio would reduce the oxidation capacity of the atmosphere. In the northern hemisphere CO is a tracer of anthropogenically influenced air masses. With an atmospheric residence time of approx. 3 to 4 months, CO is one of the longer-lived reactive trace gases.

Overall the CO time series at Hohenpeissenberg shows a negative trend. Starting around the year 2000 the mixing ratio seems to increase again. Sinking concentrations can be explained either by lowering the source strengths (less biomass burning and/or effective CO emission reduction) or by an increase of the OH radical concentration as consequence of reduced ozone mixing ratios in stratosphere and an associated increase of the UV radiation. The stagnation or even increase since around 2000 could be an effect of the industrialisation in Asia.

**Sulfur Dioxide (SO\(_2\)):**

Anthropogenic emissions are the main source for SO\(_2\). It is a tracer for emissions of combustion plants. Sinks of SO\(_2\) are reaction with OH radicals and wet deposition, i.e. by solution in cloud droplets, in which it is converted to sulphurous and sulphuric acid. SO\(_2\) is the most important source for sulphate aerosol (anti-greenhouse effect, acid rain). The mean life time in the atmosphere is about 3-4 days.

The whole time series shows a pronounced decreasing trend. That is consistent to the decreasing sulphate concentration in precipitation. Since around the year 2000 the mixing ratio is slightly increasing (similar to CO). The overall decreasing trend is caused by flue gas desulphurisation of most power plants and large industrial plants in the mid 90's. By use of sulfur-poor and/or free fuels also traffic reduces the SO\(_2\) emissions. An enhancement in tropospheric OH
concentration would also lead to lower SO$_2$ levels. The slight increase in the last years is probably a combination of increased emission in the east of Europe and more frequently arising eastern wind directions.

![SO$_2$ monthly mean, 12 month running mean, and Linear (SO$_2$ monthly mean)](image)

**Figure 2:** Time series of sulfur dioxide at Meteorological Observatory Hohenpeissenberg.

**Nitrogen Oxides (NO, NO$_2$, NO$_y$):**

![NO, NO$_2$, NO$_y$ monthly mean, 12 month running mean NO$_2$, and 12 month running mean NO$_y$](image)

**Figure 3:** Time series of nitrogen oxides at Meteorological Observatory Hohenpeissenberg.
The nitrogen oxides are emitted mainly as NO (in the northern hemisphere 90% from anthropogenic sources). They determine (beside radiation and VOC) tropospheric ozone production (summer smog). In the atmosphere they are converted into higher oxidised compounds. An important product thereby is the nitric acid (HNO$_3$), which contributes to the acid rain. The mean lifetime is between some hours up to 1-2 days.

There is no recognisable trend. The pronounced seasonal concentration fluctuations are caused by effective photochemical removal in summer and enhanced source strengths in winter. With an almost quantitative implementation of three-way catalytic converter in gasoline motor vehicles in the last years a decreasing trend of atmospheric mixing ratios has been expected, but this is possibly compensated by an enlargement of the number of vehicles, an increase of mileage, an increase of average speed or by an enhanced ratio of diesel operated vehicles.

Another possible explanation is, that at very low mixing ratios (this is mostly the case at the Hohenpeissenberg site) the influence by biogenous sources (i.e. nitrogen oxide emissions from soils, grass, fields and forests) may not be neglected.

**Tropospheric Ozone (O$_3$):**

![Graph showing time series of ground based ozone at Meteorological Observatory Hohenpeissenberg.](image-url)

Ozone is not emitted directly into the troposphere, but produced by precursor substances (secondary trace gas). Due to its participation in important chemical reactions O$_3$ is a key component in troposphere. The mean lifetime in the atmosphere is about 3-4 days.

The monthly average values show a clear positive trend over the total time series since 1971, which is justified however mainly by the rise in the first half of the observation period. Since beginning of the 90's there is no significant increase. To that extent a linear trend function does not reflect the actual conditions. A polynomial trend function reflects the situation better.

Analysing the maximum and minimum concentrations (here not shown), it is noticeable that the minima have also a positive, the maxima however a slight negative trend. Due to that fact the frequency distribution of ozone becomes narrower.
Reason for this could be decreasing nitrogen oxide mixing ratios (even if this cannot be verified from the observations at the MOHp), since thereby very high O$_3$ concentrations in summer become rarer and concentrations are raised in the winter by smaller titration effects. Also the so-called "ozone background concentration", which is determined by correlation with the wind velocity (O3-Bulletin No. 75), is still rising.

While the reduction of the maximum concentrations entails rarer and/or shorter summer smog episodes so that health risks for humans decrease, is an increase of the background concentration precariously, since already concentrations above 40 ppb are harmful for plants and crops. A further forceful emission reduction of the precursor substances (nitrogen oxides and hydrocarbons) is essential.

References
Berresheim, H., this issue.
Plass-Dülmer, C., this issue.

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Volatile organic compounds (VOC) are measured at Hohenpeissenberg since 1998. They were included into the GAW reactive gases programme due to their substantial impact on ozone, photooxidants, oxidizing capacity, aerosol, climate and health. VOC are emitted into the atmosphere by a large number of anthropogenic and natural sources and are a major source of reduced compounds (500-1000 Mt/y) in our oxidizing atmosphere. They are primarily oxidized by OH and other free radicals, initiating an oxidation chain with numerous short and long lived intermediates and products including alcohols, carbonyls and organic acids. The GAW measurement strategy aims at data on global distribution and seasonality in order to understand the biogeochemical cycling (sources, sinks, transport, and chemistry) and analyze trends to detect changes in atmospheric composition [WMO, GAW report No. 111, 1995].

According to GAW-WMO report No. 111 [1995], at Hohenpeissenberg a staged measurement programme was set up using three different gas chromatography instruments (GC’s, [Plass-Dülmer et al., 2002 and in preparation, 2006]). All three measurement techniques involve an initial concentration step on suitable adsorbents or on a cryo-trap to concentrate the VOC from typically 1 liter of air, thermal desorption, refocusing in a capillary (GC#2), separation of the various VOC on a GC column, and detection. The instruments GC#1 and GC#2 are routinely operated at 1:00 and 13:00 CET to measure online 90 different VOC compounds including C2-C12 hydrocarbons, monoterpenes, several oxygenated hydrocarbons (OVOC), and selected halocarbons (see Table 1 and references for details). Detailed quality assurance procedures have been developed [Plass-Dülmer et al., 2002], and the analytical systems have proven their capabilities to accurately measure VOC within several international intercomparison experiments, i.e. NOMHICE, AMOHA [Plass-Dülmer et al., 2006], and recently an intercomparison by WCC-VOC [Rappenglück et al., in preparation].

Table 1: Analytical systems used in analysis of VOC at Hohenpeissenberg.

<table>
<thead>
<tr>
<th>System</th>
<th>Compounds</th>
<th>Detectors</th>
<th>Detection Limit</th>
<th>Accuracy</th>
<th>Cycle time</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC#1</td>
<td>C2-C8 hydrocarbons</td>
<td>FID</td>
<td>&lt; 3 ppt</td>
<td>5-20% or 10 ppt</td>
<td>75 min</td>
</tr>
<tr>
<td>GC#2</td>
<td>C5-C12 hydrocarbons, C6-C12 OVOC’s</td>
<td>MS, FID</td>
<td>0.1 – 1 ppt</td>
<td>5-20% or 1 ppt</td>
<td>65 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 – 3 ppt</td>
<td>15-30% or 3 ppt</td>
<td></td>
</tr>
<tr>
<td>GC#3</td>
<td>C1-C2 halocarbons</td>
<td>PD-HID, FID</td>
<td>0.1 – 0.4 ppt</td>
<td>10% or 0.4 ppt</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C1-C4 OVOC’s</td>
<td></td>
<td>10-50 ppt</td>
<td>10-30%</td>
<td>35 min</td>
</tr>
</tbody>
</table>

Mixing ratios of VOC in atmosphere range between some 10 ppb (parts per billion) in urban areas down to levels well below 1 ppt (parts per trillion) in remote areas. Mixing ratios are determined in a complex interaction of sources, transport, mixing, and atmospheric removal by chemical transformation and dry or wet deposition. Most of these processes depend on the meteorological situation, e.g. biogenic emissions of VOC depend on temperature and light, transport and mixing on the wind fields and turbulent mixing, chemical processing on UV-light initiated radical formation [see Berresheim, this issue], and wet deposition on precipitation. Atmospheric life times of VOC range between less than one hour for the reactive monoterpenes and isoprene to more than a month for ethane or perchloroethene, and thus enable to separate local atmospheric processes (short lived compounds) from hemispheric scale processes.

In Figure 1 the time series of selected C2 hydrocarbons and BTX aromatics (BTX= benzene, toluene, and xylene) are shown for 1998-2005, all originating predominantly from anthropogenic emissions, i.e. traffic exhaust, solvent use, biomass burning and natural gas
leakage. Anthropogenic VOC generally show high concentrations in winter and factor 2-6 lower concentrations in summer, a consequence of higher atmospheric removal in summer due to correspondingly higher concentrations of OH radicals. The time series show negative trends of -2 to -8%/year for the anthropogenic hydrocarbons, more pronounced (-6 to -8%) for the short lived aromatics toluene and xylene (lifetimes less than 2 days at [OH] = 1 \times 10^6 \text{ cm}^{-3}\). This points toward decreasing regional emissions of these compounds. Ethene is a compound of similar lifetime but does not show significant change. Probably, reduced ethene emissions from catalyst cars have been compensated for by increased emissions from Diesel powered vehicles (increasing fraction of car fleet). The longer lived compounds (ethane, acetylene and benzene with lifetimes > 10 days) show less pronounced trends, indicating more constant emissions on the larger scale, i.e. continental to hemispheric. However, such interpretations are preliminary and need to be complemented under consideration of potentially changing transport and chemical removal processes.

![Figure 1: Time series of selected VOC at Hohenpeissenberg, monthly mean values (dots) of noon time concentrations and sine curves (lines) with linear trends fitted to the data.](image)

In Table 2, the mean annual mixing ratios (2005) and preliminary trends of a number of VOC are compiled for our measurements at Hohenpeissenberg. Anthropogenic alkanes, alkenes, aynes and aromatics generally show lower concentrations with increasing reactivity (shorter life time), thus indicating a strong impact of chemistry on the abundance of VOC in atmosphere. The trends of anthropogenic VOC obtained from the fit procedure are generally in the range shown in Figure 2, i.e. –2% to –9% with stronger trends for the more reactive compounds.

