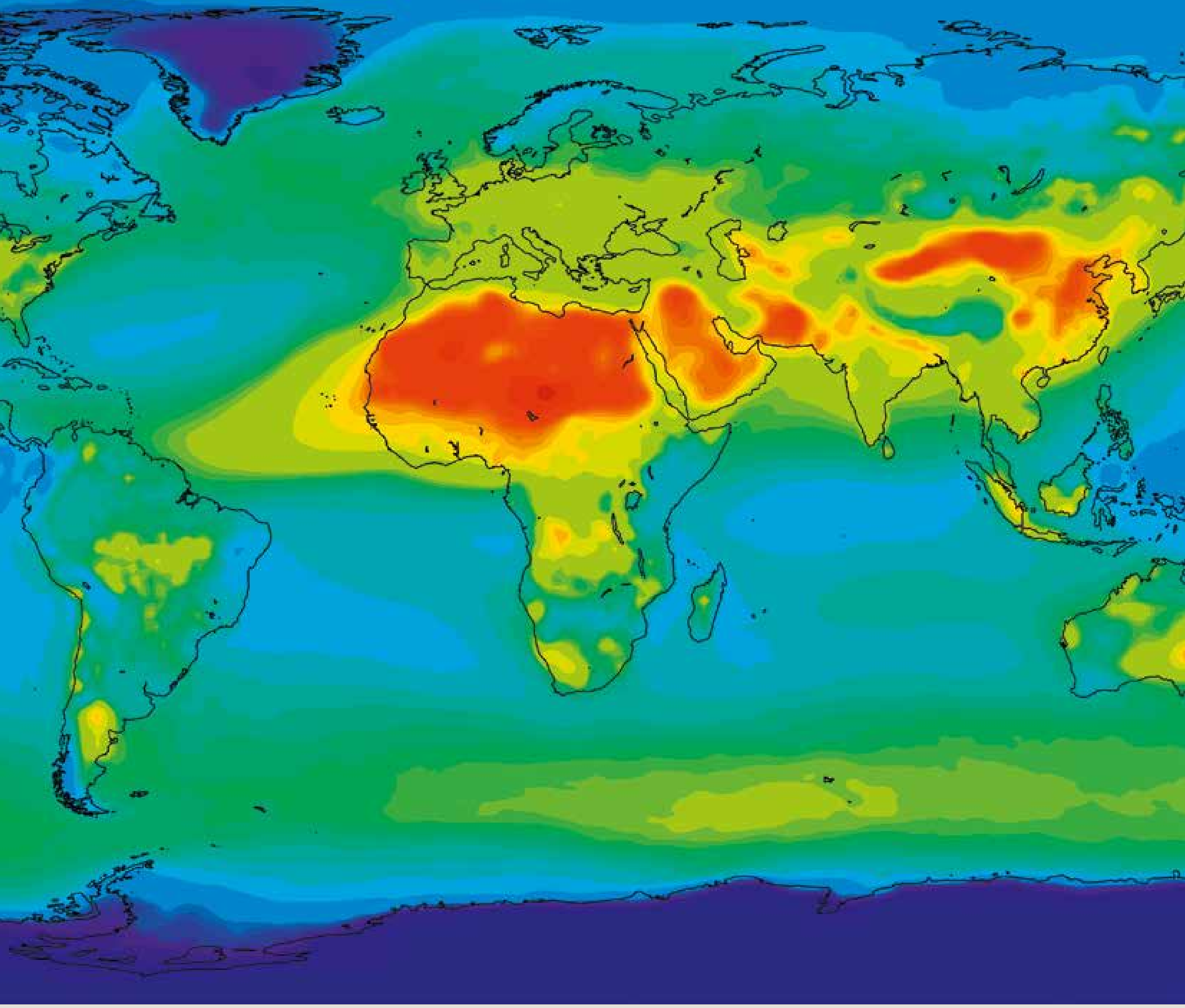

# SCIENTIFIC REPORT 2015-2017

## Max Planck Institute for Chemistry
## (Otto Hahn Institute)

MAX PLANCK INSTITUTE
FOR CHEMISTRY

MAX PLANCK INSTITUTE
FOR CHEMISTRY

*Atmospheric Chemistry · Biogeochemistry · Climate Geochemistry ·*
*Multiphase Chemistry · Particle Chemistry*

# SCIENTIFIC REPORT

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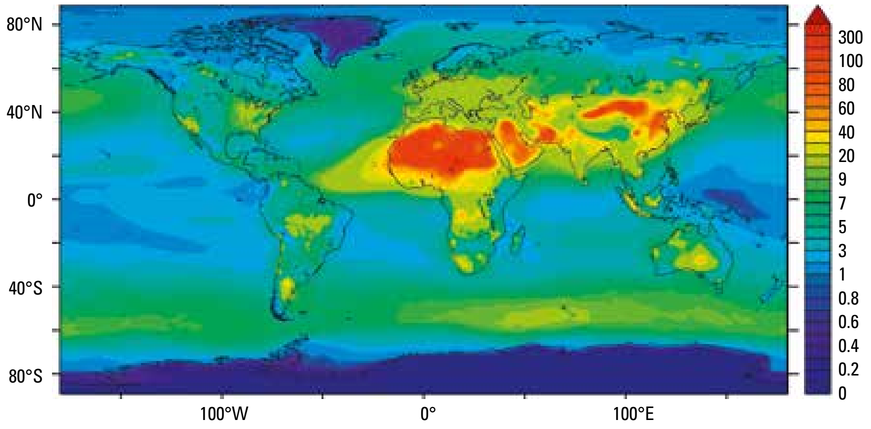
*2015–2017*

# CONTENT



*Cover picture:*
*Annual average surface concentration of PM2.5 at 50% relative humidity in µg m$^{-3}$, simulated by the EMAC model (www.messy-interface.org) (Credit: Andrea Pozzer).*

# *PREFACE*

The years 2015–2017 have been both a very challenging and a highly successful period for the Max Planck Institute for Chemistry (MPIC).

First and foremost, the Climate Geochemistry Department of Gerald H. Haug was launched in 2015 and has swiftly grown to full size. Gerald and his team bring exciting new research directions to the Institute, addressing Earth history and climate change over time scales from decades to millions of years. Excellent new members have joined the team, and new state-of-the-art laboratories and equipment for elemental, isotopic, and molecular tracer analysis have been installed and brought into operation for the investigation of ocean sediments and plankton. The climate history and ocean science perspectives of the new Department are greatly strengthening and extending the scientific scope of the MPIC and its collaboration with the MPI for Biogeochemistry, the MPI for Meteorology, and further partners in the Earth System Research Partnership (ESRP).

On the other hand, the Biogeochemistry Department of Meinrat O. (Andi) Andreae has gradually downscaled its activities and was closed in 2017, after 32 years of pioneering research on the atmosphere-biosphere exchange of aerosols and gases and their influence on clouds, precipitation, and climate. The great success of the Department's truly interdisciplinary research and international collaborations was reflected in a farewell symposium on the "Facets of Biogeochemistry", attended by scientific colleagues and friends from all around the world. One of the Department's major achievements and legacies is the Amazon Tall Tower Observatory (ATTO), which includes a 325 m measurement tower that is the highest construction in South America. After more than a decade of preparation and development led by Andi Andreae and Jürgen Kesselmeier, the ATTO project now yields unique insights into the climate and ecosystem of the Amazon rainforest. Accordingly, the investigations will continue with Andi as an emeritus member and with other ATTO researchers who have moved to different MPIC departments. Special thanks go to Andi and his entire team for their great contributions to scientific progress, to the Institute's success, and to the smooth organizational rearrangements of the past years.

In addition to establishing ATTO, the MPIC has successfully carried out a wide range of other challenging field measurements and expeditions as detailed in this report. In particular, the Atmospheric Chemistry, Multiphase Chemistry, and Particle Chemistry Departments have closely collaborated and have received excellent support from the Institute's Joint Services to undertake an exceptionally challenging ship measurement campaign around the Arabian Peninsula to unravel the effects of natural and anthropogenic emissions on air quality, climate, and public health in the Middle East (AQABA). Moreover, a series of challenging airborne measurement campaigns, ranging from tropical to polar regions, were performed with a variety of research aircraft (HALO, Geophysica, AWI Polar 5 & 6, DLR Falcon). The field observations were complemented by physical, chemical, and biological laboratory experiments and numerical model studies investigating the sources and interactions of air pollutants that influence climate and public health.

A special research highlight was the discovery of superconductivity at record-breaking temperatures of up to 203 K in hydrogen sulfide under high pressure (>1 Mbar) by Mikhail Eremets and his team. These findings were a milestone and a large step on the way to achieving room temperature superconductivity. They sparked enormous excitement in the physical, chemical, and materials science communities, triggering a wave of follow-up studies that confirmed and extended the spectacular results.

Another scientific outcome that continues to gain momentum is the notion of the Anthropocene, as established by Paul Crutzen and colleagues to describe the present era of globally pervasive and steeply increasing influence of human activities on planet Earth. It helps our society recognize that humans are indeed shaping the planet and should take care to get things right with regard to global change, climate, and public health.

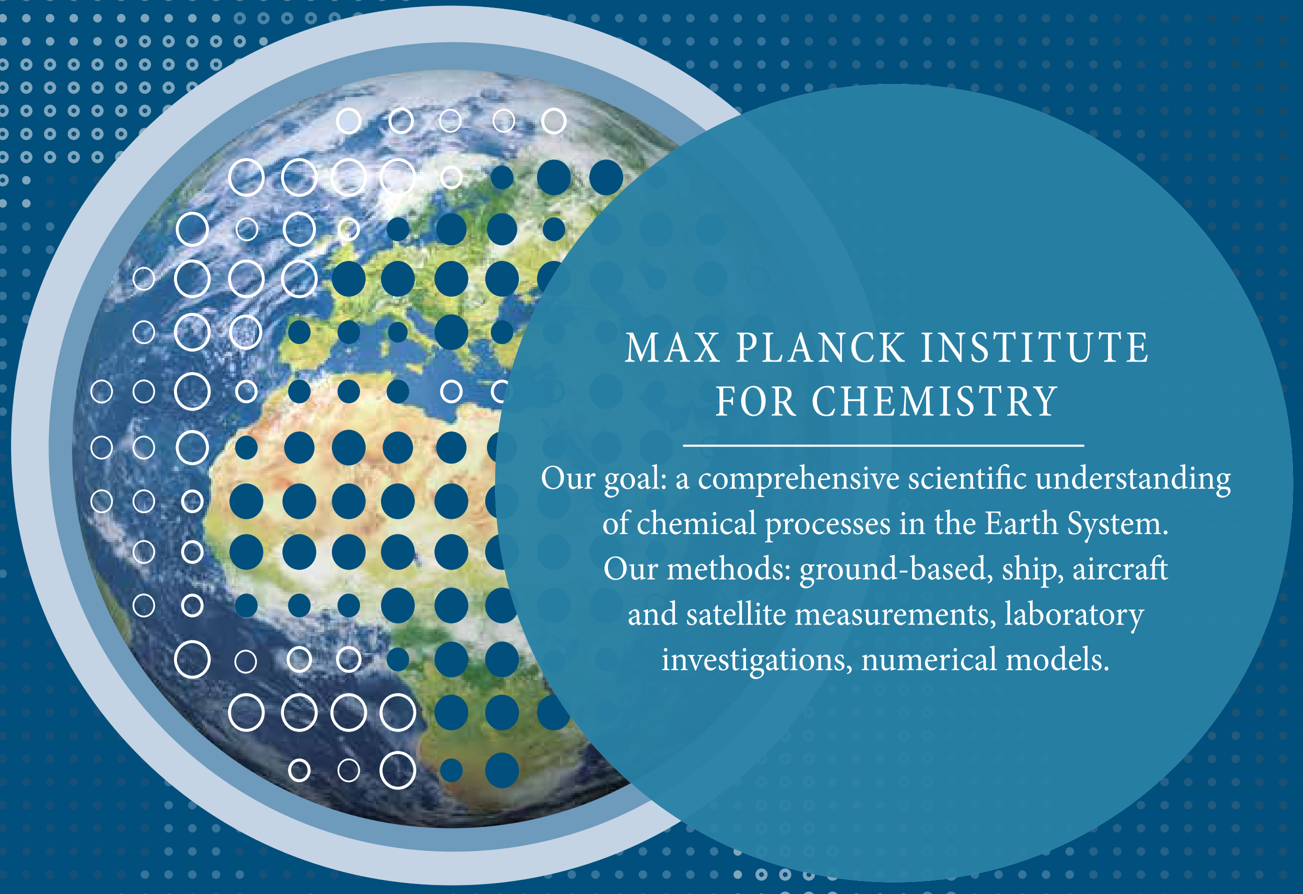
For efficient communication of scientific findings and insights, MPIC researchers have pioneered the concepts of interactive open access publishing and public peer review, which are now spreading across the sciences and humanities. Institute members play key roles in international initiatives for a science-oriented large-scale implementation of open access to research publications. As the increasing share of open access to MPIC publications in peer-reviewed scientific journals approaches 50%, the Institute continues to be a pacemaker of open science for the benefit of scientific and societal progress.

Overall, the scientific and societal impact of the Institute confirms the high value of scientific freedom and fundamental research according to the Harnack principle and traditions of the Max Planck Society.

*Ulrich Pöschl, Managing Director*
*December 2017*

*From the left: Sediment laboratory in the Climate Geochemistry Department, Farewell symposium for Meinrat O. Andreae, Institute building, ATTO measurement tower, Meeting of the Anthropocene Working Group.*

# GENERAL INFORMATION



MAX PLANCK INSTITUTE
FOR CHEMISTRY

Our goal: a comprehensive scientific understanding of chemical processes in the Earth System. Our methods: ground-based, ship, aircraft and satellite measurements, laboratory investigations, numerical models.

## OBJECTIVES & ORGANIZATION

### THE INSTITUTE

The Max Planck Institute for Chemistry has a long tradition of multidisciplinary research at the interfaces between chemistry, physics, biology, and the geosciences. Current research at the MPIC is focused on a comprehensive understanding of chemical processes in the Earth system, including the atmosphere, biosphere, and oceans.

Investigations address a wide range of interactions between air, water, soil, life, and climate over the course of Earth history up to the Anthropocene – today's human-driven epoch. Scientists conduct laboratory experiments and use ground-based observatories, vehicles, ships, airplanes, and satellite instruments to obtain measurement data and collect samples during long-term observations and expeditions. Mathematical models that simulate chemical, physical, and biological processes from molecular to global scales complement the experimental studies. One of the common themes of research at MPIC is to determine how air pollutants, including reactive trace gases and aerosols, affect the atmosphere, biosphere, climate, and public health. Other key topics are the air-sea exchange and biogeochemical cycling of greenhouse gases, oceanic nutrients, and related substances.

At present, the Institute employs some 300 staff in four departments and four additional research groups. Each department is led by a director who is a scientific member of the Max Planck Society and has the responsibility of defining the scientific objectives and guiding the research of the department. The directors jointly guide the Institute's development and take turns in serving as the spokesperson of the board of directors and managing director of the Institute. Ulrich Pöschl has been serving in this position since 2014, and Gerald Haug is expected to take office for the next term.

*Gerald H. Haug, Meinrat O. Andreae, Jos Lelieveld, Ulrich Pöschl and Stephan Borrmann (from left to right).*

### DEPARTMENTS

The **Atmospheric Chemistry Department** directed by Jos Lelieveld focuses on ozone chemistry and radical reaction mechanisms, and their role in atmospheric oxidation pathways and the global cycles of trace compounds. These processes, which are important for the self-cleaning capacity of the atmosphere, are studied through laboratory investigations and field measurement campaigns, in particular with aircraft. Computer models that simulate meteorological and chemical interactions are used to support and analyze the field measurements. Models are also applied to assess the impacts of natural and anthropogenic emissions of gases and particles on air quality and climate.