Biogenic hydrocarbons (Table 2) measured at Hohenpeissenberg are predominantly emitted from coniferous and deciduous trees and plants growing on the slopes of the mountain Hohenpeissenberg and in the surrounding countryside (about 40% forests and 40% pasture). Annual cycles (Figure 2) show pronounced maxima in summer time and typically at least an order of magnitude lower concentrations in winter due to the seasonality of emissions: Monoterpene emissions from conifers primarily depend on temperature whereas deciduous trees emit isoprene and selected monoterpenes (e.g. sabinene from beeches) depending mainly on leaf area, light and temperature. As a consequence, biogenic VOC from coniferous trees show significant concentrations in winter in contrast to terpenes emitted by deciduous trees (e.g. isoprene, sabinene, terpinene) which decline to values close to zero in wintertime, unless there are no other sources like small traffic emissions for isoprene.
Table 2: Mean noon time concentrations of selected VOC in 2005 (extension “– Bio” is used for biogenically emitted compounds), trends were calculated from a fit of a sine curve with linear trend to the data of 1999-2005, for >C8 compounds trends were derived from years 2001-2005, no trends (-) are given for those VOC where due to a reduced data base no trend can be calculated yet.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average 2005</th>
<th>Trend (year⁻¹)</th>
<th>Average 2005</th>
<th>Trend (year⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>1549</td>
<td>-2%</td>
<td>14.4</td>
<td>-</td>
</tr>
<tr>
<td>Propane</td>
<td>602</td>
<td>-4%</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>i-Butane</td>
<td>136</td>
<td>-6%</td>
<td>21.2</td>
<td>-</td>
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<tr>
<td>n-Butane</td>
<td>239</td>
<td>-5%</td>
<td>6.3</td>
<td>-</td>
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<tr>
<td>i-Pentane</td>
<td>172</td>
<td>-6%</td>
<td>8.8</td>
<td>-</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>89</td>
<td>-5%</td>
<td>9.4</td>
<td>-</td>
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<tr>
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<td>-4%</td>
<td>1.2</td>
<td>-</td>
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<tr>
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<td>-6%</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>3-M-Pentane</td>
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<td>-3%</td>
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<tr>
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<td>22.1</td>
<td>-6%</td>
<td>15.0</td>
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</tr>
<tr>
<td>C-Hexane</td>
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<td>-4%</td>
<td>161</td>
<td>-4%</td>
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<tr>
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<tr>
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<td>n-Nonane</td>
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<tr>
<td>Ethene</td>
<td>518</td>
<td>-3%</td>
<td>7.0</td>
<td>-</td>
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<tr>
<td>Propene</td>
<td>62</td>
<td>-7%</td>
<td>3.5</td>
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<td>2.2</td>
<td>-9%</td>
</tr>
<tr>
<td>i-Butene</td>
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<td>-8%</td>
<td>9.6</td>
<td>-8%</td>
</tr>
<tr>
<td>c-2-Butene</td>
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<td>-5%</td>
<td>2.3</td>
<td>-</td>
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<tr>
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<td>1155</td>
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<td>10.9</td>
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</tr>
<tr>
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<td>-</td>
<td>18.4</td>
<td>-</td>
</tr>
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<td>Isoprene – Bio</td>
<td>34</td>
<td>-</td>
<td>106</td>
<td>-</td>
</tr>
<tr>
<td>a-Pinene – Bio</td>
<td>31</td>
<td>-</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>Camphene – Bio</td>
<td>7.0</td>
<td>-</td>
<td>9.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 2: Monthly mean mixing ratios of selected biogenic VOC including isoprene and the more reactive monoterpenes; data of sabinene, myrcene, g-terpinene and terpinolene in 2004 were excluded due to instrumental artefacts.
Mixing ratios of biogenic VOC can in a first approach be parameterized by an exponential function of temperature, as shown in Figure 3. The slope is lower for monoterpenes due to their emissions by coniferous trees in wintertime. Since light and temperature are coupled to some extend, also the correlation of isoprene with temperature is reasonable although emissions are primarily light dependent. It should be pointed out that the observed temperature dependence is related to the biogenic source which overcompensates the larger sink due to enhanced OH and O3 at high insolation and temperature, partly due to the short transport time between emission and measurement.

\[ y = 4.23e^{0.15x} \]
\[ R^2 = 0.74 \]

**Figure 3:** Plot of mixing ratios of the sum of all measured monoterpenes (red) and isoprene (blue) as function of the temperature.

Any attempt to assess the impact of VOC on photo-chemistry or the importance of individual compounds is difficult since the VOC play different roles in the various atmospheric chemical processes. However, a good measure is the turn-over rate with OH radicals. This number is important for ozone and oxidant formation, production of semi-volatile products involved in aerosol growth and aerosol surface properties, and in a feed back mechanism on the self cleansing capacity of the atmosphere by potentially changing the OH concentrations [Berresheim, this issue]. In Figure 5, the relative turn-over rates of the various VOC are compared to those of inorganic trace gases measured at Hohenpeissenberg. The fractions correspond to seasonal averages of noon time values (12-14 CET), total turn over is \(10^5\) molecules cm\(^{-3}\) s\(^{-1}\) in summer (Jun-Aug) and \(3.5*10^6\) molecules cm\(^{-3}\) s\(^{-1}\) in winter (Dec-Feb). In summer, biogenic VOC contribute about a third of the total turn-over, all VOC including light aldehydes (formaldehyde and acetaldehyde, not measured) make up about half of the total turn-over. Anthropogenic VOC are of minor importance in summer, however, they comprise the dominant VOC in winter with about 20% contribution to total turn-over. It should be noted that those VOC with highest mixing ratios (Table 2), e.g. long lived alkanes, aromatics and OVOC’s, contribute fairly little to the local turn-over, underlining the important role of very reactive, mostly biogenic compounds on photo chemistry in rural, continental atmosphere.
Figure 4: Turn-over rates due to reactions with OH radicals for the months a) Jun-Aug and b) Dec-Feb, 2004; noon time mixing ratios were used with concurrently measured OH concentrations to calculate individual turn-over rates which were then averaged to obtain seasonal means (sabinene*: corrected for instrumental artifact).

Future issues of VOC measurements at Hohenpeissenberg will focus on trends of anthropogenic VOC, changes in sources of VOC, e.g. enhanced biogenic emissions due to increasing temperatures, contribution of various VOC to particulate matter, and impact of VOC on the oxidizing capacity of the lower troposphere.

References
Berresheim, H., Oxidation Efficiency of the Atmosphere - Measurements of the OH Radical, this issue

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The atmosphere has a limited capability to clean itself from gaseous pollutants, either through wet deposition (precipitation) or by chemical oxidation. Since most gases in the atmosphere are only weakly soluble or not soluble at all, the latter process is extremely important for the removal of air pollutants. The hydroxyl radical (OH) is the most important oxidizing compound in the lower atmosphere during daytime. It reacts with nearly all trace compounds including greenhouse gases such as methane and a large number of pollutants (Figure 1). Therefore, it also determines the chemical "self-cleansing" or "oxidation efficiency" of the atmosphere. In the remote atmosphere OH is primarily produced via ozone photolysis at wavelengths less than about 330 nm followed by reaction of the electronically excited O(1D) atom with water vapour:

Figure 1: Major production and removal reactions controlling the OH concentration in the atmosphere (red circles and arrows) and some examples where OH reactions determine the concentrations of the corresponding compounds and their products (blue circles and arrows).
The main removal mechanism is the reaction with carbon monoxide (CO) and methane (CH₄). However, in air masses increasingly loaded with emissions from anthropogenic or biogenic sources (e.g., CO, NOₓ, SO₂, hydrocarbons from fossil fuel combustion or hydrocarbons from vegetation) the production of OH may be overcome by its consumption (Figure 2). On a regional scale (e.g., in winter inversion layers) and even on a global scale with long-range transport of pollutants this may effectively reduce the mean oxidation efficiency of the atmosphere and further accelerate the accumulation of air pollutants and enhance their residence time in the atmosphere. Therefore it was recognized in the early 1990’s that parallel to and interactively coupled with the human-induced change of climate there may have also been a negative trend imposed on the oxidation efficiency of the atmosphere.

![Chemische Selbstreinigungskraft der Atmosphäre](image)

**Figure 2:** Simultaneous measurements of OH (units: 10⁶ molecules cm⁻³) and nitrogen oxides (NO + NO₂, units: parts-per-billion) showing the increased supply by the atmosphere of OH with increasing NOₓ and a net decline of the OH concentration (due to the reaction OH+NO₂ → HNO₃) beyond a threshold NOₓ level of about 2 ppb.

However, measurements of atmospheric OH levels proved to be extremely difficult due to the high reactivity of OH. The mean lifetime of an OH radical is typically less than one second. It can only be measured by a few sophisticated methods one of which is Chemical Ionisation Mass Spectrometry (CIMS) originally developed by F. Eisele and co-workers at Georgia Institute of Technology and the National Centre for Atmospheric Research in the USA. After working with F. Eisele for 7 years and returning to Germany in 1994 to join the German GAW programme the author initiated and organized to set up a CIMS system at the Meteorological Observatory Hohenpeissenberg. Thus, in 1998 the first long-term measurements of OH started here and were embedded in the GAW programme, and to this date this remains the only such programme in the world (Figure 3; Berresheim et al., 2000).
Since the beginning of OH measurements a rigorous quality assurance and data revaluation has been successively implemented closely coupled with measurements of photolysis frequencies (J-values) of ozone, nitrogen dioxide, and other related gases conducted by the same group. In August 2005 the DWD CIMS system participated in an international field intercomparison of radical measurements at the Research Centre Jülich (HOxCOMP). Preliminary data evaluation indicates that ambient air OH levels measured with CIMS agreed very well with OH measurements performed with quite different (optical laser) methods.

The major highlight to date are the results of a systematic and detailed analysis of the OH measurements performed between 1999-2003 which will be published in 2006 in Nature (Rohrer and Berresheim, 2006). In collaboration with F. Rohrer (Research Centre Jülich) it could be shown that OH and UV-B levels were strongly correlated, the latter being represented by the ozone photolysis frequency, J(O\(^{1}D\)), defined as the rate constant of reaction (1). Despite strong variations in other reactant concentrations such as CO, NO\(_x\), or hydrocarbons nearly all (99%) of the variability in ambient OH levels obtained over the entire 5 year period could be explained by the variability in UV-B (with instrument noise subtracted; Figure 4). Moreover, the correlation was found to be linear. The slope of the correlation characterizes the general air mass composition on a local to regional scale around Hohenpeissenberg. Similar strong correlations have been found previously in other environments (with different slopes) but only in short-term measurements of the order of one month or less. These results indicate compensating, yet unknown, processes stabilizing the relation between OH and UV-B, which can be described by a characteristic function depending on the general air mass composition. The results may thus be applied to derive the distribution of the atmospheric oxidizing efficiency on a regional scale and to determine its potential trend. As shown in Figure 5, no significant trend could be detected in the 1999-2003 period at Hohenpeissenberg.
The CIMS system has also been used in other environments during short-term field campaigns with related research objectives such as PARFORCE (New Particle Formation and Fate in the Marine Environment) conducted at the GAW station Mace Head, Ireland (Berresheim et al., 2002) or MINOS (Mediterranean Intensive Oxidant Study) conducted on Crete, Greece (Berresheim et al., 2003). However it has mainly been operated up to the present at MOHp to serve the long-term observation of the atmospheric oxidation efficiency, and the intensive study of specific processes and events in the atmosphere (e.g., the solar eclipse in 1999; Fabian et al. 2001; Winkler et al., 2000). Furthermore, the data have been intensively used by external groups conducting research campaigns at MOHp and related modelling studies. This success story is planned to be continued in the framework of the new GAW/IGACO strategic plan and will hopefully attract even more national and international collaboration with the Hohenpeissenberg GAW programme.

References

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Figure 4: Correlation of measured OH concentrations with simultaneously observed ozone photolysis frequencies, J(O¹D). The dots represent 5 min averages measured at

Figure 5: Monthly averages of the ratio of simultaneous observations of OH and J(O¹D) measured at Hohenpeissenberg. The calculated trend line has a slope of +0.9%/yr with an error
Ozone Trends
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Ozone is a key trace-gas in our atmosphere. As the strongest absorber of ultraviolet (UV) radiation, it protects life on the earth’s surface from excessive levels of this potentially harmful short-wave radiation. By absorbing and emitting thermal infrared radiation as well, ozone is also an important greenhouse gas. In general, ozone is a heat source, both in stratosphere and troposphere. Ozone is further an important player in atmospheric chemistry. It is a lead substance for urban pollution and photochemical smog, and is the precursor for the OH radical, the key atmospheric “cleaning agent” in the troposphere.

Since ozone is fairly abundant, from 50 parts per billion by volume in the troposphere to 10 parts per million in the stratosphere, and also has strong spectral absorption features, ozone measurements are relatively easy. The first beginnings of a global ozone observation network based on UV spectrometers were laid down in the 1920s (Dobson and Harrison, 1926). However, the global network of Dobson spectrometers did not start until the 1957/1958 International Geophysical Year. The realisation that anthropogenic Chloro-Fluoro-Carbons (CFCs) might destroy our stratospheric ozone layer (Molina and Rowland, 1974; Crutzen 1974), and the discovery of the Antarctic ozone hole (Chubachi, 1984, Farman et al., 1985), have raised widespread scientific interest and public awareness. They have mandated an internationally and globally co-ordinated ground- and space-based monitoring system for the ozone layer. This co-ordination was very successful and has been in place for over 20 years (WMO, 2003). The resulting WMO Global Ozone Observing System (GO3OS) has been a nucleus for the WMO Global Atmosphere Watch (GAW) programme.

The evolution of observed near global annual mean total ozone is shown in Figure 1. Since the 1960s, zonal mean ozone from 60°N to 60°S has declined by about 4%. Note that much larger...
decline has occurred near the poles, particularly in spring. Largely, this decline is a consequence of chemical ozone destruction by man-made chlorine and bromine (magenta curve for equivalent effective stratospheric chlorine, EESC, in Figure 1). However, meteorological changes related to climate change have also contributed to the decline (WMO, 2003).

Following the international ban for the production of harmful CFCs, chlorine levels in the lower stratosphere have peaked around 1996. In Figure 1 this corresponds to the minimum of the EESC curve (magenta), which is inverted to account for the negative effect on ozone. Since 1996, lower stratospheric chlorine has turned around. However, at this point it is not clear what fraction of the observed ozone levelling since 1998 (blue line in Figure 1) is due to chlorine changes, what part is due to recovery from effects of the 1991 Mt. Pinatubo volcanic eruption, causing the record low values of 1993 and 1995, or what fraction is due to transport changes, or due to the 2000 to 2003 maximum of the solar cycle (red line in Figure 1). It will take several years of additional data to resolve these ambiguities.

Most of the atmospheric total ozone column resides in the stratosphere between 12 and 40 km altitude. Over this altitude range, the time-scale on which ozone reaches photochemical equilibrium varies tremendously, from years or months near the tropopause to about one day at 40 km. Therefore, ozone in the upper stratosphere is controlled largely by photochemical reactions, whereas ozone variations in the lower stratosphere are largely determined by transport processes.

**Figure 2:** Ozone anomalies from 1967 to 2006 at three atmospheric levels above Hohenpeissenberg, measured by ozone-sondes (5 and 20 km) and laser radar (40 km). Anomalies were defined by subtracting the average annual cycle from the monthly mean time series. To reduce short-term fluctuations, the data were smoothed by a 3 months running mean. Hohenpeissenberg is located in Southern Germany at 47.8°N, 11.0°E, 1000 m a.s.l.
Examples for the evolution of ozone in two selected stratospheric layers, and one tropospheric layer, are given in Figure 2. At 40 km altitude, where ozone is largely under photochemical control, a fairly straight long-term decline is apparent. It is caused by the destruction of ozone due to increasing chlorine levels over time. Details are discussed below.

In the lower stratosphere at 20 km, in contrast, transport variations exert a major influence on ozone, although chemical depletion also plays a large role. For the long-term decline of lower stratospheric ozone from 1967 to 1996, e.g. by about 12% at 20 km, it is estimated that about two thirds are due to chlorine (and bromine) increase, and about one third is due to transport changes (WMO, 2003). As for the near global ozone (Figure 1), it is not clear which fraction of the levelling observed since 1998 is due to chlorine turning around, and which fraction is due to other factors.

While the two upper levels shown in Figure 2 are representative for ozone at mid-latitudes of the Northern hemisphere, the evolution of tropospheric ozone in Figure 2 is representative for Central Europe only. There, ozone levels have increased substantially up until the late 1980s. Largely, this increase is due to increasing emissions of nitrogen oxides and organic carbon substances. Since the 1990s, European emissions have been reduced. Tropospheric ozone levels in Europe have responded with a decrease or have remained more or less constant. For some of the finer details, measurement uncertainties of the ozone sondes may play a role. A different behaviour for tropospheric ozone is found in other parts of the world. Over Canada, for example, tropospheric ozone has been decreasing by about 10% during the 1980s, but has increased by about 10% during the 1990s (Oltmans et al., 1998; WMO, 2003). The causes for this different behaviour in various parts of the world are largely unknown.

As mentioned, for total ozone, or for ozone in the lower stratosphere, a search for beginning positive effects of the recent turnaround in chlorine (or EESC) does not provide conclusive results at this point. There are simply too many competing influence factors. More conclusive evidence for a beginning recovery can, however, be found in the upper stratosphere, where ozone levels are most closely tied to chlorine levels by efficient catalytic destruction cycles. Figure 3 shows upper stratospheric ozone residuals for five stations from mid-latitudes in the Southern hemisphere to the Northern hemisphere. These residuals were obtained by averaging all available long-term records from ground- and space-based instruments, and by subtracting the average annual cycle, as well as ozone variations due to the quasi-biennial oscillation of equatorial winds and due to the 11-year solar cycle (Steinbrecht et al., 2006). To a large degree the residuals are then determined by chlorine levels. Indeed, for most stations, the residuals follow the inverted chlorine (EESC) line in Figure 3. In particular, the levelling of chlorine since about 1996 is mirrored by a levelling of ozone, with values well above the extrapolated ozone trend-line from the 1980s. The steep decline has obviously not continued after 1997. Because most other factors can be eliminated, the levelling gives a very strong indication that ozone is following the chlorine turnaround. The Vienna convention, and the Montreal protocol, have been effective for the upper stratosphere. There the ozone layer is showing first signs of a recovery. However, as indicated by the data at the most northerly station (Hohenpeissenberg), other factors, not well understood, do interfere with the recovery signal.

Chlorine levels are expected to continue declining. They are expected to return to the near natural pre-1980 levels over the next 50 years. This should bring up ozone levels. Nevertheless, further attention to the ozone layer is required. Climate change will affect the ozone layer in the future, through both changing temperature and transports. Cooling of the stratosphere is expected to slow ozone destruction cycles in the future, and when chlorine is back to 1980 levels, total ozone and ozone in the upper stratosphere are expected to reach levels higher than in 1980. This will change the vertical distribution of atmospheric heating and may affect the global circulation. As the past has shown, surprises are always possible. One thing is clear, however: An accurate, co-ordinated, and global ozone measurement system, i.e. a Global Atmosphere Watch programme, will be required, in order to know about the true evolution of our ozone layer in the future.
Figure 3: Upper stratospheric (35 to 45 km) ozone residuals obtained by a mix of ground- and space-based instruments for five stations of the Network for the Detection of Stratospheric Change (NDSC). Ozone residuals were defined by subtracting the average annual cycle, as well as effects from the 11-year solar cycle and the quasi-biennial oscillation. Residuals very closely follow the chlorine (EESC) loading. Results from fitting at linear trend, and a change of trend term after 1996, are shown as well (red line). After Steinbrecht et al. (2006).