The **Biogeochemistry Department** directed by Meinrat O. Andreae investigated interactions between the terrestrial and marine biosphere and the chemistry of Earth. It performed field experiments to study exchange processes of trace gases and aerosols between the soil-vegetation system and the atmosphere. This included the environmental effects of vegetation fires. Laboratory studies were performed to analyze geological records to elucidate the past states of the Earth System. Upon the retirement of Meinrat O. Andreae, the Biogeochemistry Department expired in May 2017.

The **Climate Geochemistry Department** directed by Gerald H. Haug addresses climate-ocean-atmosphere processes and large-scale dynamics in global biogeochemical cycles as revealed by sedimentary and fossil records. To quantify the mechanisms and causes of major changes in Earth's environmental conditions the department employs a diverse geochemical toolbox that includes light stable isotopes of foraminifera shells and organic matter, biomarkers, and trace metals, as well as high-resolution non-destructive analytical techniques.

The **Multiphase Chemistry Department** directed by Ulrich Pöschl investigates chemical reactions, transport processes, and transformations between solid matter, liquids, and gases. These processes are essential for the interplay of the Earth system, climate, life, and public health. Among the focal points are gas-particle interactions in aerosols and clouds as well as the health effects of fine particulate matter. The applied methods include laboratory experiments, field measurements, and model studies using physical, chemical, and biological techniques.

The **Particle Chemistry Department** is directed by Stephan Borrmann who is also Full Professor at the Johannes Gutenberg University of Mainz. Its research focuses on the composition and physical properties of micro- and nanoparticles in Earth's environment, and on interactions between atmospheric aerosols, clouds and climate. Methodologies employed include single and multiple particle mass spectrometry in the laboratory and in field measurement campaigns, mostly using aircraft.

## FURTHER RESEARCH GROUPS

The **Aerosols and Regional Air Quality** group led by Yafang Cheng and supported by the Minerva program of the Max Planck Society addresses central questions of environmental research and Earth system science, such as the influence of soot particles and other aerosols on air quality and climate.

The **High Pressure Chemistry and Physics** group led by Mikhail Eremets studies matter at extremely high pressures. This research has been supported by an Advanced Grant from the European Research Council and central funds of the Max Planck Society.

The **Terrestrial Palaeoclimates** group led by Kathryn Fitzsimmons and supported by the Max Planck Research Group program of the Max Planck Society studies loess deposits in Eurasia to gather information on past climates.

The **Satellite Remote Sensing** group led by Thomas Wagner analyzes spectral data obtained from satellite instruments that measure the atmospheric absorption of solar radiation, with the goal of retrieving and studying the global distributions of trace gases, aerosols, and clouds.

### External Scientific Members

For scientific collaboration and networking, the Max Planck Society also appoints renowned scientists as external scientific members. The two external scientific members currently affiliated with the Max Planck Institute for Chemistry are Stuart A. Penkett from the University of East Anglia, United Kingdom, and Ulrich Platt from the University of Heidelberg, Germany.

## SCIENTIFIC ADVISORY BOARD

An international Scientific Advisory Board that reports to the President of the Max Planck Society evaluates the Institute's research every three years. The Scientific Advisory Board consists of internationally renowned scientists and their evaluation serves to ensure the appropriate and effective use of the Institute´s resources. The members are:

**Jonathan P. D. Abbatt,** Department of Chemistry, University of Toronto, Toronto, Canada

**Edouard Bard,** Climate and Ocean Evolution, Collège de France, France

**Maria Cristina Facchini,** Institute for Atmospheric and Climate Science, Italian National Research Council, Bologna, Italy

**John M. C. Plane,** School of Chemistry, University of Leeds, United Kingdom

**Joyce E. Penner,** Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbour, United States of America

**Yinon Rudich,** Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel

**Mary Scholes,** Animal, Plant and Environmental Sciences, University of the Witwatersrand, Johannesburg, South Africa

**James Zachos**, PBSci-Earth & Planetary Science Department, Institute of Marine Sciences, University of California, Santa Cruz, USA

# *ORGANIZATION CHART*

*Board of Directors: Stephan Borrmann, Gerald H. Haug, Jos Lelieveld, Ulrich Pöschl | Managing Director: Ulrich Pöschl*

| ATMOSPHERIC CHEMISTRY<br>*J. Lelieveld* | BIOGEOCHEMISTRY<br>*(until May 2017)*<br>*M. O. Andreae* | CLIMATE GEOCHEMISTRY<br>*G. Haug* | MULTIPHASE CHEMISTRY<br>*U. Pöschl* | PARTICLE CHEMISTRY<br>*S. Borrmann* | FURTHER RESEARCH GROUPS | JOINT SERVICES |
|---|---|---|---|---|---|---|
| Kinetics and Photochemistry<br>*J. Crowley* | Fire Ecology<br>*J. Goldammer* | Isotope Biogeochemistry<br>*S. Galer* | Biomolecular Analyses and Interactions<br>*J. Fröhlich* | Instrumental Aerosol Analytics<br>*F. Drewnick* | Aerosols and Regional Air Quality<br>*Y. Cheng* | Communications<br>*S. Benner* |
| Optical Spectroscopy<br>*H. Fischer* | Plant Physiology<br>*J. Kesselmeier* | Paleoclimate Research<br>*K. Jochum* | Organic Pollutants and Exposure<br>*G. Lammel* | Nano and Micro-Particle Research<br>*P. Hoppe* | High Pressure Chemistry and Physics<br>*M. Eremets* | Administration & Technical Services<br>*J. Egler* |
| Radical Measurements<br>*H. Harder* | Microscopy and Spectroscopy on Biogenic Aerosols<br>*C. Pöhlker* | Organic Isotope Geochemistry<br>*A. Martinez-Garcia* | Inflammatory Processes<br>*K. Lucas* | Aerosol and Cloud Chemistry<br>*J. Schneider* | Terrestrial Palaeoclimates<br>*K. Fitzsimmons*<br>*(since Dec. 2016)* | Information Technology<br>*T. Disper* |
| Fire Emissions<br>*J. Kaiser* | GEOROC Database<br>*B. Sarbas* | Geoscientific Databases<br>*B. Sarbas* *(since June 2017)* | Aerosol Analysis and Microscopy<br>*C. Pöhlker* *(since June 2017)* | Atmospherical Hydrometeors<br>*M. Szakáll, K. Diehl,*<br>*(JGU Mainz)* | Satellite Remote Sensing<br>*T. Wagner* | Administration<br>*J. Egler* |
| Atmospheric Modelling<br>*A. Pozzer* | Reactive Nitrogen Species<br>*M. Sörgel* | Micropaleontology<br>*R. Schiebel* | Organic Aerosols and Oxidants<br>*M. Shiraiwa*<br>*(until July 2016)* | Aerosol and Cloud Physics<br>*R. Weigel,*<br>*(JGU Mainz)* | | Instrument Development & Electronics<br>*F. Helleis* |
| Organic Reactive Species<br>*J. Williams* | | Inorganic Gas Isotope Geochemistry<br>*H. Vonhof* | Aerosol, Cloud and Surface Interactions<br>*H. Su* | | | Facility Management<br>*C. Pallien* |
| | | | Microbial Communities and Processes<br>*B. Weber* | | | Graduate Schools<br>*K. Sulsky* |
| | | | | | | Workshops<br>*R. Wittkowski* |

December 2017

*Group picture during the Institute meeting in June 2017.*

# *MAJOR COLLABORATIONS & PROJECTS*

The research departments and groups of the Institute collaborate with a large number of international partners and projects. Major collaborations involving multiple departments and groups are listed below. Further projects are described in the departmental and group reports.

## CROSS-DEPARTMENTAL LARGE-SCALE PROJECTS

### Earth System Research Partnership

The Earth System Research Partnership (ESRP) between the MPI for Chemistry in Mainz, the MPI for Meteorology in Hamburg, and the MPI for Biogeochemistry in Jena was established more than a decade ago, in the year 2003, to foster scientific collaboration between the Institutes and associated partners (www.earthsystem.de). Among the associated partners are the MPI for Solar System Research (Göttingen), the MPI for Dynamics and Self Organization (Göttingen), the MPI for Marine Microbiology (Bremen), the MPI for Terrestrial Microbiology (Marburg), and the Institute for Advanced Sustainability Studies (Potsdam).

The objective of the ESRP is to understand how planet Earth functions as a complex system and to improve the predictability of the effects of human actions. Over the last century, there have been marked changes in climate, air quality, biodiversity, and water availability. Additional, and potentially more rapid, changes are predicted. To find solutions to the challenges these changes pose, the ESRP studies the complex interactions and feedbacks of land, ocean, atmosphere, biosphere, and humans in the field, in the lab, and through numerical models. For this purpose, the ESRP develops, maintains, and utilizes joint research infrastructures for Earth System Science for computing (DKRZ), airborne in-situ measurements (HALO), and ground-based long-term observations (ATTO, BCO, ZOTTO etc.).

### HALO Aircraft

To optimize atmospheric research and Earth observations, the Institute uses the HALO aircraft, a research aircraft stationed at the Deutsches Zentrum für Luft- und Raumfahrt, DLR. The aircraft has a range of 12,000 km, and is able to operate at an altitude of up to 15.5 km. The aircraft was cleared for flying scientific missions in 2012 after eight years of building and approval time. Since then, MPIC has been involved primarily in the following scientific missions.

**2014** – Mid-Latitude-Cirrus (ML-CIRRUS)
The objectives of this mission over Europe and the North Atlantic included investigated indirect aerosol effects on cirrus clouds, the quantification of the contribution of aerosol particles from ground-level sources and air traffic pollution as well as the clarification of processes in the formation of cirrus clouds.

**2014** – Aerosol, Cloud, Precipitation, and Radiation Interactions and Dynamics of Convective Cloud Systems (ACRIDICON-CHUVA)
This mission over the Amazon rainforest in Brazil was aimed at elucidating aerosol-cloud interactions and their effects on atmospheric dynamics, radiation, and precipitation. In particular, the differences between unpolluted air and polluted air as well as the impact of biomass burning and other anthropogenic aerosols on the formation and evolution of clouds were studied and quantified.

**2015** – Oxidation Mechanism Observation (OMO)
The mission addressed the “self cleaning capacity” of the atmosphere and how natural and anthropogenic compounds are chemically transformed in the upper troposphere. The OMO aircraft measurement campaign focused on oxidation processes and air pollution chemistry downwind of South Asia during the summer monsoon.

**2017** – Effect of Megacities on the Transport and Transformation of Pollutants on the Regional to Global Scales (EMERGE)

This mission addresses the impact emissions from major population centers have on air pollution at local, regional, and hemispheric scales. EMERGE conducts dedicated airborne measurement campaigns, as well as coupled interpretation and modeling studies primarily of short-lived climate pollutants (i.e., reactive gases, temporary reservoirs, and aerosol particles). The first part of the campaign was conducted in summer 2017 with flights over Europe. The second part, planned for 2018, will operate flights over Asia.

Further missions of the HALO aircraft in which the MPIC is involved as a leading or contributing institution are planned as follows:

**2018** – Chemistry of the Atmosphere: Field Experiment in Africa (CAFE-Africa)
The main objective of the CAFE-Africa mission is to study the influence of the massive biomass burning emissions from southern Africa on the atmospheric oxidation capacity over the tropical and South Atlantic Ocean.

**2020** – Chemistry of the Atmosphere: Field Experiment in Brazil (CAFE-Brazil)
This mission will study tropospheric oxidant photochemistry in combination with particle formation and growth mechanisms under clean, pristine conditions over the Amazon rainforest, operating HALO from Manaus.

**2021** – Formation, Lifetime, Properties and Radiative Impact of High-Latitude Cirrus Clouds (CIRRUS-HL)

### Air Quality and Climate Change in the Arabian Basin (AQABA)

During summer 2017, an international research team coordinated by the Atmospheric Chemistry Department at MPIC collected data on the chemical composition of the atmosphere along a ship track between Malta and Kuwait that went around the Arabian Peninsula. The aim of the research project was to study the influence of air pollution on public health, climate, and the natural environment using a comprehensively instrumented research vessel to simultaneously characterize atmospheric chemistry and aerosol processes.

The team was joined by colleagues from the Kuwait Institute for Scientific Research and the Cyprus Institute as well as from Saudi Arabia, France, and the USA.

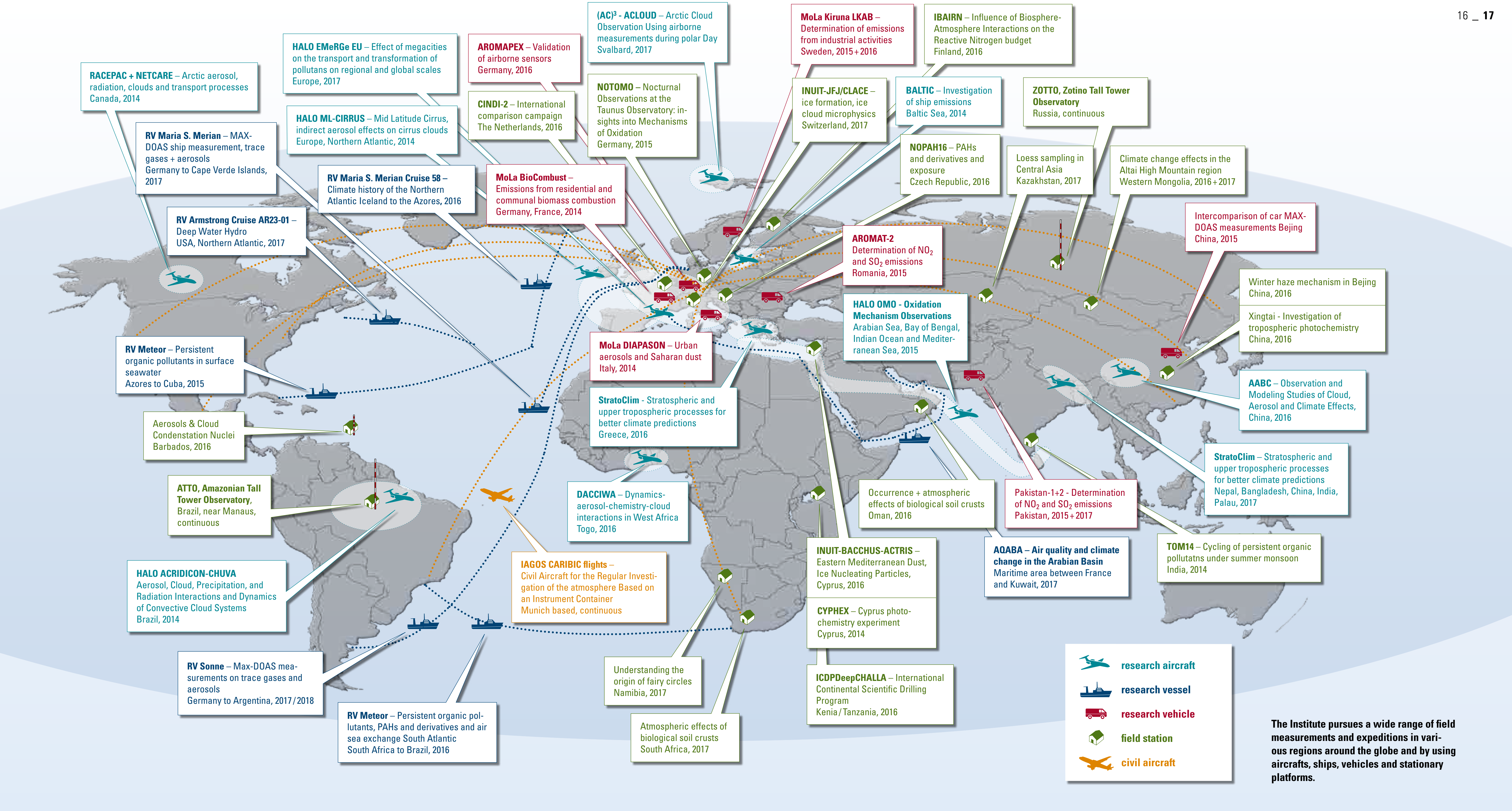
During the two-month expedition, AQABA encountered a unique environmental "spectrum", ranging from pristine conditions over the Arabian Sea, unpolluted but dusty air over the Red Sea that originated in Africa, to moderately polluted conditions over the Mediterranean that were downwind from urban areas (e.g., Cairo) and the Middle East, to ship exhaust in the Suez Canal, to petrochemical emissions in the Arabian Gulf area. The measurements, complemented by model calculations, will help determine the complex effects of natural and anthropogenic emissions on the atmosphere in the Middle East.