References

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Aerosol Measurements at the GAW Global Station Hohenpeissenberg

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Aerosol activities have developed into a core component of GAW because of their importance to a wide range of issues from global climate change to regional and local air quality (WMO, 2001a). Aerosols influence the atmospheric energy budget through direct and indirect radiative effects. Direct effects include the scattering and absorption of radiation and the subsequent influence on planetary albedo and the climate system. Indirect effects involve the influence of anthropogenic aerosol on available cloud condensation nuclei (CCN). An increase in aerosol number concentration tends to increase the CCN which in turn, leads to increased cloud albedo and to changes in the Earth’s radiation budget. Cloud lifetimes and precipitation frequencies can also be affected. This alters the hydrological cycle and water supply. Scientific evidence indicates that in regions with high anthropogenic aerosol concentrations, aerosol forcing is of the same magnitude, but opposite in sign to the combined effect of all greenhouse gases (IPCC, 2001).

Due to the recommendations of the Scientific Advisory Group (SAG) for aerosols (WMO, 2003) the intensive aerosol programme (including optical depth measurements) at Hohenpeissenberg covers numerous parameters for the characterization of the physical, optical and chemical characteristics of the atmospheric aerosol and addresses both climate and health issues. Aerosol mass and its toxic chemical components as well as “Nano particles” are known to have links to chronic respiratory and acute cardio-vascular problems.

The following documentation is an exemplary presentation of interesting aerosol features measured at the Hohenpeissenberg station:

Number Concentration

Integral particle measurements of number concentrations across a wide size range serve various purposes: 1. Indication of local anthropogenic aerosol sources, 2. Long term changes, 3. “Gas-to-particle” conversion events.

1. Because high number concentrations of CN are produced mainly by anthropogenic activities, and in particular by combustion processes a rapid rise in particle number concentration (d >11 nm) can be used as an indication of a local aerosol source. In addition aerosol absorption measurements can be taken (provided the local pollution aerosol is absorbing) to be sure that the increase is of anthropogenic origin.

![Figure 1: Example of instruments response to biomass burning (CN concentration: upper curve and left axis, black carbon: lower curve and right axis).](image-url)
2. It is the goal of the Global Atmosphere Watch programme to ensure long-term measurements in order to detect trends in global distributions of chemical constituents in air and the reasons for them (WMO, 2001a). CN concentration gives an indication of the instantaneous balance between particle production and removal in the sampled air and hence, CN is responsive to changes in the net result of these processes.

![Graph showing particle concentration at Hohenpeissenberg, 1995 - 2005](image)

**Figure 2:** Number concentrations (monthly mean) of different particle counters at Hohenpeissenberg:
- orange: CN larger than 3 nm; (TSI 3025)
- blue: CN larger than 11 nm (TSI 7610 and 3762)
- red: DMPS system of IFT Leipzig, size range 10-730 nm
- green: DMPS system of IFT Leipzig, size range 3-730 nm.

The data record of CN measurements at Hohenpeissenberg started in June 1995 for Aitken particles larger than 3 nm (Figure 2; orange line) and in January 1998 for CN larger than 11 nm (Figure 2; blue line). The comparison of the two CN counters, associated with a DMPS system operated by the Institute for Tropospheric Research (Leipzig) at Hohenpeissenberg show that data from the particle counter > 3 nm before 2001 may have been affected by experimental errors. Due to these difficulties a trend in CN particle concentration cannot yet be determined.

3. The sub-micrometer fraction ("fine particles") originates from condensation sources (both high and low temperature) and from atmospheric gas-to-particle conversion processes. We use a basic counter (11 nm) and also a counter with a lower size-cut of 3 to 4 nm (ultra-fine counter). The difference of these two measurements is a measure of particle production by nucleation. In urban and rural air, these ultra fine particles generally comprise the major fraction of the CN number concentration. Figure 3 gives an average impression about the occurrence of gas-to-particle conversion events. Ultra fine particles are mainly produced in March during midday when UV-intensity is high.
Aerosol Radiative Properties – Light Scattering

Knowledge of aerosol radiative properties is needed for evaluation of aerosol effects on climate and visibility. The fundamental quantity of interest for these applications is the aerosol cross-section for light extinction per unit volume of air, commonly called the aerosol light extinction coefficient reported in units of \( \text{m}^{-2} \text{m}^{-3} \) (i.e., \( \text{m}^{-1} \)) or \( \text{Mm}^{-1} \). The light extinction coefficient is the sum of the light scattering and light absorption coefficients. For radiative climate studies, information on the angular distribution of scattered light and on the relative amounts of scattering vs. absorption is required. The aerosol light scattering coefficient is measured with an integrating 3 wavelength nephelometer (e.g., Heintzenberg and Charlson, 1996). Figure 4 shows the monthly mean values and the linear trend for the total scattering from 1999 to 2005.

Aerosol Radiative Properties - Light Absorption (Black Carbon)

In 1996 we started deriving black carbon (BC) from absorption measurements of an aethalometer. The aethalometer is based on the rate of change of transmission through a fibre filter as particles are deposited on the filter (Hansen et al., 1984). Calibration of these filter-based methods is difficult, but is required because the relationship between change in light transmission
and aerosol absorption optical depth on the filter depends on many factors, including the particular filter medium and the light-scattering nature of the particles.

Interpretation of aethalometer absorption data in terms of black carbon requires a value for the mass absorption efficiency of the black carbon particles. A value of 19 m$^2$ g$^{-1}$ is commonly recommended by the manufacturer. However, mass absorption efficiencies ranging from 5 to 20 m$^2$ g$^{-1}$ have been reported for aerosols from different regions (Liousse et al., 1993), which implies that the mass absorption efficiency must be determined experimentally at every site where aethalometers are used to estimate black carbon concentrations. The mass absorption efficiency at Hohenpeissenberg was determined to be 5.9 m$^2$ g$^{-1}$. But the aethalometer has other uncertainties as for example the “shadowing effect” (Weingartner et al., 2003). Since August 2003 we are running an additional filter-based instrument - the Multi-Angle Absorption Photometer (MAAP). The MAAP uses a different optical configuration than the aethalometer, with measurements of the filter reflectivity at two different angles in addition to the filter transmission measurement (Petzold et al., 2002). The two reflectivity measurements allow correction for multiple scattering processes involving the deposited particles and the filter matrix. This approach eliminates the need for a correction scheme based on independent measurements of aerosol light scattering coefficient. The MAAP operates at a wavelength of 670 nm.

![Figure 5: Black Carbon at Hohenpeissenberg (monthly averages) with trend line derived from aethalometer aerosol absorption observations.](image)

**Single-Scattering Albedo (SSA)**

The aerosol single-scattering albedo describes the relative contributions of scattering and absorption to the total light extinction. Purely scattering aerosols (e.g., sulphuric acid) have values of 1, while very strong absorbers (e.g., black carbon) have values of around 0.3.

As the aethalometer measurements contain errors, an algorithm was derived from the parallel run of aethalometer and MAAP, which makes a retrospective correction of the aethalometer data possible. Figure 6 shows the temporal course of the SSA, calculated from corrected aethalometer data (rhombi) and the MAAP data (triangles in magenta). The small degree of deviations shows the quality of the corrective procedure. A high uncertainty in measuring the scattering is due to the fact that the aerosols are measured under dry conditions (approx. 30 % relative humidity), although in the atmosphere the relative humidity has a large influence on the scattering characteristics of the aerosol. The critical SSA value, which decides whether the
radiative forcing by aerosols leads to a warming or a cooling is seen to be above 0.95 and below 0.9 (Hansen et al., 1997). With an SSA of > 0.95 the atmospheric aerosol will cause a cooling in almost all cases. If the SSA is < 0.9, the aerosol particles will heat up the troposphere distinctively and intensify global warming. At Hohenpeissenberg the SSA changed from 0.85 to 0.91 in the time period 1999 to 2005, i.e. the regional aerosol as a whole is dominated by scattering rather than absorbing particles. This means that in the initial years the aerosol did not diminish the temperature rise, but rather caused it to increase.

![Figure 6: Temporal course of the calculated "Single Scattering Albedo" (relationship of scattering to extinction, whereby extinction represents the sum of scattering and absorption) at Hohenpeiissenberg. The rhombi represent SSA values by which the absorption term was calculated from corrected aethalometer measurements, the measured values of the "Multi Angle Absorption Photometers" were used for the triangles in magenta.](image)

At present the value of the SSA indicates a transient area. The future will decide whether the atmospheric aerosol will increase or diminish the greenhouse effect here. High concentrations of scattering sulphate aerosols (SSA > 0.95), as emitted from mega cities, for example, diminish the temperature rise (Andreae et al., 2005). If the cooling decreases due to air pollution control measures (reduction of the aerosol emission, especially scattering sulphate aerosols), the warming could turn out to be all the greater. However, what has caused the change in the SSA in the Hohenpeissenberg area? Was it a change in the scattering or a change in the absorption? While the soot concentrations and thus the absorption in the period under investigation have remained constant (Figure 5), aerosol particles have increased the proportion of scattering (Figure 4), i.e. regional aerosol, as a whole, is made up of more scattering than absorbing particles.

Measurements of scattering and absorption and calculation of the SSA are necessary for estimating the local contribution to the radiative forcing by aerosol particles. Different types of aerosol cause very differing radiative forces. The differences are large compared to the values that are presently being used in climate models. To simplify matters, one is trying to classify the aerosols that are important for the direct radiation effect: scattering sulphate aerosol, scattering and absorbing mineral particles and absorbing aerosol from the burning of fossil fuel and biomass. This means great uncertainties in the forecasts from climate models. The SSA shows a low variability in the vertical, which is why ground measurements such as those at the GAW station Hohenpeiissenberg can be seen as being representative for the lower air column in the surrounding area. Whether or not the results also reflect the large-scale situation can only be shown in a comparison of the data of a global network such as the GAW.
From current aerosol trends at the GAW global station Hohenpeissenberg it is possible to analyze their relevance for air pollution control and possible influences on climate. Aerosol particles scatter and absorb solar radiation and thus cause a cooling or warming in the atmosphere.

References
Precipitation Acidity Trend at Hohenpeissenberg

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One of the main objectives of GAW is to examine the success of global and regional mitigation strategies. As a consequence of the public awareness of forest decline in Germany and neighbouring countries, measures for reduction of SO₂ emissions were taken in the 1980’s, mainly through desulfurization of coal and oil fired power plants. Before these actions were taken, annual average pH values in Germany ranged from 4.2 to 4.5, depending on the amount of precipitation. In the frame of a research project at the Juelich Research Centre weekly wet-only precipitation samples at Hohenpeissenberg observatory were analyzed in the early and mid-eighties. At that time, the average pH value was close to 4.4 (Figure 1). Note that low pH values reflect high acidity.