### Amazon Tall Tower Observatory (ATTO)

The Amazon Basin plays a key role in the carbon and water cycles, climate change, atmospheric chemistry, and biodiversity. It is affected by human activities, and more pervasive change is expected to occur in the future. Thus, it is essential to establish long-term measurements that provide a baseline record of present-day climatic, biogeochemical, and atmospheric conditions and continue to monitor changes in the Amazon region related to global change and the Anthropocene as the current era of globally pervasive and steeply increasing human influence on planet Earth.

The Amazon Tall Tower Observatory (ATTO) has been set up in a pristine rain forest region in the central Amazon Basin, about 150 km northeast of the city of Manaus, Brazil. Two 80 m towers have been operated at the site since 2012, and a 325 m tall tower has been completed in 2015. The ATTO project is a Brazilian-German collaboration between the Instituto Nacional de Pesquisas da Amazonia (INPA), the Universidade do Estado do Amazonas (UEA), the Max Planck Society (MPG), and further research partners. On the German side, the project had been initiated and established by the MPIC, and it continues to be coordinated in collaboration between the MPI for Biogeochemistry and the MPIC.

# *FIELD MEASUREMENTS & EXPEDITIONS 2014–2017*



**RACEPAC + NETCARE** – Arctic aerosol, radiation, clouds and transport processes
Canada, 2014

**HALO EMeRGe EU** – Effect of megacities on the transport and transformation of pollutans on regional and global scales
Europe, 2017

**AROMAPEX** – Validation of airborne sensors
Germany, 2016

**(AC)³ - ACLOUD** – Arctic Cloud Observation Using airborne measurements during polar Day
Svalbard, 2017

**MoLa Kiruna LKAB** – Determination of emissions from industrial activities
Sweden, 2015 + 2016

**IBAIRN** – Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget
Finland, 2016

**CINDI-2** – International comparison campaign
The Netherlands, 2016

**NOTOMO** – Nocturnal Observations at the Taunus Observatory: insights into Mechanisms of Oxidation
Germany, 2015

**INUIT-JFJ/CLACE** – ice formation, ice cloud microphysics
Switzerland, 2017

**BALTIC** – Investigation of ship emissions
Baltic Sea, 2014

**ZOTTO, Zotino Tall Tower Observatory**
Russia, continuous

**RV Maria S. Merian** – MAX-DOAS ship measurement, trace gases + aerosols
Germany to Cape Verde Islands, 2017

**HALO ML-CIRRUS** – Mid Latitude Cirrus, indirect aerosol effects on cirrus clouds
Europe, Northern Atlantic, 2014

**RV Maria S. Merian Cruise 58** – Climate history of the Northern Atlantic Iceland to the Azores, 2016

**MoLa BioCombust** – Emissions from residential and communal biomass combustion
Germany, France, 2014

**NOPAH16** – PAHs and derivatives and exposure
Czech Republic, 2016

Loess sampling in Central Asia
Kazakhstan, 2017

Climate change effects in the Altai High Mountain region
Western Mongolia, 2016 + 2017

**RV Armstrong Cruise AR23-01** – Deep Water Hydro
USA, Northern Atlantic, 2017

**AROMAT-2**
Determination of $NO_2$ and $SO_2$ emissions
Romania, 2015

Intercomparison of car MAX-DOAS measurements Bejing
China, 2015

Winter haze mechanism in Bejing
China, 2016

Xingtai - Investigation of tropospheric photochemistry
China, 2016

**HALO OMO - Oxidation Mechanism Observations**
Arabian Sea, Bay of Bengal, Indian Ocean and Mediterranean Sea, 2015

**RV Meteor** – Persistent organic pollutants in surface seawater
Azores to Cuba, 2015

**MoLa DIAPASON** – Urban aerosols and Saharan dust
Italy, 2014

**StratoClim** - Stratospheric and upper tropospheric processes for better climate predictions
Greece, 2016

**AABC** – Observation and Modeling Studies of Cloud, Aerosol and Climate Effects,
China, 2016

Aerosols & Cloud Condensation Nuclei
Barbados, 2016

**ATTO, Amazonian Tall Tower Observatory**,
Brazil, near Manaus, continuous

**DACCIWA** – Dynamics-aerosol-chemistry-cloud interactions in West Africa
Togo, 2016

Occurrence + atmospheric effects of biological soil crusts
Oman, 2016

Pakistan-1+2 - Determination of $NO_2$ and $SO_2$ emissions
Pakistan, 2015 + 2017

**StratoClim** – Stratospheric and upper tropospheric processes for better climate predictions
Nepal, Bangladesh, China, India, Palau, 2017

**HALO ACRIDICON-CHUVA**
Aerosol, Cloud, Precipitation, and Radiation Interactions and Dynamics of Convective Cloud Systems
Brazil, 2014

**IAGOS CARIBIC flights** –
Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container
Munich based, continuous

**INUIT-BACCHUS-ACTRIS** –
Eastern Mediterranean Dust, Ice Nucleating Particles,
Cyprus, 2016

**AQABA** – **Air quality and climate change in the Arabian Basin**
Maritime area between France and Kuwait, 2017

**TOM14** – Cycling of persistent organic pollutatns under summer monsoon
India, 2014

**CYPHEX** – Cyprus photochemistry experiment
Cyprus, 2014

**RV Sonne** – Max-DOAS measurements on trace gases and aerosols
Germany to Argentina, 2017/2018

**RV Meteor** – Persistent organic pollutants, PAHs and derivatives and air sea exchange South Atlantic
South Africa to Brazil, 2016

Understanding the origin of fairy circles
Namibia, 2017

Atmospheric effects of biological soil crusts
South Africa, 2017

**ICDPDeepCHALLA** – International Continental Scientific Drilling Program
Kenia/Tanzania, 2016

**The Institute pursues a wide range of field measurements and expeditions in various regions around the globe and by using aircrafts, ships, vehicles and stationary platforms.**

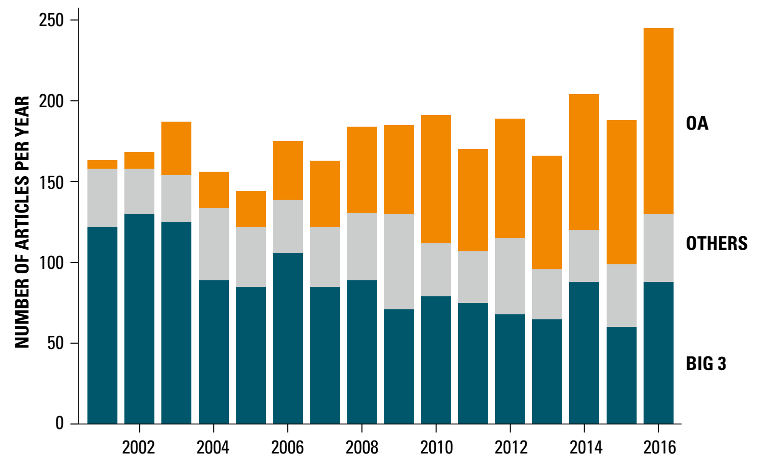
# SCIENTIFIC PUBLICATIONS

## PUBLICATION STATISTICS

The results of the fundamental scientific research conducted at the Institute are mainly published in peer-reviewed scientific journals. From 2006 to 2016, 2,062 peer-reviewed journal articles and reviews were published at the MPIC; on average, 188 publications per annum (see figure 1). Through the end of 2016, MPIC-authored publications from 2006 to 2015 were cited 61,245 times. This is an average of 33.7 citations per paper, an increase of about 14 % compared to an average of 29.5 citations per paper in the years 2003 to 2012.*

Between 2006 and 2015, the Institute published papers that belong, on average, to the top fourth (27.0%) most cited papers within their subject categories. A value of 50 % represents the median and thus an average citation impact compared to all publications from the same subject areas and publication years. Thus, the MPIC citation impact is far above the average of the relevant scientific community.

Approximately one-quarter (23.6%) of the MPIC papers belong to the 10% most cited papers within their subject categories. In 11 out of 17 relevant subject categories, the Institute has achieved a subject-based observed-to-expected citation ratio far above the international standard of the corresponding field (>1.5); in six categories the ratios are higher than 2.0, which indicates a very high performance. The MPIC citation impact is significantly higher than the country averages of Germany and the United States of America, and also higher than the average of the Chemistry, Physics and Technology Section (CPTS) of the Max Planck Society.



*Publication output of the MPIC in the years 2000 to 2016 (peer-reviewed journal articles per year). Blue green: major traditional subscription publishers (Elsevier, Springer Nature, Wiley); grey: other subscription publishers, orange: open access publications (Source: Max Planck Digital Library, 2017).*

In summary, the metrics used to measure normalized citation impact show that the MPIC has a very high impact. Moreover, individual institute members have been ranked repeatedly as “Highly Cited Researchers”.

A comprehensive listing of scientific publications during the past decades is available on Institute’s web pages (http://www.mpic.de/en/research/publications.html), further information and citation statistics are provided on the web pages of individual researchers (Researcher ID, Google Scholar, etc.), and selected highlight studies have also been advertised in press releases (http://www.mpic.de/en/news/press-information.html).

## OPEN ACCESS

The Max Planck Society and the Max Planck Institute for Chemistry are among the leading proponents of open access to scientific publications and scholarly knowledge. Since the year 2003, the Max Planck Society is hosting and supporting a series of international meetings, the “Berlin Open Access Conferences”, which are dedicated to the promotion of open access and yielded some of the key statements and developments in the global move to open access.

The “Berlin Declaration on Open Access to Knowledge in the Sciences and Humanities” (https://openaccess.mpg.de/Berlin-Declaration) has been signed by 600 scholarly organizations from around the world and continues to receive further support.

The “Mission Statement at the Berlin 11 Open Access Conference” (2013) outlined clear perspectives and urged research organisations to develop a viable, coordinated and transparent strategy for an open access environment that returns control of scholarly publishing to the scholars (https://openaccess.mpg.de/mission-statement_en).

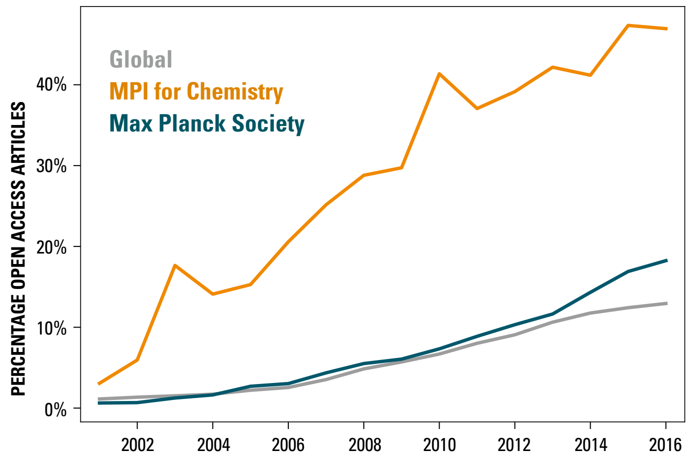


*Figure 2: Open access share among publications of the MPIC (peer-reviewed journal articles) compared to the Max Planck Society and the global scientific community (Source: Max Planck Digital Library, 2017).*

The „Berlin 12 Open Access Conference“ (2015) led to the international initiative „Open Access 2020“ (OA2020), which builds on the „OA2020 Expression of Interest“ (EoI) in the „Large-scale Implementation of Open Access to Scholarly Journals“ and aims to transform existing scholarly journals from subscription to open access publishing in a smooth, swift and scholarly oriented way.

Since its release in 2016, the OA2020 EoI has already been signed by almost 100 scholarly organizations - including the Alliance of Science Organisations in Germany, the European University Association representing more than 800 universities in 47 countries and other major organizations in Europe, Asia, and the Americas - and continues to receive swiftly growing global support.

MPIC scientists have been actively involved in this development from the beginning, and U. Pöschl has co-chaired the latest Berlin Open Access Conferences, triggered the OA2020 initiative, led the drafting of the OA2020 EoI, and continues to serve as co-chair for these and other open access initiatives of the Max Planck Society.

Already before the Berlin Declaration on Open Access, the MPIC and its researchers were pioneers in the foundation and successful development of innovative forms of open access publishing. Since the year 2001, scientists from the MPIC have led the way in the conception, development, and application of interactive open access publishing with public peer review, which is now also spreading across other fields in the sciences and humanities.

In fact, some of the very first and most successful open access journals have been founded and grown to top visibility and scientific reputation under the aegis of researchers at the MPIC: Atmospheric Chemistry and Physics (ACP) by U. Pöschl et al. since 2001; Biogeosciences (BG) by J. Kesselmeier et al. since 2004; Atmospheric Measurement Techniques (AMT) by T. Wagner et al. since 2008; and Geoscientific Model Development (GMD) by R. Sander et al. since 2008.**

Beyond the successful engagement of individual scientists in the founding, editing, and promoting of open access journals and initiatives, the MPIC continues to increase the open access share of its publications at much higher rates than the Max Planck Society and the global scientific community as illustrated in Figures 1 and 2. Swiftly approaching an open access share of 50%, the Institute indeed continues to a pacemaker for open science for the benefit of scientific and societal progress.

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*The publication list of the Institute is available at www.mpic.de/research/publications*

* *The bibliometric analysis of the MPIC is based on data retrieved from a bibliometric databases of the Max Planck Digital Library (MPDL, Munich) and derived from citation indexes provided by Clarivate Analytics (formerly ISI).*

** *For details see “A short History of Interactive Open Access Publishing” and “Multi-Stage Open Peer Review” (see: www.mpic.de/research/publications/openaccess)*

# *JUNIOR RESEARCHERS & VISITING SCIENTISTS*

The Max Planck Institute for Chemistry (MPIC) has a long and successful tradition of hosting and supporting junior researchers and guest scientists from all over the world.

The Institute is located on the campus of the Johannes Gutenberg University Mainz (JGU), and opportunities to perform research projects at the forefront of science are offered to students who can obtain a university degree in collaboration with the JGU or other German and international university partners. The education and support of graduate students is organized within the framework of two complementary programs – the Paul Crutzen Graduate School at the MPI for Chemistry (PCGS), which is open to all PhD students at the Institute, and the Max Planck Graduate Center with the Johannes Gutenberg University Mainz (MPGC), which is dedicated to particularly interdisciplinary PhD studies in collaboration with the JGU.