![Figure 1: Monthly averages of pH in precipitation at Hohenpeissenberg (wet-only).](image1)

![Figure 2: Monthly averages of conductivity in precipitation at Hohenpeissenberg (wet-only).](image2)
Measurements resumed with daily samples in 1995 in the frame of the GAW programme. The data from both periods can be compared because both were derived from wet-only samples. The pH values in 1995 had already risen to 4.8. Further desulfurization measures, especially in Eastern Germany and the former East block countries, led to a continued increase in pH up to 5.2, which is quite close to the natural background: Today's level of SO$_2$ emissions in Germany is lower than at the end of the nineteenth century. pH values in the dry and hot summer of 2003 were exceptionally high due to.

The decrease in precipitation conductivity (Figure 2) proves, that the increase of pH values was indeed caused by a decrease in anions rather than by an increase of cation concentrations. Along with that decrease, the variability in conductivity has become much smaller.

**Figure 3:** Monthly averages of SO$_4^{2-}$-S in precipitation at Hohenpeissenberg (wet-only).

Figure 3 displays the decreasing sulfate concentrations in precipitation due to the reduction of SO$_2$ emissions in the last two decades. During the first monitoring period, sulfate had only been analyzed for two years, but data from other stations in Germany confirm this trend. Most of the change in pH values can be explained by the decrease in sulfate concentrations. It can therefore be stated that the reduction of SO$_2$ emissions in Germany and the surrounding European countries was successful with respect to the mitigation of acidic precipitation.

After an increase over two decades the pH values now show a noticeable downward trend from 2003 on. Part of this is certainly due to the frequent Saharan dust events during summer 2003 on the one hand and on the cold winter of 2005/06 with frequent snowfall (snow is generally more acidic than rain) and continental airmasses on the other hand. To what extent this decrease in pH can be attributed to meteorological effects or to slightly rising emissions of SO$_2$ or other acidifying substances, will be a matter of further investigation.
In many countries, the number of dust storms is increasing to an extreme degree. In parts of North Africa, the annual dust quantity has increased tenfold over the past 50 years. Dust is transported over long distances, for example, from the Sahara as far as the Caribbean or from China as far as Europe. Every year, 2,000 to 3,000 million tons of dust are emitted into the atmosphere and act as fertiliser for coral reefs, accelerate the salinisation in some regions, neutralise acid rain, and change the radiation balance as the dust particles both reflect and absorb solar radiation. Dust particles are relevant for weather forecasting, as they affect visibility and modify the radiative forcing of the atmosphere on a larger scale.

Each year the Global Station Hohenpeissenberg is affected on a few days by Saharan Dust events. Such events leave fingerprints for a couple of parameters: Mass, size distribution, Angstrom exponent, and chemical composition of the aerosol (calcium content). Furthermore Saharan dust events are obvious in satellite images and the origin of dust clouds can be traced back by calculated backward trajectories.

Mass

The aerosol mass concentration at a background station like Hohenpeissenberg typically is in the order of 10-20 µg/m³. During Saharan Dust events the total mass concentration slowly rises up to values in the order of 50 to 100 µg/m³ and goes down to normal values of approx. 10µg/m³ after the dust cloud has passed (Figure 1).
Size Distribution

In order to distinguish the aerosols from different sources, such as sea salt or mineral particles due to mechanical generation processes, it is useful to measure aerosol size distributions, especially in combination with observations of the aerosol chemistry. Figure 2 gives an example about the changing aerosol size distribution during a Saharan dust event. Mineral dust aerosols consist of crustal materials originating mostly from suspension of exposed soil by wind in arid and semi-arid areas such as desert and agricultural regions and to a lesser extend by automobile traffic on unpaved roads. Mineral dust aerosols are primarily in the coarse mode; those with diameters >10µm fall out rapidly due to gravitational settling, while those with smaller sizes can be transported over long distances. They can impact significantly the atmospheric energy budget through scattering and absorption of solar radiation.

On the 23rd of March the aerosol size distribution at Hohenpeissenberg was mainly characterised by smaller sized aerosol particles (Figure 2) coming from local pollution. With the arrival of the Saharan dust between midnight and 9:00 a.m. on the 24th of March, the mass of giant particles (> 1 µm) increased by the factor 9.

Figure 2: Temporal changes of the aerosol volume as a function of the particle diameter at Hohenpeissenberg from 23rd to 24th March 2000.

Angstrom exponent

The Angstrom exponent describes this wavelength-dependence for scattered light. Situations where the scattering is dominated by sub micrometer particles typically have Angstrom values of approximately 2 (for the 550-700 nm wavelength pair), while values close to 0 occur when the scattering is dominated by larger particles such as mineral dust. Figure 3 shows hourly averages of the Angstrom exponent calculated from scattering measured at different wavelength with an integrating nephelometer at Hohenpeissenberg for February 2004. Hohenpeissenberg was influenced by Saharan dust on the 6th and 21st of February.
Figure 3: Angstrom exponent at Hohenpeissenberg (hourly averages). Circled values are Saharan Dust events.

Chemical composition of the Saharan dust aerosol

Calcium in aerosols is expected to come from dust in a variety of minerals. Compared to the average ion concentration for filter samples there are higher nitrate and especially calcium concentrations during Saharan dust events (Figure 4). Over continental areas, nitric acid reacts with calcium and magnesium carbonates found on crustal materials from local soil erosion or desert dust and forms calcium and magnesium nitrates.

Figure 4: Average percentage aerosol composition (filter) for non Saharan dust events (light blue) and Saharan dust events (dark red). Nitrate and especially Calcium show higher concentrations during Saharan dust events.
**Occurrence**

Saharan dust can be observed relatively frequently in Germany. Less spectacular Saharan dust events (yellow columns) can be observed especially in the spring and autumn on an average of up to five times a month. More extreme events with visible sand deposits on cars or with optical phenomena can be seen up to twice a month, mainly in the months of February, March, or October (blue columns). The occurrence of Saharan dust strongly differs from year to year.

**Figure 5:** Average number of Saharan dust events at Hohenpeissenberg (1997-2004). Weak events: light yellow, strong events: light blue.

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Climate Forcing Gases at Zugspitze

Measurement technique

Starting in 2001 carbon dioxide and methane are measured with GC FID technique using a gas chromatography unit which has been built especially by the ‘Institut für Umweltphysik’ (institute for environmental physics) at the University of Heidelberg. With the same unit, using ECD also sulfur hexa fluoride is measured with one chromatogram value every five minutes. The measurement of ozone is performed with a TE49 instrument.

Carbon Dioxide

Figure 1 shows the worldwide longest time series of CO₂ in the atmosphere which started 1955 at Mauna Loa in Hawaii plus the time series of the German GAW regional station Schauinsland which represents the longest CO₂ time series in Europe and the CO₂ time series measured at Zugspitze.

Despite the fact that the three measurement sites are at very different geographical locations the three time series are in very good accordance. This proofs that a worldwide trend of carbon dioxide is measured. The annual carbon dioxide variation which results from biologically induced mass balance has its relative minimum at the seaside station Mauna Loa, which also has the longest distance from the continentally situated sources and sinks. In contrary to this Schauinsland data taken at a continental site at 1200m asl. show the strongest annual variation because of the relative closeness to summerly carbon dioxide sinks of the vegetation and to anthropogenic carbon dioxide sources in the winter. With a lower carbon dioxide maximum in the winter Zugspitze data reflect the distinct separation from ground based measurements.

Figure 1: Worldwide trend of carbon dioxide in the atmosphere from 1955 to 2005 at the stations Mauna Loa (Hawaii), Schauinsland (Germany) and Zugspitze (Germany).
More information about carbon dioxide measurements in Germany can be obtained from the GAW letter No. 19 with the title “CO2 Messungen an den GAW Stationen Zugspitze und Schauinsland” under the following link from the internet:
www.dwd.de/de/FundE/Observator/IMK-IFU/...briefe/gaw_brief_019.pdf

**Methane**

The growth characteristics and the mean annual growth rate (2.5ppbV/yr) for the last decade of the measured methane time series (Figure 2) are in good accordance with globally averaged GAW methane measurement time series. However, due to the continental situation of the GAW station Zugspitze the time series shows an approximately 3.5% higher concentration level als the referred globally averaged time series from the world data centre for greenhouse gases.

![Methane Zugspitze 1995 - 2005](image)

**Figure 2:** 
Zugspitze Methane concentrations in the atmosphere from 1995 to 2005.

**Sulfur Hexafluoride**

Having an extremely higher atmospheric life time of about 3200 years and therefore a global warming potential for the next 100 years which is 22200 times higher than that of CO2 and a strong and steady growth sulfur hexafluoride has become an important climate forcing gas which has to be controlled. For the SF6 concentrations at Zugspitze (Figure 3) it is characteristic that for each year within the winter months the monthly mean values have concentrations which are significantly below the annual mean growth rate. This is another way to show that Zugspitze Station is strictly separated from ground sources during the winter months. On the other hand months with an considerably amount of convection – transport of lower air masses to Schneefernerhaus – clearly exceed the mean growth rate.
Ozone

Being a chemical reactive as well as a climatic forcing gas ozone is a very important atmospheric trace gas for GAW measurements. On Zugspitze summit ozone measurements have been made since 1978. Since 2001 ozone measurements have been continued at Schneefernerhaus (300 m below summit) with very good accordance to the summit data (Figure 4). In this altitude ozone measurements reflect the northern hemispheric background. The ozone concentrations of the last ten years show a stagnation on a high level at about 50 ppbV. Due to an atmospheric life time of 3 to 3 ½ weeks at this altitude ozone can be used in selected cases as an indicator for investigating intercontinental long range transport events, e.g. from northern America.
Ultra Fine Aerosols at Zugspitze

Between December 2004 and November 2005 the number concentration of fine and ultrafine particles in the range from 10 bis 800nm have been measured with the TSI SMPS 3080 electric size mobility scanner and with the CPC 3010 condensation particle counter.