## Paul Crutzen Graduate School (PCGS)

All PhD students at the MPIC are supported by the Paul Crutzen Graduate School (PCGS), which evolved from the International Max Planck Research School of Atmospheric Chemistry and Physics (IMPRS) established in 2003. The PCGS offers a structured curriculum for graduate studies that enhances academic and social exchange between the students, their supervisors, and additional advisors through seminars, lecture and soft skill courses, career orientation, and related events. Within the PCGS, every student is tutored by a PhD Advisory Committee (PAC) that comprises the main supervisor and additional mentors who follow the studies and offer advice through regular meetings, reports, and feedback forms. Currently, 81 PhD students (36 female, 45 male) from 14 different countries are enrolled in the Paul Crutzen Graduate School.

## Max Planck Graduate Center (MPGC)

The Max Planck Graduate Center was created in 2009 to promote interdisciplinary and interdepartmental research across the MPI for Chemistry, the MPI for Polymer Research, and four faculties of the Johannes Gutenberg University (JGU) in Mainz: Chemistry, Pharmaceutical Sciences and Geosciences; Physics, Mathematics and Computer Science; Biology; and the University Medical Center. To overcome limitations imposed by traditional faculty rules of graduation on the interdisciplinarity of doctoral studies, the MPGC has established a special set of doctoral degree regulations that allow for a high degree of interdisciplinarity and a broad scientific range of doctoral studies. These regulations and the excellent research environment enable the MPGC to attract outstanding PhD students from many countries and diverse scientific backgrounds. Currently, 21 PhD students pursuing their research projects at the MPIC are members of the MPGC. Since the launch of the MPGC in 2009, 14 PhD students from the MPIC received the degree “Doctor rerum naturalium of the University of Mainz” with a certificate co-issued by the Max Planck Society. Three of the students have also received the prestigious Otto Hahn Medal of the Max Planck Society for outstanding scientific achievements.

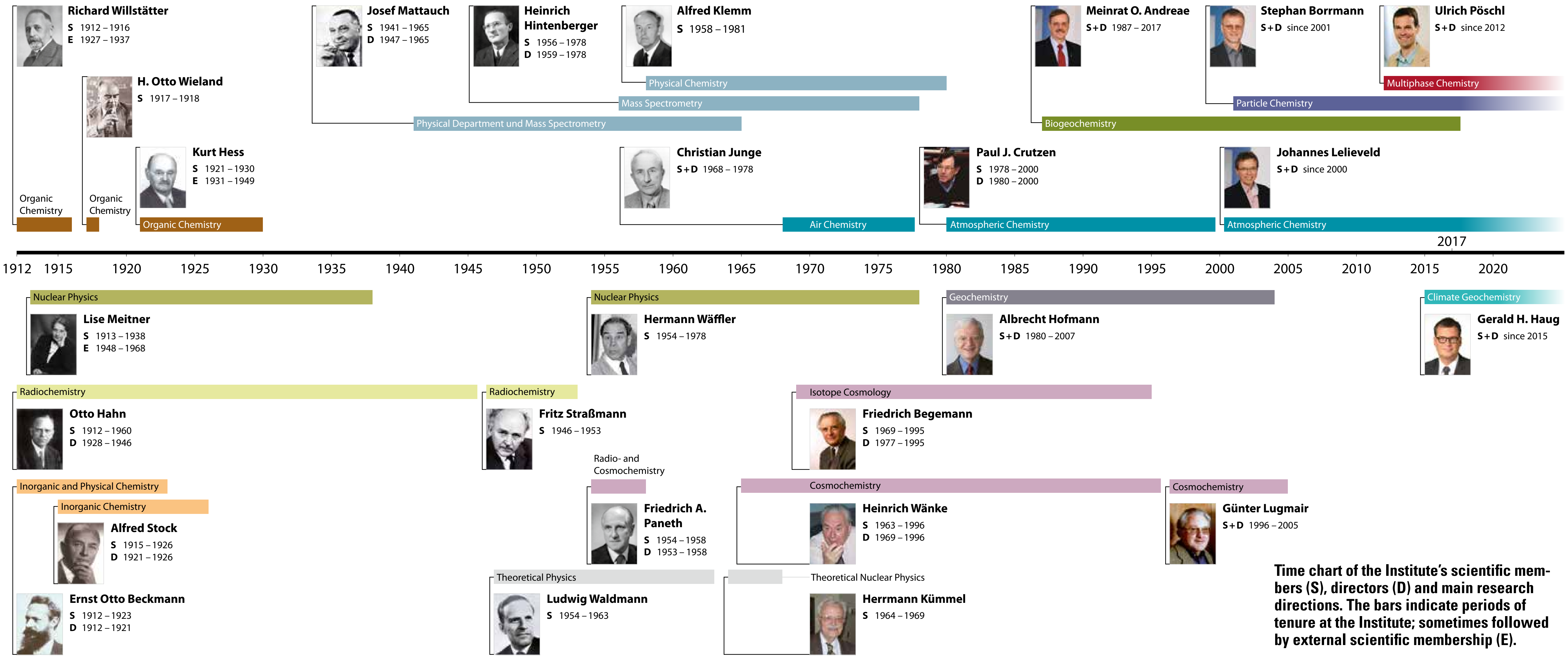
## MPIC Guest Program

To foster international scientific exchange, the MPIC Guest Program is supporting researchers temporarily working at the Institute, including doctoral students, postdoctoral researchers, and senior visiting scientists. The guest scientists are welcome to engage in the ongoing research, initiate new collaborative projects, use the research infrastructure, and participate in the academic and social life of the Institute. Special support is provided with regard to administrative matters, integration, and everyday life. Among the guest scientists are visitors from international cooperation partners and recipients of awards and stipends from German and international research funders (e.g.: Alexander von Humboldt Foundation, German Academic Exchange Service, Chinese Scholarship Council). Guest scientists who are not externally funded can also receive a stipend from the Institute. The MPIC Guest Program has a long and successful history of providing opportunities for flexible and free scientific exchange, mobility, and development to junior researchers as well as senior visiting scientists.

## *FACESTS OF BIO-GEOCHEMISTRY*

## *FAREWELL SYMPOSIUM FOR 'ANDI' ANDREAE, 19 MAY 2017*

# HISTORY



**Time chart of the Institute's scientific members (S), directors (D) and main research directions. The bars indicate periods of tenure at the Institute; sometimes followed by external scientific membership (E).**

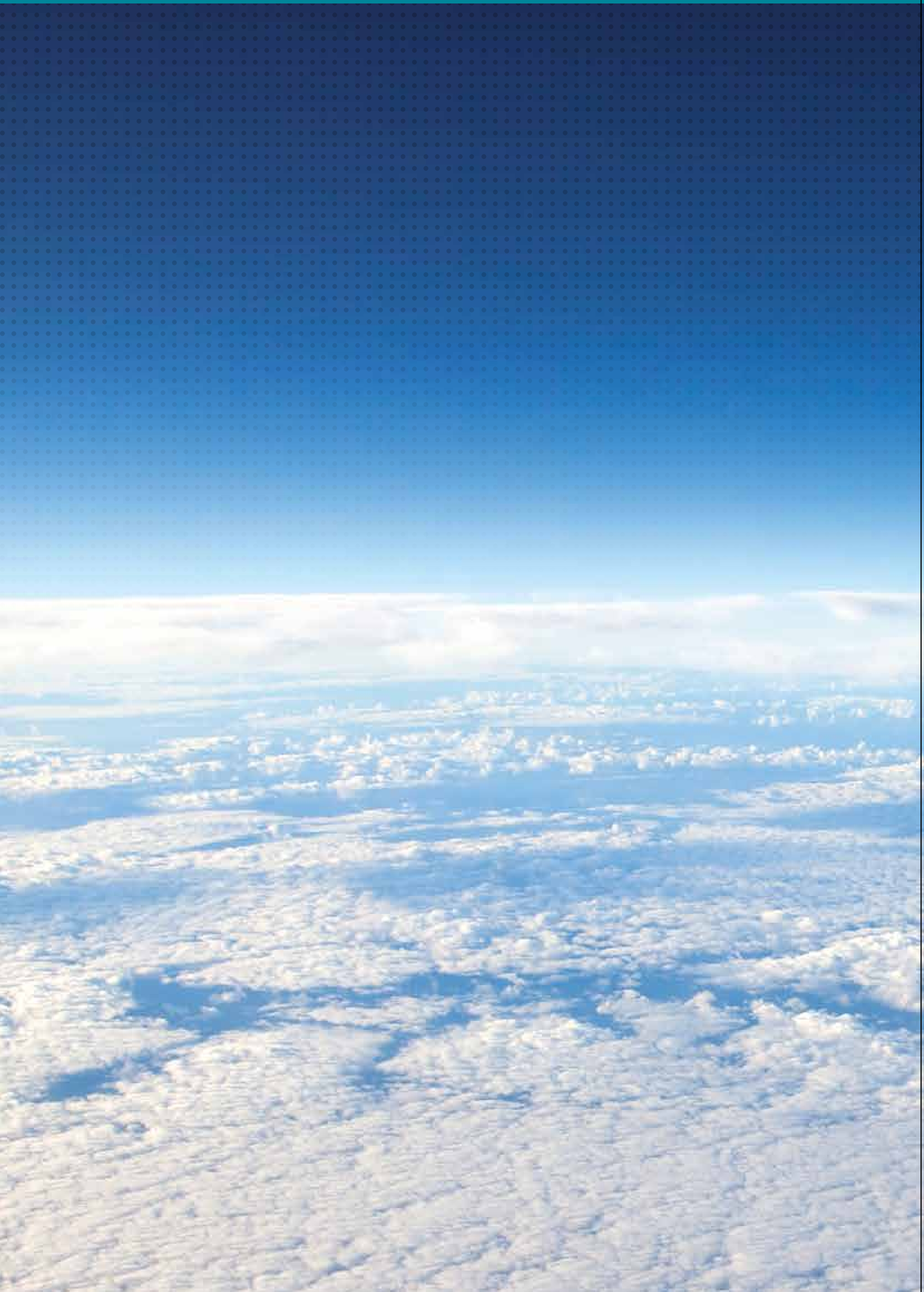
Research at the Max Planck Institute for Chemistry has been at the forefront of science throughout its existence. Since the Institute's foundation in 1912, three of its directors were awarded with the Nobel Prize for Chemistry: Richard Willstätter in 1915 for the revelation of the structure of chlorophyll and other plant pigments, Otto Hahn in 1944 for the discovery of nuclear fission, and Paul Crutzen in 1995 for the elucidation of atmospheric ozone chemistry.

The research departments and focal points of the Institute have gone through a history of change and scientific evolution as illustrated in the time chart above. What began in 1912 with classical organic, inorganic and physical chemistry at the Kaiser Wilhelm Institute for Chemistry in Berlin evolved into radiochemistry and nuclear physics in the 1930s, leading to the discovery of nuclear fission by Otto Hahn, Lise Meitner and Fritz Strassmann.

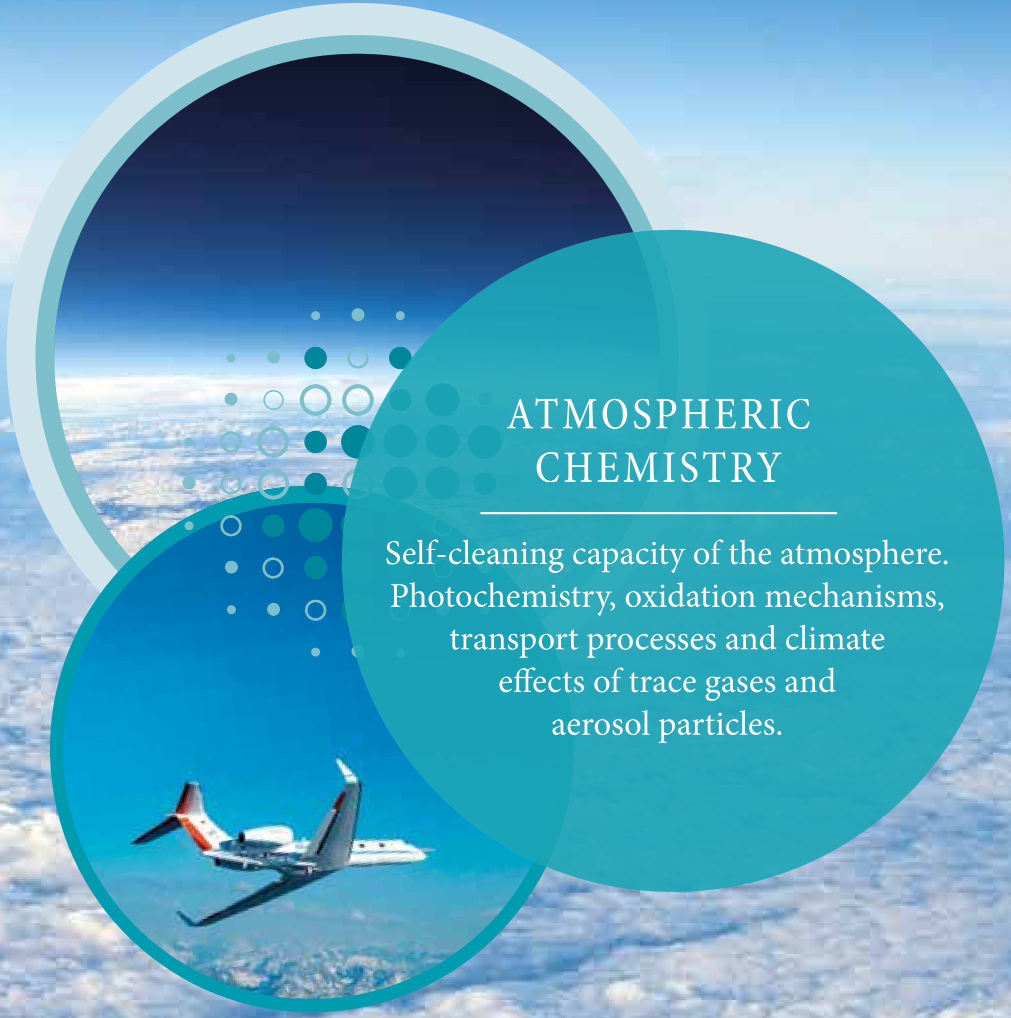
As the Institute was severely damaged towards the end of World War II it was moved to the Swabian Alps in today's Baden-Wuerttemberg. There the chemists worked provisionally from 1944 to 1949 until the Institute moved a second time to the campus of the newly founded Johannes Gutenberg University in Mainz. At the same time it was integrated into the Max Planck Society, the successor of the Kaiser Wilhelm Society, and reopened as the Max Planck Institute for Chemistry. Since 1959 the Institute also carries the name “Otto Hahn Institute” in honor of its previous director and the first president of the Max Planck Society.

In the 1960s and 1970s the Institute's research portfolio was extended from Physical Chemistry, Nuclear Physics and Mass Spectrometry to Cosmochemistry, Isotope Cosmology and Air Chemistry. Meteorites and moon dust samples were studied and the interplay of atmospheric gases, particles and meteorology were investigated. In the 1980s new departments for Geochemistry and Biogeochemistry were founded, in 2001 the Particle Chemistry Department was established jointly with the Institute for Atmospheric Physics at the Johannes Gutenberg University of Mainz, in 2012 the Multiphase Chemistry Department, and in 2015 the Climate Geochemistry Department was founded.

Nowadays, the research focus of the Max Planck Institute for Chemistry is on Earth System science, in particular on the chemical processes occurring in the atmosphere and their interactions with the biosphere and oceans. It also includes the influence of humans, as unprecedented urbanization and industrialization in the past centuries have changed the course of natural processes on our planet, in an epoch now known as the Anthropocene.



# ATMOSPHERIC CHEMISTRY



ATMOSPHERIC
CHEMISTRY

Self-cleaning capacity of the atmosphere. Photochemistry, oxidation mechanisms, transport processes and climate effects of trace gases and aerosol particles.

# *ATMOSPHERIC CHEMISTRY DEPARTMENT*

## ATMOSPHERIC "AGEING": OXIDATION PROCESSES CLEANSE THE ATMOSPHERE THROUGH THE CHEMICAL PROCESSING OF NATURAL AND ANTHROPOGENIC EMISSIONS

The atmosphere removes millions of tons of natural and human-induced emissions each year through oxidation. This critical self-cleansing mechanism profoundly changes the characteristics of freshly released gases and particles, referred to as "primary emissions". Many of the emitted gases react with radicals, predominantly hydroxyl (OH), which results in less volatile and more soluble products that can be more easily removed by precipitation and deposition to the Earth's surface. Secondary pollutants are formed during the oxidation process, which can potentially deteriorate air quality and exacerbate climate change. For example, fine particulate matter and ozone ($O_3$), with atmospheric lifetimes of days to weeks, can be transported over hundreds to thousands of kilometers. Thus, air pollution is not necessarily a local, and often not a national, phenomenon. Our department studies the mechanisms in the atmosphere that chemically process natural and anthropogenic emissions, and especially combinations of them, on regional to global scales.

Our research groups use instrumented mobile platforms such as aircraft and ships to gain insight into interdependencies between emissions, chemical conversions and atmospheric transport. The instruments target different categories of reactive species, and the data together are used to constrain the chemistry.

Groups 1 and 3 (Harder and Crowley) use laser-based fluorescence and absorption techniques to measure radicals, including OH and $NO_3$. Group 2 (Fischer) uses optical detection and wet-chemical methods to measure primary emissions and atmospheric reaction intermediates, for example aldehydes and peroxides. Group 3 uses laser-cavity methods and chemical ionization mass spectrometry combined with thermal dissociation to measure atmospheric nitrogen oxide chemistry. Group 4 (Williams) uses proton-transfer mass spectrometry to measure organic compounds and their reaction products. In addition, Group 5 (Kaiser) characterizes vegetation fires and their atmospheric impacts using global satellite remote sensing. Group 6 (Pozzer) employs a hierarchy of local to regional to global models to analyse the measurements collected from diverse environments. Group 7 (Lelieveld) interprets the results in terms of consequences for global air quality and climate.

Results show how the atmosphere regulates concentrations of OH and other oxidants, and how reactive gases alter the properties of aerosols, including aeolian dust, organics and sea spray. The chemical transformation of particles, also called "atmospheric ageing", affects the lifetime of the aerosols, and thus cloud formation, climate, nutrient cycles, and public health. The latter research area is an emerging focus of our groups' field measurements and modeling, in collaboration with other departments.

The Atmospheric Chemistry Department studies "natural pollution" by measuring the vast amounts of volatile organic compounds (VOCs) emitted by vegetation in forests. The pristine atmosphere manages this abundance in intriguing ways. One research theme compares tropical with boreal environments, where the characteristics of VOCs can be very different. The VOC isoprene, released by the canopy, dominates tropical forest emissions. Our measurements collected from aircraft over the Amazon rainforest suggest that the OH radical is recycled in the atmosphere after it oxidizes isoprene. These measurements indicate that a multitude of higher generation reaction products can explain the OH recycling. Furthermore, our laboratory and field experiments identified hitherto unknown soil emissions of highly reactive terpenes, another group of VOCs. The combination of the primary VOCs and their reaction products can account for the observed OH reactivity, which was previously severely underestimated.

In contrast, boreal forest emissions of terpenes appear to recycle OH less efficiently while maintaining oxidation capacity through reactions with $NO_3$ and $O_3$, also during the night. In this environment, Criegee intermediates, or carbonyl oxides, are formed by the ozonolysis of unsaturated organic compounds, which contribute directly to oxidation reactions and also indirectly by releasing OH.

For decades, the chemistry of Criegee intermediates has been investigated with theoretical and indirect experimental methods, while their concentration in ambient air was unknown. Our measurements in the boreal forest have provided the first estimate of ambient Criegee intermediate concentrations, corroborating their importance in atmospheric chemistry, including the formation of aerosols.

Over the past several years, we have developed a comprehensive suite of instrumentation for the institute's new High Altitude Long Operation (HALO) aircraft. The instruments were first deployed during the "Oxidation Mechanism Observation" campaign in 2015. HALO flew through the outflow of deep convective clouds during the wet season in South Asia, and our data revealed that the monsoon sustains an effective cleansing mechanism in which contaminants are rapidly oxidized into products that can be removed by rain. However, some pollutants are lofted above the monsoon clouds, and can reach the stratosphere. In the coming years, HALO will be engaged in studies of emissions in West Africa and South America.

## *JOS LELIEVELD*

**25 July 1955** Born in The Hague, The Netherlands

**1984** Study of natural sciences Leiden University

**1984–1987** Research associate at Geosens B.V.

**1987–1993** Research scientist at the Max Planck Institute for Chemistry

**1990** PhD in Physics and Astronomy Utrecht University

**1993–2000** Professor of Atmospheric Physics and Chemistry University of Wageningen and Utrecht

**since 2000** Director at the Max Planck Institute for Chemistry and Scientific Member of the Max Planck Society

Professor in Atmospheric Physics, University of Mainz, and Professor at the Cyprus Institute, Nicosia

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# *RADICAL CHEMISTRY AND THE SELF-CLEANING CAPACITY OF THE ATMOSPHERE*

**HARTWIG HARDER**

**“Understanding the impact of changes in composition of the atmosphere on its self-cleaning capability.”**

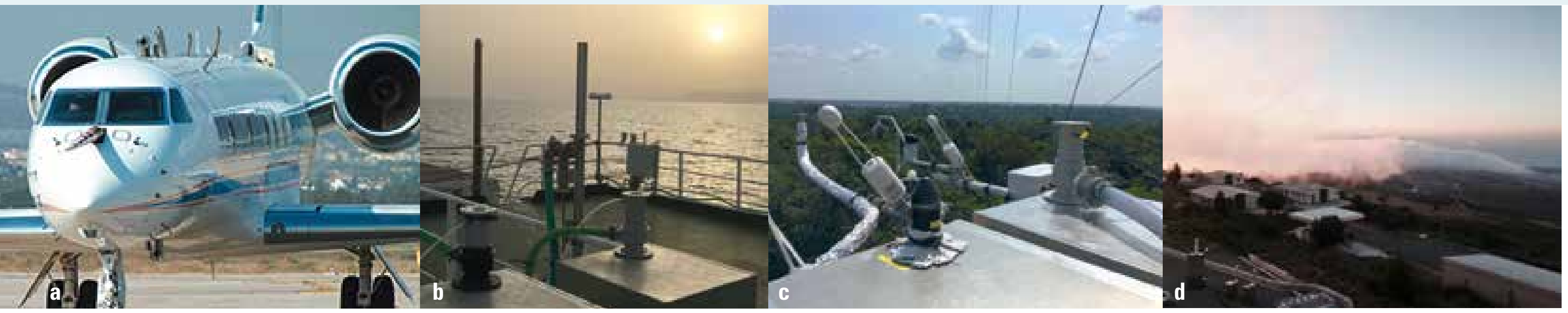

*Figure 1: a) HALO research aircraft during OMO, b) sunset in the red sea observed through a thick dust layer in the atmosphere during AQABA, c) high-frequency measurements 10 m above the Amazon rainforest during ATTO/CLAIRE IOP- 1, d) polluted boundary layer during CYPHEX on Cyprus.*

Volatile species emitted into the atmosphere do not built up to toxic concentrations thanks to self-cleaning processes. The self-cleaning process is initiated mainly by the OH radical, which is buffered by the $HO_2$ radical. In summer 2014, the CYprus PHotochemical EXperiment (CYPHEX) conducted a research campaign on the island of Cyprus to investigate the impact of pollution emissions from central Europe, transported to the eastern Mediterranean, on regional air quality during a period of intense photochemistry. Measurements of the OH and $HO_2$ concentration are generally in good agreement with results from a data-constrained chemical box model. However, in air masses containing elevated terpene concentrations, the box model underestimates $HO_2$ concentrations. Sensitivity studies using the Master Chemical Mechanism (MCM) based model show improved agreement if the applied terpene mechanism is altered to allow for auto-oxidation of organic peroxy radicals ($RO_2$). This reaction reduces the loss of $HO_2$ and also brings the model results close to the measurements of organic peroxides, which are the products of $RO_2$+$HO_2$ reactions. This finding suggests that auto-oxidation of terpene-generated $RO_2$ plays an important role in terminating the radical chain propagation, and can suppress ozone formation in high terpene environments. To pursue the impact of auto oxidation on maintaining the self-cleaning capability of the atmosphere further, we are developing an instrument that measures $RO_2$ directly, and reexamining our high-terpene data from the boreal forest in Finland from 2010.

To study the self-cleaning capability of the atmosphere at the interface to the biosphere, we collected high-resolution (5 Hz) measurements of OH and $HO_2$ along with fast measurements of wind speed and direction, water vapor, ozone, NOx, $J(O^1D)$, isoprene, kOH, and other relevant parameters in the Amazon rainforest during fall 2015. The measurements were collected 40 meters above ground, and 10 meters above the tropical rainforest canopy at the Amazon Tall Tower Observatory (ATTO) site in Brazil. We found that segregation by turbulent transport of isoprene and OH occurs on similar scales as previously observed in central Germany. The derived upward flux of $HO_2$ revealed that the initial oxidation of volatile organic compounds (VOCs) in the sunlit atmosphere above the canopy, together with upward transported NO from soil emissions, led to fast radical formation that impacted ozone production and oxidation reactions at this interface. In addition to the net upward flux of $HO_2$ from the canopy, we observed that the oxidation capacity at the surface was driven by turbulent downward transport of $HO_2$ and $O_3$ through the canopy into the dark understory, where about 97% of the sunlight was attenuated.

We investigated possible spurious OH measurements by instrument-internal interferences in this environment above and below the canopy. From our previous studies in the boreal forest, we knew that the interfering species can react with $SO_2$ in the gas phase and decompose into OH within our instrument. Whereas in the boreal forest in Finland this reaction contributed up to 50% to total gas phase $H_2SO_4$ production, in the rainforest the contribution was negligible. We determined the reaction rate constant of this species with $SO_2$ in the rainforest to be of the same order as that of $SO_2$ with stabilized Criegee intermediates. Further investigations are being conducted to identify species or groups of species that can produce spurious OH, and to what degree they contribute to the oxidation capacity of the atmosphere. By applying our new inlet pre-injector (IPI) system, we can distinguish the atmospheric OH signal from spurious OH, which in turn provides a basis for quantitative studies of Criegee intermediates.

To investigate the impact of uplifted polluted boundary layer air by the South Asian monsoon on the upper troposphere and lower stratosphere, we conducted the aircraft-based Oxidation Mechanism Observations (OMO) campaign during summer 2015. We measured OH, $HO_2$, and $NO_2$ in very clean air masses outside the anticyclone that are established by large-scale monsoon convection, and contrasted the data with that of polluted air masses influenced by monsoon outflow within the anticyclone. To quantify the OH background signal, often found in ground-based campaigns, we applied the IPI technique for the first time to atmospheric samples collected while on the High Altitude Long Range Research Aircraft HALO. To characterize the pressure and temperature dependent sensitivity, we constructed a low-pressure and low-temperature calibration system that allows us to replicate the inflight conditions to characterize OH, $HO_2$, and $NO_2$ measurements on HALO in the laboratory. While the $NO_2$ and OH channel have been extensively characterized, that of the $HO_2$ channel is being finalized.

The impact of airborne desert dust on the radical budget of the lower troposphere has been the focus of the ship campaign AQABA (Air Quality and climate in the Arabian Basin), conducted during summer 2017. We measured OH and $HO_2$ radicals across the Mediterranean Sea and around the Arabian Peninsula. The environmental conditions varied tremendously. We observed very clean air southeast of the Arabian Peninsula in the monsoon-driven flow with very low $O_3$, and with NOx mixing ratios less than 15 ppt and CO below 60 ppb, which is characteristic of large areas of the marine Southern Hemisphere.
In contrast, we measured very high $O_3$ mixing ratios above 160 ppb with unusually high VOC and $NO_x$ loadings in the Suez Canal and over the Arabian Gulf. With dust events observed in nearly all environmental conditions that we encountered, both in clean and polluted air masses, the dataset provides a unique basis to address the impact of atmospheric dust on atmospheric chemistry.

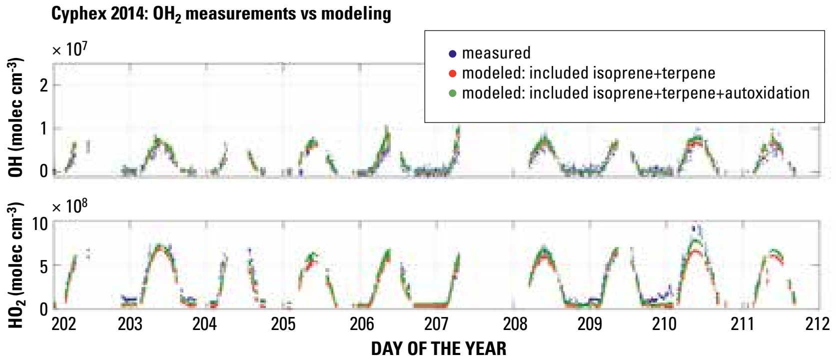

*Figure 2: Modeled and measured OH and $HO_2$ concentrations during the CYPHEX campaign.*

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# *THE IDENTIFICATION OF AIR MASSES AFFECTED BY THE INDIAN SUMMER MONSOON DURING THE OXIDATION MECHANISM OBSERVATIONS (OMO) CAMPAIGN*

**HORST FISCHER**

**“The South Asian summer monsoon strongly affects the composition of the upper troposphere from the Western Pacific to the Mediterranean.”**

*Figure 1: TRIHOP is an Instrument that measured $H_2O_2$ and total hydroperoxides, as well as CO, HCHO and $CH_4$ on board the High Altitude Long Operation (HALO) aircraft during the 2015 Oxidation Mechanism Observations (OMO) mission. TRIHOP stands for the combination of the instruments TRISTAR (TRacer In-Situ Tdlas for Atmospheric Research) and HyPHOP (Hydrogen Peroxide and Higher Oraganic Peroxides) (Credit: Uwe Parchatka).*

The optical spectroscopy group develops instruments based on infrared (IR) laser absorption, chemiluminescence, and fluorescence spectroscopy and uses them to detect atmospheric trace gases. Target molecules are $O_3$, NO, $NO_2$, $N_2O$, CO, $CO_2$, $CH_4$, HCHO, $H_2O_2$, and organic hydro-peroxides (ROOH). To investigate the South Asian monsoon outflow, in July-August 2015, the Oxidation Mechanism Observations (OMO) campaign successfully deployed a quantum-cascade laser absorption spectrometer (HCHO, CO, and $CH_4$) along with a dual enzyme fluorescence monitor ($H_2O_2$ and ROOH) on a High Altitude Long Operation (HALO) aircraft (Figure 1).