Particle Distribution
The percentiles of the annual mean particle size distributions show clearly that the number concentration in the size distribution for all particle sizes has an annual variation of two magnitudes. Further the size distribution is bimodal with a mode separation at approx. 80 nm (Figure 5). The larger mode representing older particles and air masses is named “accumulation mode” whereas younger particles with a size below 80 nm are belong to the “aitken mode”. The number concentrations of particles in the range from 10 to 20 nm representing the formation process of new particles have to be treated separately.

Figure 5: Mean particle size distributions and percentiles at site Schneefernerhaus 300m below Zugspitze summit. Vertical lines show the interval boundaries at 20 and 80nm.

Correlation analysis shows that the number concentrations of different size classes have an independent behaviour. Therefore the size distribution from 10 to 540 nm contains real information and can not be substituted by a measurement of the total particle number. Moreover, the concentrations of the size classes over 50 nm and below 20 nm are anticorrelated. Thus only in very clean air masses the formation process of new particles starts.

Aerosol climatology
Figure 6 shows the monthly mean daily variation of particle number concentrations for Schneefernerhaus site in the time from December 2004 to November 2005. These data mirror detailed information about the aerosol dynamics and relating meteorological processes throughout the year.

This analysis shows clearly that the site lies above the atmospheric boundary layer for about half a year from autumn to spring in the months from October to march. The change between situations upwards boundary layer and below boundary layer occurs in the months April and September. May to august are typical months when the air masses of the dijournal variation are influenced by local convection processes of lower air masses with higher particle concentrations, especially in the time from noon to early evening with a maximum in July and august. It also can be stated that throughout the spring and summer months with strong influence of convection a time window exists in the time range from midnight to morning which enables a representative measurement of the conditions of the lower free troposphere.
Figure 6: Monthly mean daily variation with an abscissa showing the 24 hours daily time range, an ordinate with the size range from 10 to 800nm and a colour code representing the particle number concentrations in the range from 1 to 2000 dN / d log Dp cm$^{-3}$ particles per size class from blue to red.
Results from GAW Station Neumayer

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The observations at Neumayer cover the following types of GAW-measurements: Aerosol, greenhouse gas, meteo, ozone, radionuclide, solar radiation. In the following, some examples from the long-term measuring programme will be shown. More information is available at http://www.empa.ch/gaw/gawsis/reports.asp?StationID=54 or http://www.awi.de/Polar/neumayer2.html.

Air Temperature

Antarctica is frequently regarded to be very sensitive to climate changes. The positive albedo feedback mechanism between temperature and sea-ice extent is taken as one reason. The collapse of the Larsen Ice Shelf in 1995 and 2002 may be seen as an example. The event took place at the Antarctic Peninsular where a significant warming over the last 50 years was recorded.

The annually averaged air temperature 2 m above the snow surface from Neumayer is depicted in Figure 1. Within the last 25 years remarkable year to year variations were measured but no significant trend can be observed. This finding is in contrast to the measurements at the Antarctic Peninsular, but typical for the majority of all other Antarctic stations.

Recent publications denote a significant warming of the Antarctic winter troposphere [Turner et al., 2006]. The authors analysed long-time radiosonde measurements of 9 Antarctic stations covering the whole continent. The data from Neumayer - which have not been taken into account in this publication – show a comparable trend, but vice versa! Thus, at this moment it seems to be questionable whether the proposed warming of the Antarctic winter troposphere is significant or not.

![Figure 1](image)

**Figure 1:** Time series of the annually averaged air temperature 2 m above the snow surface of Neumayer.
Radiation

The radiation measurements at Neumayer are performed within the framework of the “Baseline Surface Radiation Network” BSRN [Ohmura et al., 1996]. One goal of this network is to monitor the background short-wave and long-wave radiative components and their changes with the best methods which are currently available. Furthermore, the network is used to validate and evaluate satellite-based estimates of the surface radiative fluxes and for comparison to climate models.

Since 1992 validated high quality data are available from about 40 BSRN-stations around the whole world. The Neumayer data show slight increase of the global radiation and a slight decrease of the long-wave downward radiation. The significance of these trends is still under discussion.

Ozone Profiling

The dynamic of the upper atmosphere in Antarctica is strongly influenced by a belt of strong westerly winds which form a circumpolar vortex surrounding the whole continent. This vortex is normally rather stable and separates the air masses within the vortex from the air at lower latitudes. Although the lower boundary of this vortex lies within the middle of the troposphere the vortex is called Antarctic stratospheric vortex since it dominates the dynamic of the whole stratosphere including the ozone layer. Only during polar day the vortex vanishes completely.

While the vortex is established, the advection of ozone rich and warm air from lower latitudes into the stratosphere of Antarctica is strongly reduced. Thus, during polar night, when no solar uv-radiation can get absorbed from the ozone layer, the stratosphere cools down to temperatures below -78°C which allow the formation of polar stratified clouds. With the increasing meridional temperature gradient across the polar vortex the wind velocities of the vortex increase. This thermal wind has mean zonal values well above 50 m/s and lead to a further separation of the air-masses inside the vortex.

After the Antarctic winter, when the sun rises above the horizon and polar stratified clouds are frequent, the solar radiation has the potential to destroy ozone molecules very efficiently. This happens normally during the first half of September. Afterwards, the ozone layer within the whole vortex is severely depleted or locally destroyed completely. The area with a vertically integrated ozone amount of less than 200 Dobson is called ozone hole.

The ozone hole frequently covers the total area within the stratospheric vortex. The worldwide increasing anthropogenic CFC concentration lead to an increasing ozone depletion.

The decreasing ozone concentrations in the Antarctic stratosphere lead to a diminished absorption of uv-radiation. Thus, the warming of the Antarctic stratosphere during spring is reduced. The isolating polar vortex – a thermal wind – resists longer and the possibility for polar stratospheric clouds – needed for further ozone depletion – is rising.

This positive feedback mechanism ends when the stratosphere gets warm enough that polar stratified clouds cannot exist any longer. The temperature gradient across the polar vortex gets weaker till the vortex looses its isolating character and warm, ozone rich air from lower latitudes can penetrate into the Antarctic stratosphere. This happens normally during November. In rare cases the stratospheric vortex is dynamically unstable and gets destroyed during winter. Comparable high temperatures and high ozone concentrations during the following spring are the consequences.

Since 1982 daily upper air soundings take place at Neumayer. In 1992 a weekly ozone sounding programme – started in 1985 at the near by station Georg-Forster – was moved to Neumayer. Both stations are situated comparable within the area normally surrounded by the Antarctic stratospheric vortex. The measurements contribute to the “Global Atmospheric Watch” (GAW) as well as to the “Network for the Detection of Stratospheric Change” (NDSC).
As can be seen clearly in Figure 2, the ozone layer above Neumayer shows a pronounced annual cycle. High ozone partial pressures are measured at heights about 20 km from December/January till end of August. This ozone originates from lower latitudes while the polar stratospheric vortex did not exist. Later, it stays more or less without major concentration changes inside the isolated vortex. The ozone layer descents from January to August about 3 km. The prevailing katabatic winds at the surface of Antarctica – leading to a mass transport outside the area of the polar vortex - are the reason. During Antarctic spring (September till November) the ozone layer vanishes more or less completely.

**Figure 2:** Time-height section of ozone partial pressure above Neumayer from 1992 to 2005.

Within the troposphere the ozone partial pressure is comparable constant with time and height. Close to the surface an annual variation with maxima during polar night and minima during polar day is evident.

The ozone layer during Antarctic spring shows remarkable inter-annual variations as well as an overall reduction of the ozone partial pressure with time. If the time series from Neumayer gets extended with the measurements taken from the near by station Georg-Forster these effects are even more pronounced, see Figure 3. The ozone reduction is strongly correlated with a cooling of the stratosphere. Corresponding variations or a significant trend during other seasons could not be ascertained.

From 1985 till 1989 a biannual oscillation of the spring ozone concentrations is evident. It is strongly correlated with the temperature in the height of the ozone layer. Labitzke et al. [1992] explained this behaviour as dynamically induced from the quasi biannual oscillation of stratospheric wind above the equator.

In the nineties, no biannual oscillation of the spring ozone concentration was measured any longer. The data show a more or less continuously reduction of the ozone concentration and a cooling of the air around 70 hPa. Crutzen et al. [1986] explained this kind of behaviour as a chemically effect with respect to the worldwide rising anthropogenic CFC concentrations.

During spring 2002 very high temperatures and ozone concentrations were measured. They result from a dynamically break down of the Antarctic stratospheric vortex during winter. This behaviour has nothing to do with a recoverage of the ozone layer after the worldwide ban of nearly any CFC product. Although the CFC concentrations in the troposphere are significantly falling and
start to fall in the stratosphere the recovery of the ozone layer will most probably not take place within the next decade.

![Figure 3: Time series of seasonal averaged stratospheric parameters (at 70 hPa) above Georg-Forster and Neumayer from 1985 to 2005.](image)

**Tropospheric Ozone**

It is generally accepted that the photooxidation of trace gases to water soluble compounds, followed by rainout, is the major cleaning procedure of tropospheric air. Photooxidation in the troposphere consists of typical radical chain reactions which need to be initiated, mainly by OH radicals. OH in turn is primarily generated via ozone photolysis and subsequent reaction of the so produced O¹D (i.e. electronically excited oxygen) atoms with water vapour. Thus tropospheric ozone is certainly a key trace gas in controlling the chemical composition of the troposphere.

Surface ozone is continuously measured since 1982 at Neumayer Station by electrochemical concentration cells (ECC, until 1994) and uv-absorption from 1994 ongoing (Figure 4). O³ mixing ratios measured at the former Georg-von-Neumayer-Station by ECC seem to be significantly lower before 1987, a probably artificial peculiarity which is not yet clarified. Nevertheless from this record, covering now 24 years of observation, no significant trend can be deduced.

A more detailed section of this times series is depicted in Figure 5. Maximum ozone values of about 32 ppbv are generally observed in August while during polar summer (December-January) a distinct minimum of around 13 ppbv is typical. In strong contrast to urban areas where nitrogen oxides (NOₓ) levels are about three orders of magnitude higher, photochemical ozone destruction and not formation occurs in summer leading to surface ozone minima in pristine regions like Antarctica.