Deep convection over India and the adjacent region strongly affects the trace gas composition within the South Asian summer monsoon anticyclone. During the 2015 OMO campaign, 17 HALO measurement flights from Paphos (Cyprus) and Gan (Maldives) investigated the trace gas composition of anticyclones from the Eastern Mediterranean, across the Arabian Peninsula, to the tropical Indian Ocean. To differentiate background air masses from those affected by the monsoon, the instruments aboard HALO collected vertical profiles of relatively long-lived trace gases (Figure 2). Background profiles for CO and $CH_4$ were collected over Germany and the Western Mediterranean where anticylones were absent. At altitudes above 300 hPa (about 9 km), we observed background mixing ratios of 77.3 ± 12.9 ppbv and 1841.4 ± 16.2 ppbv for CO and $CH_4$, respectively. In air masses over Egypt and Bahrain that were affected by the summer monsoon, mixing ratios for both species were enhanced (Fig. 2). Although CO mixing ratios are only slightly elevated (99.7 ± 9.4 ppbv) compared to background levels, the mixing ratios for methane are significantly enhanced (1908.5 ± 18.3 ppbv). Thus, we use a methane mixing ratio of 1879.8 ppbv deduced from the tropospheric background mixing ratio plus the $2\sigma$ standard deviation to define a threshold value for monsoon-influenced air masses.

To establish a dynamic connection between enhanced $CH_4$ mixing ratios in the anticyclone and potential methane sources in Southeast Asia, 10-day backward trajectories were calculated along the flight path. These trajectories indicated that convective transport from the atmospheric boundary layer to the upper troposphere over India and the Bay of Bengal was responsible for the observed trace gas enhancement. Satellite images of cloud top heights confirm the back-trajectory results by connecting strong vertical transport deduced from the trajectories with the occurrence of deep convective clouds. The convective towers, observed as very cold and bright spots in satellite imagery, are often found close to strong methane sources, mostly rice paddies, in India and Bangladesh.

To investigate the influence of the South Asian summer monsoon on the oxidizing power of the upper troposphere, we measured $H_2O_2$ and ROOH inside and outside the anticyclone above the Arabian Peninsula. We use the methane threshold discussed above to differentiate between monsoon-affected and background air masses. At altitudes higher than 300 hPa, the $H_2O_2$ mixing ratio in background air was 100 ± 53 pptv. Enhanced mixing ratios found in the anticyclone (144 ± 58 pptv) indicate active radical chemistry and high $HO_2$ levels. The difference between background air and the monsoon-influenced air masses was even larger for ROOH: 220 ± 86 pptv vs. 336 ± 74 pptv. Using a steady-state model to calculate the ratio of $H_2O_2$ to the assumed dominant ROOH species methyl hydrogen peroxide (MHP) permits us to estimate MHP mixing ratios from ROOH measurements. Outside the anticyclone, the deduced MHP mixing ratio is 168 ± 83 pptv, while the monsoon-affected air masses have a higher mixing ratio of 190 ± 78 pptv. This enhancement indicates that the observed increase in ROOH is not due to MHP, but instead is due to an unidentified organic peroxide. The mixing ratio of this peroxide is low in background air (52 ± 82 pptv) and increases greatly in the anticyclone (145 ± 42 pptv). A correlation analysis with a large number of measured trace gases indicates that the unknown ROOH peroxide correlates strongly with acetone. We deduce that peroxyaceticacid (PAA), a photochemical degradation product of acetone, and an important source of radicals, is most likely the unidentified peroxide.

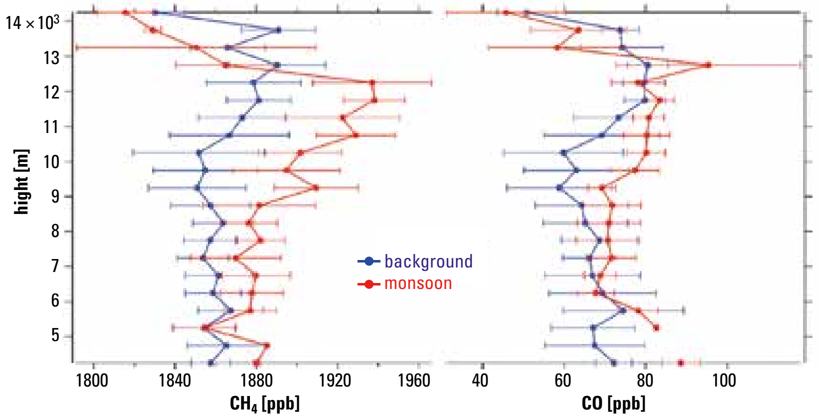

*Figure 2: Vertical profiles for (left) $CH_4$ and (right) CO. Background mixing ratios (in parts per billion) of the gases collected over Germany and the Western Mediterranean are shown in blue and mixing ratios in monsoon-influenced air masses over Egypt and Bahrain are shown in red.*

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*Bozem, H., Butler, T. M., Lawrence, M. G., Harder, H., Martinez, M., Kubistin, D., Lelieveld, J., Fischer, H.: Chemical processes related to net ozone tendencies in the free troposphere. Atmos. Chem. Phys., doi: 10.5194/acp-17-10565-2017 (2017).*

*Bozem, H., Pozzer, A., Harder, H., Martinez, M., Williams, J., Lelieveld, J., Fischer, H.: The influence of deep convection on HCHO and $H_2O_2$ in the upper troposphere over Europe, Atmos. Chem. Phys., doi: 10.5194/acp-17-10565-2017 (2017).*

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# *RADICAL INDUCED OXIDATION OF ORGANICS: FIELD AND LABORATORY STUDIES OF $NO_3$ AND OH CHEMISTRY*

**JOHN CROWLEY**

**“Unravelling the complexity of radical-induced oxidation in the troposphere by combining in-situ observations and laboratory kinetics. “**

*Figure 1: Measurement site of the Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget (IBAIRN) campaign in the boreal forest (Credits: Nils Friedrich).*

The troposphere is like an enormous chemical reactor in which megatons of organic material generated by both anthropogenic and biogenic activity at ground level are annually emitted and processed. The fate of organic trace gases in the troposphere is remarkably varied; some less reactive species (e.g., methane, $CH_4$) can reside for several years and build up to appreciable concentration levels, while others are rapidly removed in a number of reactions initiated by the $NO_3$ radical (during nighttime) and the OH radical (mainly during daytime).

The reaction of $NO_3$ with hydrocarbons, which is most important for unsaturated organic trace gases, proceeds most efficiently by electrophilic addition, leading to the formation of organic nitrates (ON). This reaction complements the formation of ON (both as alkyl-nitrates [AN], and peroxy-nitrates [PN]) via daytime reactions of OH with organics in the presence of NO*x* (NO + $NO_2$). The organic nitrates that are formed may partition to the particle phase, at the same time removing NO*x* from the gas phase and contributing to the formation and growth of secondary organic aerosol.

In order to investigate the relative importance of $NO_3$ and OH reactions in the formation of organic nitrates, we built a two-color, 5-channel, cavity-ring-down spectrometer that measures $NO_2$, $NO_3$, $N_2O_5$, ΣPN (total peroxy nitrates), and ΣAN (total alkyl nitrates). The instrument relies on the thermal dissociation of $N_2O_5$ to $NO_3$ (100°C) and PN and AN to $NO_2$ (at 200°C and 400°C, respectively). This instrument was first deployed at a local mountain site during the 2015 NOTOMO (NOcturnal chemistry and the Taunus Observatory: insights into Mechanisms of Oxidation) campaign. Organic nitrates were recorded at levels of up to a few parts per billion by volume (ppbv). The fraction of NO*x* sequestered as organic nitrates was found to be highly variable and as large as 75% in air for which the time between release of NO*x* and arrival at the measurement site was sufficient for chemical processing to occur (Figure 2). Although the night- and daytime production rates of alkyl nitrates were similar, the daytime concentrations were higher, indicating relatively more efficient nighttime loss of organic nitrate, a result of a larger rate of gas-to-particle conversion. The efficient nighttime loss reflects the fact that alkyl nitrates formed by the reaction of $NO_3$ with biogenic hydrocarbons have low vapor pressures and thus high yields of secondary organic aerosol.

The role of $NO_3$ as an atmospheric oxidant can be assessed by measuring its mixing ratio. However, in regions where the rate of $NO_3$ production (via the reaction between $NO_2$ and $O_3$) is slow and its loss rate is large, $NO_3$ mixing ratios are frequently below the detection limit of modern instruments. For this particular situation, we developed a novel reactor that measures the total reactivity of $NO_3$ in ambient air, summed over all its gas-phase loss processes. Our observations of $NO_3$ reactivity in the Finnish boreal forest during the 2016 IBAIRN (Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget) campaign represent the first-ever direct measurements of this parameter and revealed that the lifetime of $NO_3$ was not only very short (at times just one second), but also highly variable and dependent on altitude. The vertical gradient in reactivity indicated that $NO_3$ lifetimes were shortest close to the ground and increased above canopy height. The short $NO_3$ lifetimes encountered in remote forested environments where there is little anthropogenic influence are due to the presence of high levels of biogenically emitted volatile organic compounds (BVOCs), especially terpenes. Although BVOCs efficiently remove $NO_3$, the converse is also true: the major loss process for these traces gases is via their nighttime reaction with $NO_3$, which generally outruns the loss due to daytime OH reactions.

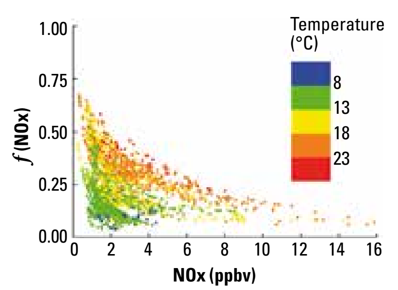

*Figure 2: NOx sequestered as organic nitrate at the Taunus Observatory. The fraction of NOx sequestered as organic nitrates, f(NOx), can approach 75 % and is larger for aged air masses (low NOx) and for warmer conditions (day v. night).*

Our laboratory studies of organic trace-gas degradation in the troposphere have focused on the reactions of fluorinated hydrocarbons with the OH radical. We have deployed real-time kinetic studies (pulsed laser-photolysis formation of OH and its detection via laser induced fluorescence) with chamber experiments to derive both rate coefficients and products. The laser-based experiments have enabled us to investigate the temperature dependence of OH reacting with vinyl ethers R-OCF=$CF_2$, where R is either $C_2F_5$ or $C_3F_7$. The reaction was found to proceed via addition of OH to the double bond, with a rate coefficient at room temperature of ≈ $3 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The major products formed (Figure 3), identified using infrared absorption spectroscopy and quantum-chemical calculations, were a fluoro-formate, ROC(O)F and carbonyl fluoride, $F_2CO$. The rate coefficient implies that R-OCF=$CF_2$ will be efficiently removed in the troposphere, with a residence time of a few days. The carbonyl products will transfer to the aqueous phase, leading to the formation of fluorinated acids, with their lifetimes limited by precipitation.

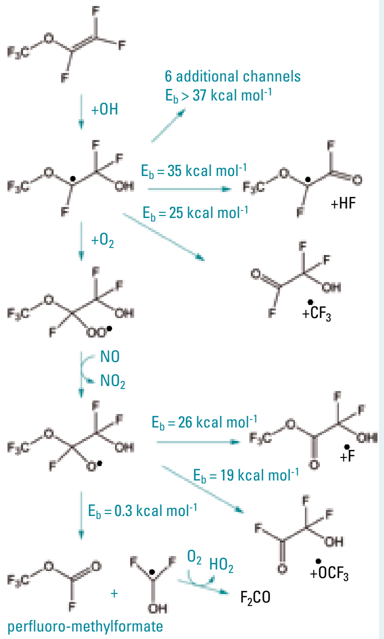

*Figure 3: Atmospheric degradation of perfluoro propyl vinyl ether. The main products are perfluoro-methylformate ($CF_3OC(O)F$) and perfluoro-phosgene ($F_2CO$).*

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# *VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE*

**JONATHAN WILLIAMS**

**"We aim to understand the atmospheric chemistry of volatile organic compounds."**

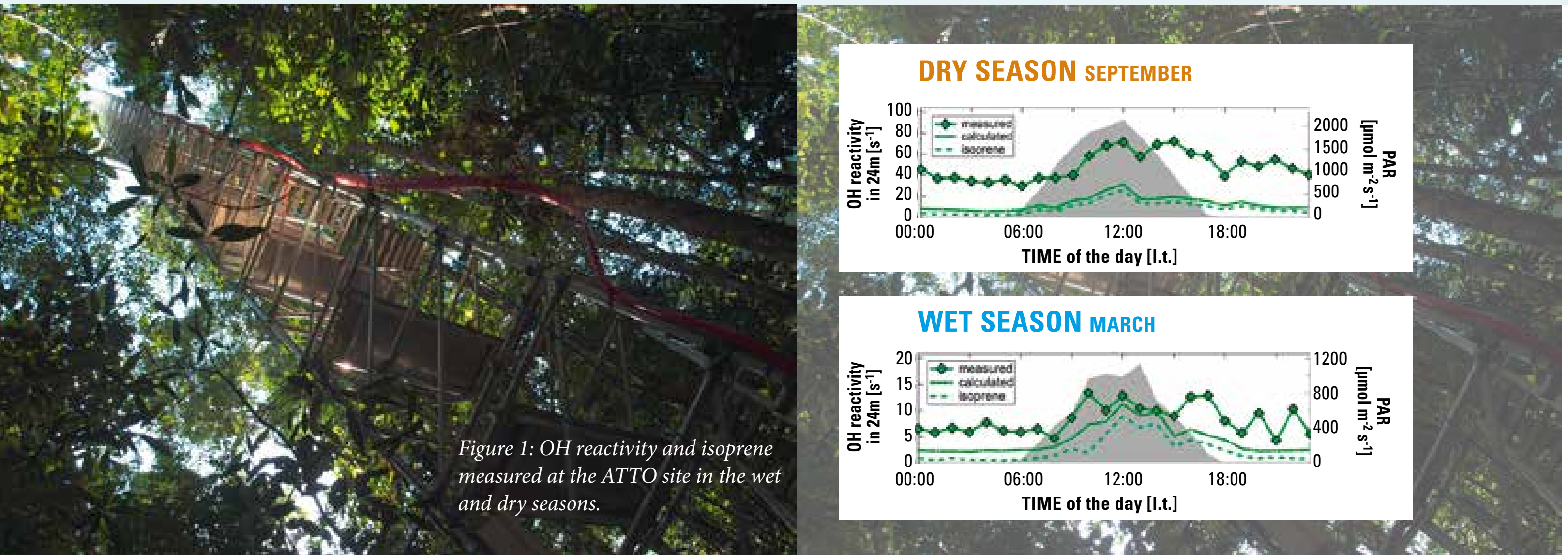

*Figure 1: OH reactivity and isoprene measured at the ATTO site in the wet and dry seasons.*

## INTRODUCTION

Our group specializes in the measurement of volatile organic compounds (VOC). We use highly sensitive mass spectrometers to identify and quantify hundreds of VOC species in multiple environments, from deep in the Earth's mantle to the stratosphere, and from megacities to pristine rainforests. We develop instruments and deploy them in the field at remote ground sites (Amazon Tall Tower Observatory [ATTO]), on ships (M/V Kommander Iona) and on aircraft (High Altitude Long Operation [HALO] and Lufthansa Civil Aircraft for Regular Investigation of the atmosphere Based on an Instrumentation Container [CARIBIC]). Recently, we applied our techniques in the novel setting of a cinema to investigate several aspects of indoor chemistry.

## RESULTS

The Amazon rainforest is the largest source region of VOCs to the Earth's atmosphere. Accordingly, our group has been active in characterizing this source in terms of individual VOCs (including isoprene, monoterpenes, and oxygenates). In parallel, we measured the reactivity presented by all gas phase species to the atmosphere´s primary oxidant OH. This quantity is termed total OH reactivity Our measurements from at the ATTO site (see Figure 1) characterized VOC and total OH reactivity as a function of time of day, height, and season. Notably, in 2015 we measured VOC emissions during the unusually dry conditions associated with an El Niño event. We showed that despite collecting a large suite of VOC measurements, many VOC species remained undetected in this environment. By collecting similar measurements in the megacity of Beijing, China, we revealed how ozone relates to OH reactivity in both environments. Despite the rainforest emitting gases that are in total three times more reactive OH than found in Beijing, ozone remains stable throughout the day. In Beijing, $NO_x$ released in the morning rush hour kick-started a rapid ozone increase that persisted through the daylight hours. In order to establish a community of OH reactivity measurement specialists and to initiate an intercomparison of techniques, we organized the first international OH reactivity meeting at the Max Planck Institute for Chemistry in Mainz in 2015.

For airborne measurements we successfully deployed a custom-built fast gas chromatography–mass spectrometer (GC-MS) on the HALO research aircraft for the first time within the Oxidation Mechanism Observations (OMO) airborne campaign. Monsoon outflow plumes from the South Asian continent were successfully intercepted at 15 km altitude and characterized for oxygenates and organohalogen compounds by virtue of the high measurement frequency. In addition, we continue to measure VOCs in canisters collected monthly from a commercial Lufthansa passenger aircraft in the CARIBIC program. By analyzing this long-term data-set we revealed evidence for significant chlorine (Cl) radical chemical reactions in polluted outflow from East Asia. This finding is important, as Cl radicals were not previously thought to be significant oxidants in the anthropogenically influenced atmosphere, and the Cl radicals can produce chlorine-containing compounds in-situ that are not included in emissions inventories. Such species can nevertheless be transported to the stratosphere and destroy ozone.

Finally, in view of increased interest in indoor chemistry, we characterized the typical real-world VOC emission spectrum from human beings by measuring the composition of air in a cinema. In addition to quantifying VOC emission rates from people, we discovered that audiences release specific chemicals into ambient air depending on the scenes in the film, for example, isoprene peaks were associated with moments of high anxiety (Figure 2). The effect was reproducible over multiple screenings of the same film. This discovery has generated international press interest and from fields as diverse as neuroscience, psychology, and consumer research. Intriguingly, it seems that the emotional responses of a crowd can be measured in the air, opening a new field of research.

## OUTLOOK

Using the established institute´s infrastructure in the Amazon rainforest and two newly acquired mass spectrometers, we will extend the characterization of VOCs at the ATTO site, including measuring reactivity and the emissions from different components of the ecosystem. In the next three years, we will comprehensively characterize VOC species in ambient Amazon air. Furthermore, we will deploy two field measurement mass spectrometer systems (GC-MS and a proton transfer reaction-mass spectrometer, or PTR-MS) on the 2018 HALO aircraft campaign investigating African air-outflow. We will continue to look for innovative applications of measurements to further our knowledge of volatile organic compounds in the atmosphere.

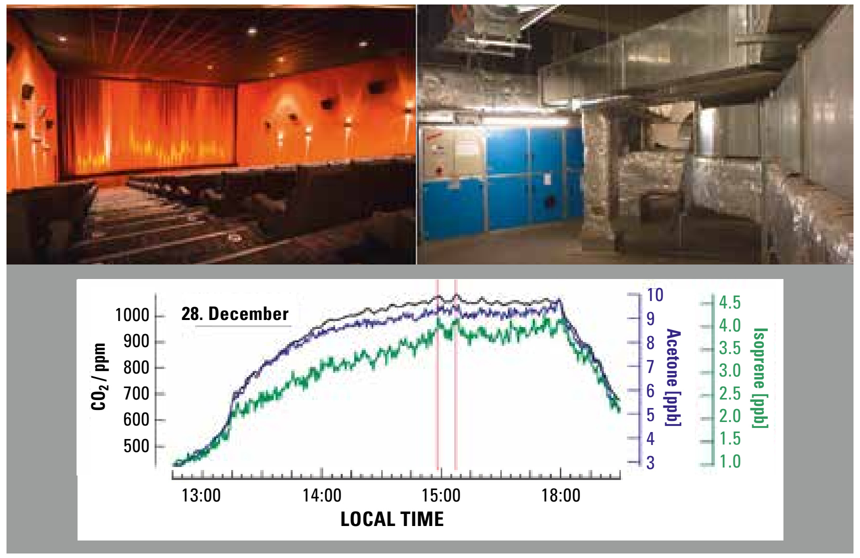

*Figure 2: Variation of isoprene and acetone in a public cinema in Mainz (Credits: Jochen Wulf, CineStar).*

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# *VEGETATION FIRES AND THEIR EMISSIONS TO THE ATMOSPHERE*

**JOHANNES W. KAISER**

> **“Satellite observations uncover global vegetation fires, their smoke emission strength, composition, and injection height.”**

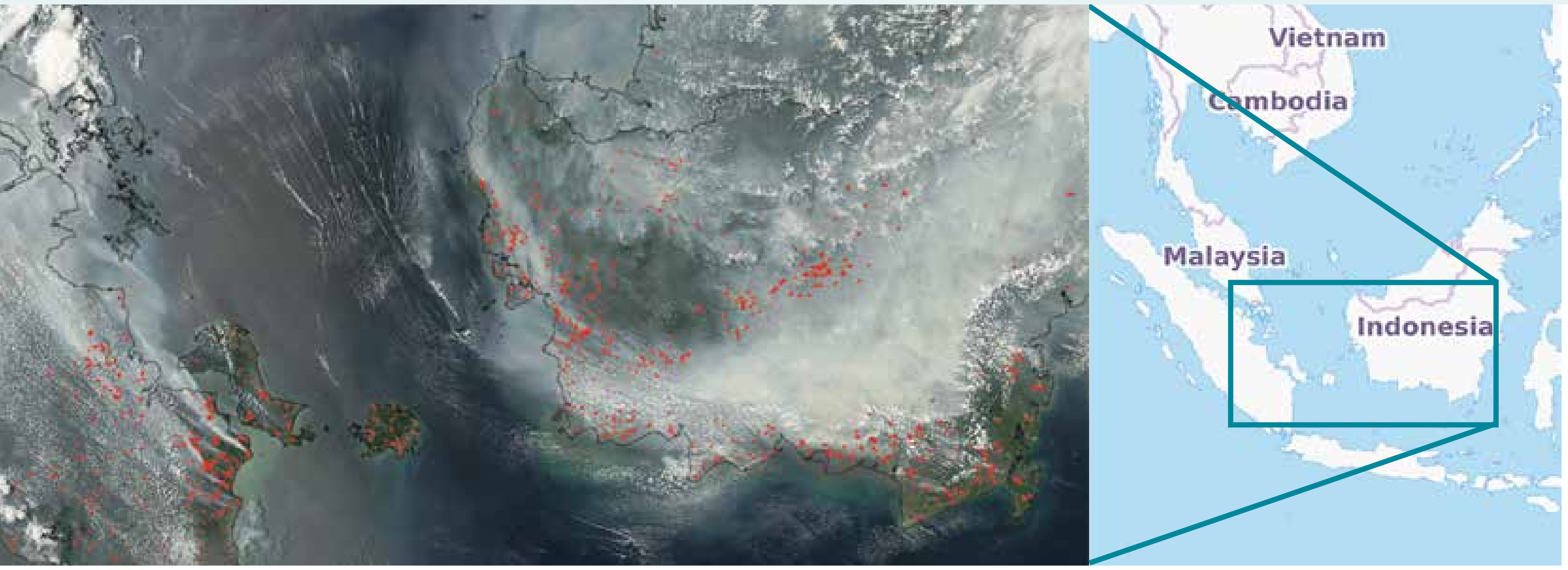

*Figure 1: Moderate Resolution Imaging Spectroradiometer (MODIS) satellite image of widespread smoke over Sumatra and Borneo with superimposed fire detections on 22 September 2015 (Credit: NASA, LANCE/EOSDIS MODIS Rapid Response Team, GSFC) and geographical map of the region (Credit: Open Street Map).*

Vegetation fires (i.e., open biomass burning) are a major source of atmospheric trace constituents such as carbon monoxide and particulate matter. They are a natural component of the Earth system ever since land plants evolved. Today, both climate conditions (precipitation, wind) and human activity (agriculture, forestry, nature conservation, deforestation, fire suppression etc.) exert strong control over the intensity and distribution of vegetation fires. Thus, vegetation fires are an important aspect of the Anthropocene. While the total carbon flux from vegetation fires is relatively well known, this is not the case for individual smoke constituents. In particular, bottom-up and top-down estimates of particulate matter emissions differ by up to an order of magnitude.

Fire occurrence and the associated emissions are traditionally quantified based on in situ observations of the burned area. Satellite-based observations now provide the burned area input data globally. Increasingly, high-resolution, accurate satellite data of the infrared radiation released by fires, the so-called fire radiative power (FRP), guide the development of fire emission inventories. Compared to burned area-based inventories, the key advantages are better sensitivity to small fires, reduced dependency on estimates of fuel type and burning conditions, better temporal resolution (e.g. Meteosat-10 satellite), and availability in near-real time.

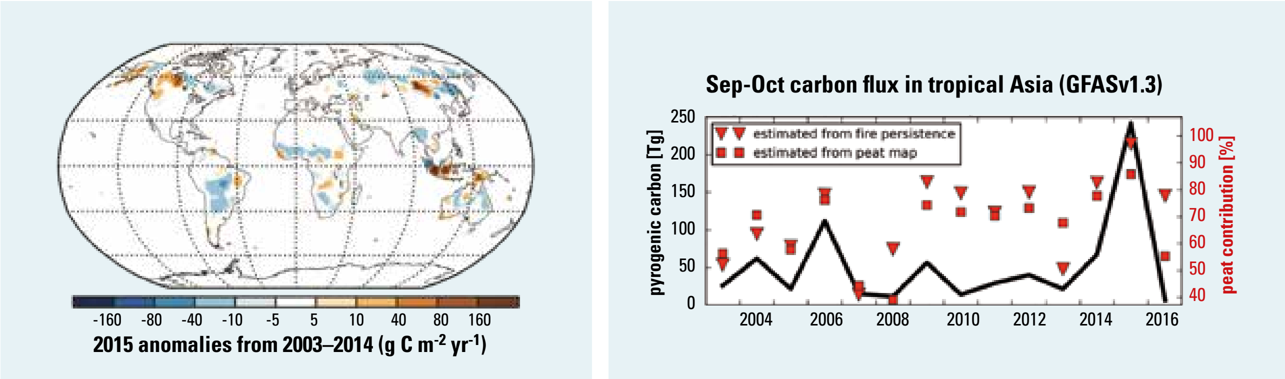

*Figure 2: 2015 anomaly map for pyrogenic carbon flux (left). The time series of the flux in Southeast Asia during Sep-Oct (right, black curve) and two independent estimates for the peat contribution (right, red symbols) show that peat burning is associated with strong carbon emissions, and that 2015 was an extreme event (adapted from Kaiser et al. BAMS 2016. Credit: American Meteorological Society, used with permission).*

Our group is studying the role of vegetation fires in the Earth system by compiling global FRP distributions from satellite data and applying them to atmospheric chemistry and climate research. We lead the development of the Global Fire Assimilation System (GFAS), which is a collaboration with King's College London, the Free University of Amsterdam, the Portuguese weather service and the European Centre for Medium-range Weather Forecasts. The latter currently operates GFAS in near-real time as one of the four headline products of the operational Copernicus Atmosphere Monitoring Service (CAMS). This data product is the most widely used fire emissions inventory for operational atmospheric composition forecasting.

During the El Niño-induced drought in 2015, Indonesia experienced the worst wildfires since 1997 (Figure 1). Wildfires in Indonesia are often associated with the conversion of tropical peat forest to palm plantations. Because peat does not regrow, peat fires constitute an irreversible flux of carbon into the atmosphere. We have optimized GFAS for such fires by incorporating new peat data and quantifying night-time fire activity. We demonstrated that more than 80% of the Southeast Asian pyrogenic carbon flux of 340 Tg(C) in 2015 originated from peat fires (Figure 2). This flux even exceeds Germany's contribution to $CO_2$ emissions through fossil fuel burning, which is about 210 Tg(C) $year^{-1}$.

We participated in several comparisons and inversion studies of fire emission datasets and atmospheric modeling with satellite observations of CO, $CO_2$, aerosols, $NO_2$, and formaldehyde, which underscored the importance of FRP observations, in addition to burned area data.

We provided fire emission information for the coordinated IPCC climate modeling (CMIP6), in preparation of the next assessment report, and contributed fire disturbance assessments to the annual state of the climate reports by the US National Oceanic and Atmospheric Administration (Figure 2). Within the ESA Climate Change Initiative, we investigated how burned area and FRP can be combined to achieve a comprehensive description of fire properties. In the validation team of the Copernicus Sentinel-3 satellite, we analyzed additional near- and shortwave infrared data to determine fire size and temperature at night. We also developed a new gas flaring inventory, and participated in atmospheric chemistry studies conducted by research groups within several departments at our institute. J. Kaiser is co-chairing the Interdisciplinary Biomass Burning Initiative (IBBI), an activity of the WMO and the international projects IGAC and iLEAPS.

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> **“Numerical models are developed to analyze and interpret observational datasets from field campaigns, distributed networks, and long-term monitoring stations.”**

# NUMERICAL MODELING OF ATMOSPHERIC CHEMISTRY

**ANDREA POZZER**

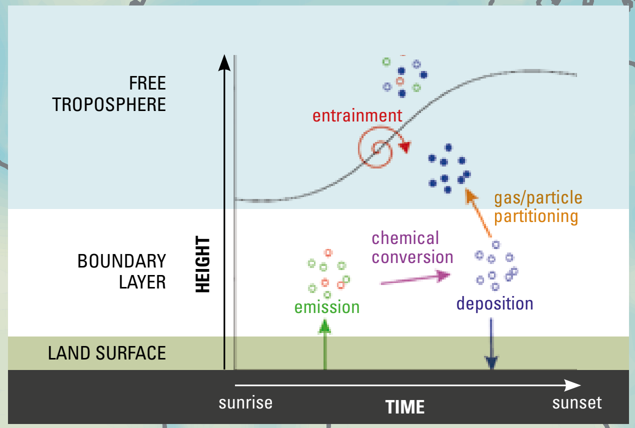

*Figure 1: Structure of the physical-chemical implementations of the newly developed numerical model VERTICO.*

An intricate interplay of photochemical reactions and physical processes controls the concentrations of trace species in the atmosphere. Thus, to study and predict the distribution and the temporal development of trace gases and aerosols, and advance our understanding of the composition of the atmosphere, numerical models that calculate atmospheric chemistry, radiation transfer, transport, and exchanges with Earth’s surface, are needed.

The numerical modeling group develops and maintains a hierarchy of numerical models at different scales and resolutions, and applies them in a wide range of chemistry, air quality and climate studies, and supports experimental groups with the interpretation of observational datasets.

In recent years, our group has developed VERTICO, a numerical model for the lowest part of the atmosphere (up to the tropopause), whose physical and chemical algorithms are compatible with other large-scale models that we operate. VERTICO combines a mixed layer model for the detailed diurnal dynamics of the convective boundary layer together with modules that calculate photochemistry and surface exchange processes (Figure 1). Using VERTICO, local field campaigns conducted in approximately homogeneous environments, such as a forest, can be simulated efficiently, and the observations interpreted without using complex models that need high-performance computing infrastructure. The model is user-friendly and can be operated by experimentalists to simulate the local meteorology and perform sensitivity calculations. For example, VERTICO was applied to field measurement data collected in and around Paris to study atmospheric chemistry in a megacity. It showed that planetary boundary layer dynamics in the urban environment plays a fundamental role in determining the mixing ratios of organic gases and aerosols. The model also showed that local emissions largely control the formation of secondary organic aerosols (SOA), although entrainment of air from the free troposphere strongly influences concentrations. Further, diel boundary layer dynamics  mostly control the concentrations of primary organic aerosols (POA), with other physical phenomena (such as dry deposition) playing only a minor role.