In addition, from August to September extraordinary tropospheric ozone depletion events can frequently be detected (Figure 5). Neumayer Station was the first Antarctic site where this peculiarity was described [Wessel et al., 1998]. Comparable to stratospheric ozone depletion, reactive halogen compounds, here especially BrO, are responsible for this anomaly [Friess et al., 92]
2004]. However, in contrast to the chemical processes occurring in the stratosphere, tropospheric ozone depletion in polar regions is a natural phenomenon most probably caused by release of reactive bromine compounds eventually derived from sea-salt over sea-ice. There is some recent evidence that frost flowers, which frequently grow on newly-formed sea ice, play an important, if not crucial role as a source for reactive tropospheric halogen compounds [Kaleschke et al., 2004].

![Figure 4: Surface ozone mixing ratios (daily means) record at Neumayer from 1982 to 2005.](image.png)

![Figure 5: Surface ozone mixing ratios (daily means) record at Neumayer from 1992 to 1999. The enlarged section on the right hand side shows typical tropospheric ozone depletion events (shaded areas) in more detail (hourly averages).](image.png)

**Condensation Nuclei Concentrations**

Condensation nuclei (CN) comprise all atmospheric particles which can act as nuclei for condensation of low volatile gaseous compounds most notably water vapour. Generally particles >3 nm in diameter can act as CN.
CN concentrations at Neumayer exhibit a stepwise increase from polar winter (below 100 particles/cm³) to a maximum in late austral summer of around 1000 particles/cm³ (Figure 6). During summer the chemical composition of these particles is mainly methane sulfonic acid (MSA) and non-sea salt sulfate (nss-sulfate), thus CN are formed in the marine troposphere by photooxidation of dimethyl sulfide (DMS) emitted by the phytoplankton.

During winter and stormy weather conditions, however, sea salt aerosols dominate. Interestingly, the maximum of condensation particle concentration typically appears in late February to early March, i.e. shifted by around 4-6 weeks compared to the MSA and nss-sulfate maxima. Our measurements suggest that during late summer the concentration of very small particles between 3 and 5 nm diameter (nucleation mode) is significantly enhanced, indicating new particle formation.

DMS could act via its photooxidation product sulfuric acid as gaseous precursor for nucleation mode particles, a process known as gas to particle conversion. Due to the relatively short atmospheric lifetime (a few hours) of nucleation mode particles, regional sources should dominate the measured signal. We believe that following the retreat of sea ice in the nearby Atka bay during late February, considerable amounts of DMS are released by the now emerging phytoplankton bloom in this area. Note that nucleation mode particles do not contribute much to the total aerosol mass due to their small size, therefore nss-sulfate and MSA concentration maxima must not coincide with the particle number concentration maximum!

**Figure 6:** Daily means of condensation nuclei (particle diameter larger than 10 nm, measured with a TSI CPC 3022) concentrations at Neumayer. The bold yellow line is a low-pass smoothed representation of the data by a 30 points Gaussian filter.
References
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Measurement of Radionuclides at the GAW Station Zugspitze/Hohenpeissenberg

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The radioactivity measuring programme for the global station Zugspitze/Hohenpeissenberg (2962 m a.s.l) is carried out on the Zugspitze platform as well as at the Environmental Research Station Schneefernerhaus (UFS-Schneefernerhaus, 2650 m a.s.l.) and comprises the determination of atmospheric activity concentrations of the radionuclides tritium as $^3$H in $^3$HOO, (half-life 12.32 a), $^{85}$Kr (half-life 10.76 a), $^{14}$C as $^{14}$CO$_2$ (half-life 5730 a), $^7$Be (half-life 53.3 d), $^{222}$Rn (half-life 3.8 d) and its daughter products $^{212}$Pb (half-life 10.64 h) and $^{214}$Pb (half-life 26.8 min).

Some of these radionuclides are formed naturally by the interaction of cosmic radiation with the atoms of the upper atmospheric layers, such as, for example, $^{14}$C and $^3$H which are also emitted by nuclear power plants. The continual new formation and the radioactive disintegration result in a balance of concentration on these radionuclides in the atmosphere, and in the oceans and biological systems that are in constant exchange with the atmosphere.

$^{85}$Kr is formed as fission product from $^{235}$U or $^{239}$Pu with differing amounts. In the processing of fuel elements the majority of noble gases reaches the atmosphere. The operation of nuclear reactors and the chemical reprocessing of the fuel rods causes the concentration of $^{85}$Kr in the atmosphere to increase continuously world-wide.

The natural radioactive noble gases $^{222}$Rn and $^{220}$Rn escape from the ground and disintegrate in the air into the daughter products $^{212}$Pb respectively $^{214}$Pb. The relationship between $^{222}$Rn, $^{85}$Kr and $^7$Be shall be used to make statements on the origin of the air masses (classification as local or long-distance transported air masses, vertical transports).

Meteorological Significance of $^7$Be, $^{212}$Pb and $^{214}$Pb

The stratosphere is the main reservoir of atmospheric $^7$Be. During tropopause folding events $^7$Be enriched stratospheric air penetrates into the troposphere. High $^7$Be concentrations indicate air masses of stratospheric origin and occur in dry air descending from the tropopause to the lower troposphere.

$^{212}$Pb and $^{214}$Pb are produced in the lower troposphere by the radioactive decay of the gases $^{222}$Rn and $^{220}$Rn. These gases are emitted in the atmosphere at the ground. The concentrations of $^{212}$Pb and $^{214}$Pb usually decrease from the ground to higher elevations. $^{212}$Pb and $^{214}$Pb are transported to higher elevations by convection developing during daytime, which indicates transport of boundary layer air to higher elevations.

The radionuclides are quickly attached to aerosol particles suspended in the atmosphere. This is why, apart from the transport, cloud and processes forming precipitation must also be taken into consideration when interpreting the data. The table below summarises three important meteorological processes and their effect on the activity concentration of the radionuclides. The changes in the activity concentration of the radionuclides refer to high elevated locations like the Zugspitze.
Large-scale descending (process 1) prevails in a high pressure region. The activity concentration of $^7$Be increases at the Zugspitze due to the sinking, that of $^{212}$Pb and $^{214}$Pb and the concentration of the aerosol particles decrease. Descending air causes an increase in temperature and a decrease in the relative humidity at the Zugspitze. Only in winter does the sinking movement remain undisturbed from other transport processes. In spring and especially in summer the descending is superimposed by convection (process 2), which is enhanced by mountains. The convection developing during daytime causes part of the air at the Zugspitze to come from the atmospheric boundary layer. The concentrations of $^{212}$Pb and $^{214}$Pb and the aerosol particles increase at the Zugspitze due to the portion of air from the boundary layer. The relatively long half-life of $^7$Be in comparison to the fast convective exchange makes the identification of intrusions more difficult. The convective transport can be recognised with the aid of $^{212}$Pb and $^{214}$Pb, thus making it possible to separate the ascents of $^7$Be caused by intrusion from those caused by convection. The activity concentrations of the radionuclides decrease when clouds and precipitation form, because the aerosol particles to which the radionuclides are attached are removed from the atmosphere (process 3).

March 2002 – Case studies on the radionuclide-supported interpretation of atmospheric transport processes
Measurements of the relative humidity, precipitation (Figure 1) and the radionuclides (Figures 2 and 3) from March 2002 clearly show the relation between vertical transport and the concentration of radionuclides. From March 1 - 19 and 26 - 30 very dry air masses dominated over the Zugspitze, which were only seldom interrupted by short phases of precipitation. In this period the concentration level of \(^7\)Be was above average, which was due, on the one hand, to the air masses sinking from higher layers in the atmosphere and, on the other, to the low degree of precipitation activity. The rise in the \(^{212}\)Pb- \(^{214}\)Pb-concentration (Figure 3) and the relative humidity (Figure 1) from the 11\(^{th}\) - 16\(^{th}\), as well as towards the end of the month, suggests that, during the course of this fine weather period, thermal convection and thus the influence of surface air increased (Process 2). In March the high mountains are already under the influence of convective transport from the boundary layer. The marked \(^7\)Be peaks on March 4 and 26 in connection with the minima for \(^{212}\)Pb and \(^{214}\)Pb suggest an air mass from the upper troposphere/lower stratosphere (Process 1). The increases in ozone concentration (Figure 3) during both these occurrences indicate, on the basis of radionuclide measurements, ozone\(^∗\) of stratospheric origin. The ozone concentration rose gradually from March 11 - 16. As the \(^{212}\)Pb and \(^{214}\)Pb concentrations also increased during this period, the air mass over the Zugspitze was influenced by surface air, within which ozone had probably formed photo-chemically.

On March 19 cloudy and rainy weather set in which lasted until March 25. The radionuclides were almost completely removed from the atmosphere with the aerosol particles (Process 3). Air sampling at the Zugspitze is done by separating the aerosol particles on filters that are changed every 12 hours to determine the activity concentration of \(^7\)Be and \(^{212}\)Pb and every 2 hours for \(^{214}\)Pb. The activity concentration of \(^7\)Be and \(^{212}\)Pb is given in mBq/m\(^3\), that of \(^{214}\)Pb in Bq/m\(^3\).

### Measurements

The measurements according to the GAW-programme were started in 2000. \(^7\)Be, \(^{212}\)Pb and \(^{214}\)Pb have been measured continuously since then. \(^{222}\)Radon has also been measured but the concentration of \(^{222}\)Radon is very low at the sampling site UFS-Schneefernerhaus so that the limit of detection of the measuring device was not reached often. Therefore a new measuring system has been developed and will be ready to continue measuring in summer 2006. Additionally the measurements of \(^{210}\)Pb have been started in 2005.

Due to limitations of personal staff the measurements of \(^{85}\)Kr and \(^{14}\)CO\(_2\) were terminated in 2004. The sampling of tritium in humidity has been started in the beginning of 2004 but the samples are not yet analysed because of above mentioned reasons. The time series of \(^{85}\)Kr and \(^{14}\)CO\(_2\) are presented with figure 4 and 5.

The present \(^{85}\)Kr activity concentration in the air is approx. 1.4 Bq/m\(^3\) in the northern and approx. 1.2 Bq/m\(^3\) in the southern hemisphere. In 1973 the measured values were around 0.6 Bq/m\(^3\) [1].

The sampling site Zugspitze is particularly suitable for recording long-distance transported \(^{85}\)Kr without local influence. Since 2000 an analysis system for radioactive noble gases has been in operation at the central laboratory of the DWD in Offenbach for the further processing of the samples. The activity concentration in the air is calculated from the beta activity of \(^{85}\)Kr in relation to the amount of total non-radioactive krypton which is 1.14 ppmV.

The comparability of the analytical method is tested as follows: Two parallel samples are taken at the Offenbach site, one sample to be analysed in the laboratory of BfS, the other sample in the DWD laboratory. Both measurement series agree well [2]. The data are recorded and are supposed to be fed continuously into a GAW data base for scientific use.

\(^∗\) ozone data from UBA (Federal Office for the Environment)
References

Figure 4: Results for $^{85}$Kr at the sampling site UFS-Schneefernerhaus: 2000 – 2004.

Figure 5: Results for $^{14}$CO at the sampling site UFS-Schneefernerhaus in 2003 – weekly samples.
Climate Forcing Gases

**Carbon Dioxide (CO₂)**

Germany has a long tradition in continental observation of climate forcing gases in the atmosphere. The first continental measurements of CO₂ were established by the 'Deutsche Forschungsgemeinschaft' (German Science Foundation) at Schauinsland in the beginning of the 1970s. Therefore, the Schauinsland record is the longest available continental time series of CO₂ mixing ratios. Today several stations in Germany, operated by the 'Umweltbundesamt' (Federal Environment Agency), add to GAW with continuous measurements. The Schauinsland continuous measurements are supplemented by flask sampling (University of Heidelberg) and are - together with the results of other sites - currently integrated in the EU-funded Project CarboEurope-IP (www.carboeurope.org).

This international effort aims at intercomparing and harmonising all European CO₂ observations, in order to make them available for (inverse) modelling which use the small but significant observed CO₂ gradients over Europe to derive the European budget of CO₂ sources and sinks. Figure 1 and Figure 2 show the CO₂ records at the Schauinsland and Neuglobsow stations, respectively.

Figure 1: Upper panel: Daily mean wind-selected CO₂ mixing ratios at the German GAW station Schauinsland in the Black Forest (1205 m asl); lower panel: Long-term trend of the annual growth rate (see also Schmidt et al. 2003).
CO₂ mixing ratios over the continents are much more variable than measurements at marine baseline stations but they capture the signals from regional and continental sources and sinks. Still they follow the trend at marine sites (dotted curve in Figure 1). The CO₂ mixing ratios at the Schauinsland and Neuglobsow stations show a strongly increasing trend, with a mean growth rate of approximately 2 ppm/yr. The inter-annual variations of the growth rate are mainly due to the variations of the exchange fluxes between atmosphere, biosphere and the oceans.

Figure 2:  Wind-selected CO₂ concentrations in the atmosphere at Neuglobsow station.

Figure 3:  Long term trend of the unselected monthly means of carbon dioxide mixing ratio at Schauinsland station in comparison with measurements at the GAW global stations Mauna Loa and Zugspitze.
Figure 3 shows that CO₂ concentration levels increase worldwide with the same rate. The seasonal variations of the mixing ratios observed at mid northern latitudes are caused by photosynthesis and respiration of the continental biosphere. As expected, the unselected CO₂ record at Schauinsland station has more distinct seasonal variations due to the biogenic and anthropogenic impact in the surrounding area of the station (Figure 1).

Other Climate Forcing Gases

Similar monitoring efforts as for CO₂ concern measurements of other climate forcing gases such as methane (CH₄), nitrous oxide (N₂O) and sulfurhexafluorid (SF₆) which are conducted at the Schauinsland, as well as at the Zugspitze station. The GAW regional station Neuglobsow runs a GC system for CO₂ and methane.

Methane (CH₄)

Besides CO₂ methane is the most important anthropogenic greenhouse gas. CH₄ mixing ratios have been measured since 1991 at the Schauinsland station, and since 1994 at the GAW regional station Neuglobsow. At both stations a GC system with FID detector is used. Figure 4 shows the comparison of the mixing ratios between both stations.

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\text{Figure 4: Comparison of the unselected monthly mean methane mixing ratios at the GAW regional stations Neuglobsow and Schauinsland.}
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The large seasonal variation of the CH₄ mixing ratio at Neuglobsow is probably due to the stronger influence of local sources at this site compared to the mountain station Schauinsland. Maximum concentrations are reached in the winter months, the minimum is observed in summer. At the Schauinsland station there is no systematic seasonal variation detectable. Both records show a distinct increase of CH₄ concentrations in the atmosphere.

Sulfurhexafluoride (SF₆)

Since the beginning of the observation of the greenhouse gas Sulfurhexafluorid (SF₆) at the Schauinsland station in 2000, annual mean concentrations have increased from about 5 ppt up to almost 6.5 ppt. This corresponds with a percentile increase of 30% within 5 years. In comparison with CO₂, SF₆ has a 22000 times higher greenhouse potential. It is very inert, and has a lifetime in the atmosphere of about 3000 years. Due to this long lifetime, any additional SF₆ emission will cause an increase in the atmosphere and stabilisation of this greenhouse gas is only possible when emissions are completely stopped. Due to its physical properties SF₆ is mainly used in electrical equipment and in high voltage areas, in electric switches and isolations.
Figure 5: Development of the monthly mean concentrations of sulfurhexafluoride (SF$_6$) at the Schauinsland station.

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A Simple Data Filter for Increased Spatial Representativity

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One of the objectives of the measurements made within GAW is to calculate and track large-scale changes in air pollutant concentrations. In order to be able to recognize in their early stages such trends in locally measured time series, local influences must be filtered out. A simple filter developed at the Hohenpeissenberg observatory uses the changes in concentration with time and relates each value, with the aid of the wind speed measured simultaneously, to so-called "representation distances" (RD). A detailed description of this filter method can be found under Fricke et al. (2000). Using this approach it is possible to give the distance from the monitoring site, within which the measured concentration of a pollutant remained in a given concentration interval, and is thus representative for this parcel of air.

Figure 1: Time series of the hourly mean CO concentration at Hohenpeissenberg for various representation distances (concentration interval: 15 ppb).
Figure 1 shows the variation in time from January 1997 to April 2004 of all hourly CO mean values at the top. The large span of CO concentration with maximum values in winter of almost 1 ppm can be seen. The seasonal variation with higher values in winter and lower concentrations in summer is also conspicuous. If these data are filtered and the values shown only with RD values of more than 70 km, this results in the courses shown below. High CO concentrations are no longer found here, the highest values being almost all under 400 ppb. The range of the other values has also decreased considerably and is only half as large as the whole data set. From the originally over 57000 data, around 28000 values still remain, i.e. a good half of the CO values had, according to this filtering, a spatial representation of more than 70 km in the years 1997 to 2004. The diagram on the bottom contains only CO data with a representation distance of more than 250 km (approx. 15% of the total data set). Apart from very few exceptions, all values lie between 80 and 250 ppb, which are values that according to Novelli et al. (1998) are observed at background stations of the northern hemisphere.

Figure 2: Time series of the hourly mean NOx concentration at Hohenpeissenberg for various representation distances (concentration interval: 0.3 ppb).
The concentration trend of all NOₓ hourly values from 1997 to 2004 are shown in Figure 2 and below that, the filtered data with a related RD of more than 70 and more than 250 km. These components also show very well how the high concentrations fall away with increased RD. Only between November and January do some hours with concentrations of over 3 ppb occur, which is related to a high RD. In corresponding representation distances more values are filtered out of the NOₓ data than the CO data. Due to the shorter residence time of NOₓ in the atmosphere as compared to CO, this result is plausible.

When calculating a linear trend for the CO data, it shows only a significant (i.e. trend > standard deviation) decrease of 1.7% per year for the unfiltered data. The trend is no longer significant for filtered data. Higher RD (250 instead of 70 km) of the filter hardly lead to any changes worth mentioning (see table). That permits the conclusion that in the near vicinity the emissions decrease more than at distances further away. The linear trend for the NOₓ data shows a decrease of around 2.5% per year for the unfiltered values, and no significant trend for the filtered data. That corresponds to the decrease in concentration already found for CO in the near vicinity of the Hohenpeissenberg.

Table 1: Trends in CO and NOₓ concentration at Hohenpeissenberg for different periods and filters.

<table>
<thead>
<tr>
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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Linear trends in % per year</td>
<td>CO</td>
<td>Nox</td>
</tr>
<tr>
<td>not filtered</td>
<td>-1.7 ± 0.9</td>
<td>-2.5 ± 1.3</td>
</tr>
<tr>
<td>RD &gt; 70 km</td>
<td>-0.5 ± 0.8</td>
<td>-0.6 ± 1.0</td>
</tr>
<tr>
<td>RD &gt; 250 km</td>
<td>-0.7 ± 0.8</td>
<td>-1.0 ± 1.1</td>
</tr>
</tbody>
</table>

If the trends established for the period given above (January 1997 - April 2004) are compared with the period until December 2001, then the CO trends have clearly changed (see Table 1). Over the shorter period the trends were plainly more pronounced and for all 3 filter stages a definite negative trend was recorded. For NOₓ on the other hand, the trends for both periods showed very similar results.

The great changes observed for CO indicate that the period taken for the evaluation is till too short to discern a long-term trend. A similar behaviour would then, however, be expected for NOₓ.

On the other hand, these results are consistent with analyses of the SO₂ trend at Hohenpeissenberg, where it was established that since about the year 2000, in addition to a more frequent occurrence of east wind weather situations, an increase in the mixing ratios with easterly winds was also measured. This was suspected as being the result of possibly increased emissions in eastern Europe. In this case a definite positive trend is expected for long-lived trace gases (e.g. CO), or in the case of an already present negative trend, a clear decrease in this trend, especially for data that are representative for a greater distance. A slight positive trend is to be expected for trace gases with a medium life time (e.g. SO₂) and for trace gases with a short residence time (e.g. NOₓ) no trend is to be expected. This is consistent with the observations described above.

In addition to the filtering of local origins, the influence of meteorological quantities (e.g. shifting of advection frequency from areas of origin) will also have to be taken into account in further trend analyses. Changes in meteorological parameters, as part of the climate change, could feign or disguise trends in air pollution records.
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*Formation and Chemistry of Atmospheric Oxidants*

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*GAW lead scientist: H. Berresheim*

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