In addition to the development of new numerical tools, a large effort is dedicated to the advancement of the EMAC (ECHAM/MESSy for Atmospheric Chemistry) model. EMAC was initiated in our department, and has been further developed as an international community atmospheric chemistry – general circulation model. Recently, a new version of EMAC has been released, with essential contributions by our modeling group. The new model version was used in the ESCiMo (Earth System Chemistry integrated Modelling) simulations, providing long-term data to a consortium of national and international scientists from eight research centers and universities (Jöckel et al., 2016). Ensemble simulations used more than 6 million central processing unit (CPU) hours on the German Climate Computing Centre (DKRZ) supercomputer, generating approximately two petabytes of atmospheric chemistry data for the past and present century.

Based on the EMAC model results, our group has performed analyses of various datasets, for example, to investigate the causes of ozone trends in the atmosphere. Ozone in the stratosphere protects life on Earth from shortwave ultraviolet radiation. In the troposphere, ozone is important as an oxidant, an air pollutant, and greenhouse gas that contributes to climate change. Using the EMAC model, we showed that the tropopause layer can fold over intense cyclone, and the consequent intrusions of stratospheric ozone into the troposphere significantly contribute to the observed high concentrations in the lower-middle free troposphere over the Eastern Mediterranean and the Middle East in summer, which is unique for this region.

Although ozone in the upper troposphere is largely dynamically regulated through stratospheric intrusions, near Earth’s surface ozone concentrations largely depend on the amount of precursor present mostly emitted by anthropogenic emissions. Our model analysis of data from a global surface network and atmospheric column measurements supported observations of a steady decline in ethane concentrations (an ozone precursor) that began in the 1970s, halted after 2005 in most of the Northern Hemisphere, and reversed after 2010. The spatial distribution of the recent increase in ethane suggests North American oil and natural gas development from hydraulic fracturing is the primary cause. Based on EMAC model simulations and the ground-based network data, we calculated that in the Northern Hemisphere, a total non-methane hydrocarbon emission increase of 1.2 (±0.8) Tg $yr^{-1}$ due to fracking is required to reproduce the observational trends. The photochemical breakdown of these hydrocarbons is associated with ozone increases of several nanomoles per mole downwind of the oil and natural gas production regions (Figure 2).

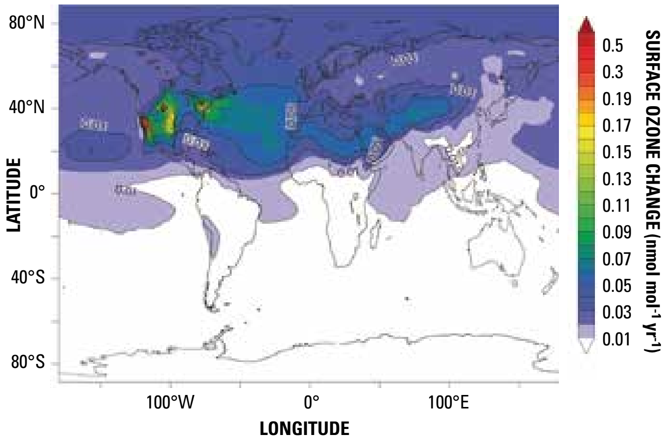

*Figure 2: Estimate for the average annual 2009-2014 June-August change in surface ozone mixing ratios based on estimated non-methane hydrocarbons increased during the same period due to North America oil and gas extraction.*

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# *ATMOSPHERIC CHEMISTRY IMPACTS ON AIR QUALITY AND CLIMATE*

**JOS LELIEVELD**

> **“Human-induced emissions in the Anthropocene drastically change the composition of the atmosphere, which affects air quality, ecosystems and climate. We developed the global atmospheric chemistry–climate model EMAC to assess consequences.”**

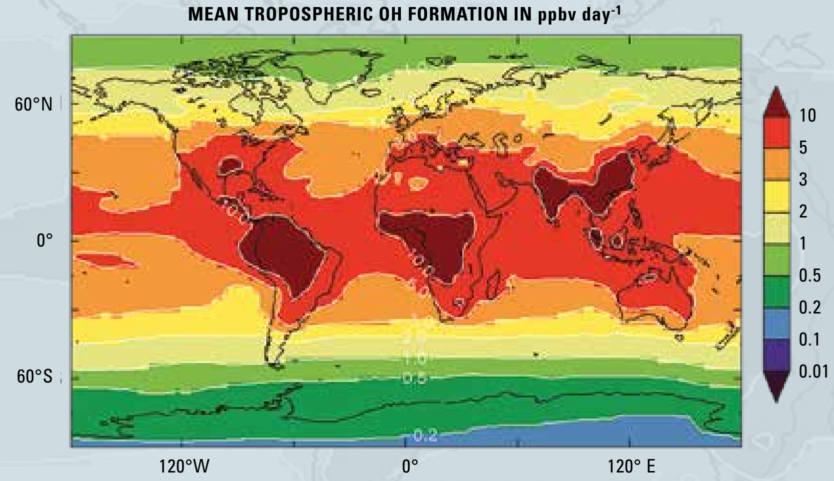

*Figure 1: Model calculations of annual mean OH formation in the troposphere, showing maxima over forested and polluted regions where OH sinks are also largest. This model illustrates the efficiency of OH recycling, which buffers OH concentrations.*

Hydroxyl (OH) radicals are the principal controls on the atmosphere’s oxidation capacity. The primary source of hydroxyl is through the photo-dissociation of ozone, and the secondary source is through OH recycling in radical reaction chains. By using the recent Mainz Organics Mechanism (MOM) with comprehensive volatile organic compound (VOC) chemistry in the global EMAC model, we demonstrated that secondary sources provide much more OH to the atmosphere than previously assumed (Figure 1). In our global computations, we included emissions of a large number of VOCs and an order of magnitude more reactions (>1,600) than commonly included in such models, and accounted for all breakdown products (>400). While earlier models found primary and secondary sources to be of similar magnitude globally, our model simulations predict that secondary sources contribute twice the OH than primary sources, mostly due to OH recycling in the free troposphere. Further, we find that OH formation at night is significant in the polluted subtropical boundary layer in summer, which complements $NO_3$ chemistry. We test these model predictions using measurements collected in the field.

Many of the breakdown products of VOCs have reduced volatility and contribute to the formation of secondary organic aerosols (SOA). This is the case for VOCs emitted by natural sources as well as by combustion of fossil fuels and biomass. We linked the MOM chemistry to volatility categories of organic aerosols, also accounting for photochemical ageing of the particles, and then directly compared the results to our global database of SOA volatility categories measured by aerosol mass spectrometry. Based on model and measurement results, we inferred missing sources of primary and secondary organics in inventories, for example, from widespread wood burning in winter. Our model calculations are used to guide measurements of SOA reactivity and solubility, as photo-oxidation converts emitted hydrophobic compounds into hydrophilic compounds. Because the SOA particles thus turn more soluble in water, their lifetime in the atmosphere is limited by precipitation. Using a new method to compute SOA phase transitions, we find that the particles are liquid in tropical and polar air at high relative humidity, semi-solid in middle latitudes, and glassy solid over dry land and in the upper troposphere and lower stratosphere. The different phases the particles assume over different regions are likely to significant affect liquid and ice cloud formation.

EMAC multiyear simulations demonstrate that the sulphur gases COS and $SO_2$ largely control the formation of stratospheric aerosols. Estimates of volcanic $SO_2$ emissions in our new, long-term database were derived from satellite observations. The calculated climate forcing, i.e. the imbalance between incoming and outgoing radiation energy caused by stratospheric background aerosols, including sulphate produced from COS oxidation, plus contributions by organic aerosols from biomass burning, is about 0.07 W $m^{-2}$. Since about 2002, stratospheric sulphate aerosol from relatively minor volcanic eruptions in the tropics temporarily cooled the atmosphere by up to 0.2 W $m^{-2}$, moderating climate warming. In comparison, short-term cooling resulting from the last major eruption, of Mt Pinatubo in 1991, reached 5 W $m^{-2}$. While anthropogenic emissions in East Asia typically do not reach the stratosphere, we find that the influence from $SO_2$ emissions by coal burning in South Asia is growing rapidly. Our model results, supported by measurements with instruments aboard the HALO aircraft in the “Oxidation Mechanism Observations” campaign in 2015, suggest that the South Asian monsoon effectively transports sulphur species from South Asia to the stratosphere.

While $O_3$ in the stratosphere indirectly affects human health by moderating the amount of solar ultraviolet radiation reaching Earth’s surface, $O_3$ near the Earth’s surface and fine particulate matter with a diameter smaller than 2.5 µm ($PM_{2.5}$) are directly hazardous because they can get trapped in people’s lungs when breathing. Using EMAC and epidemiological integrated-response functions, we estimated mortality by cardiovascular and respiratory diseases that is attributable to air pollution. Based on new data from the World Health Organization on disease incidence, and a recent downward adjustment of the “safe threshold” for $PM_{2.5}$, we estimated a global mortality due to air pollution of 4.3 million per year (±25% uncertainty). The updated number of years of life lost is 122 million annually, hence the lifespan of each individual who dies from air pollution is reduced by about 28 years (“passive outdoor smoking”). We find that residential energy use for heating and cooking is the largest source of $PM_{2.5}$ globally (>30%), mainly in China and India, where a total of 2.2 million deaths per year occur due to air pollution. However, Eastern European countries such as Russia have the highest per capita mortality attributable to air pollution (Figure 2).

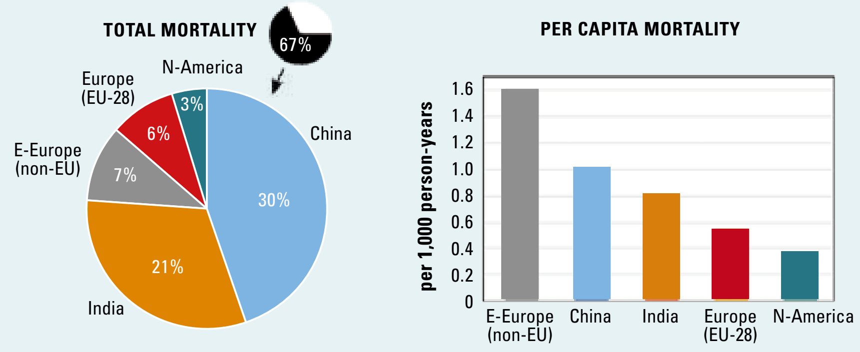

*Figure 2: About two-thirds of the global mortality attributable to air pollution of 4.3 million per year occurs in China, India, Europe, and North America (left). While China and India lead in terms of total mortality, the per capita mortality is highest in Eastern Europe (right).*

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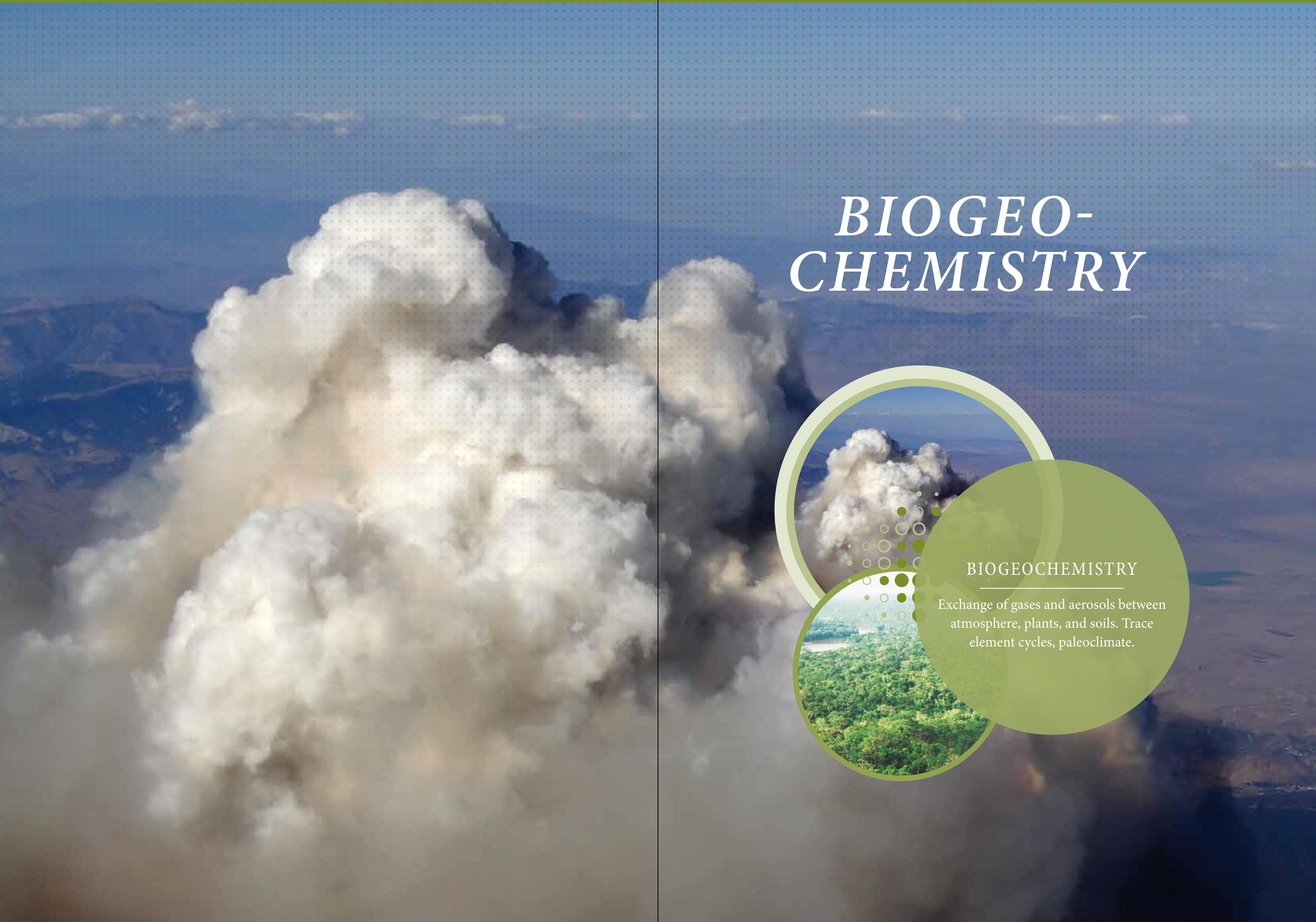


# BIOGEOCHEMISTRY

## BIOGEOCHEMISTRY

Exchange of gases and aerosols between atmosphere, plants, and soils. Trace element cycles, paleoclimate.

# BIOGEOCHEMISTRY DEPARTMENT

**BIOGEOCHEMISTRY STUDIES THE INTERACTIONS OF THE BIOSPHERE WITH EARTH'S CHEMICAL ENVIRONMENT.**

It is a central part of Earth System Science, which looks at Earth as an integral system, in which the biota interact with the atmosphere, the hydrosphere, and the solid Earth. Our department investigates a number of key aspects of global biogeochemistry: the role of the terrestrial biota as sources and sinks of climatically important trace gases and aerosols; the effect of vegetation fires on ecology, climate, and air quality; and the role of aerosols in the climate system.

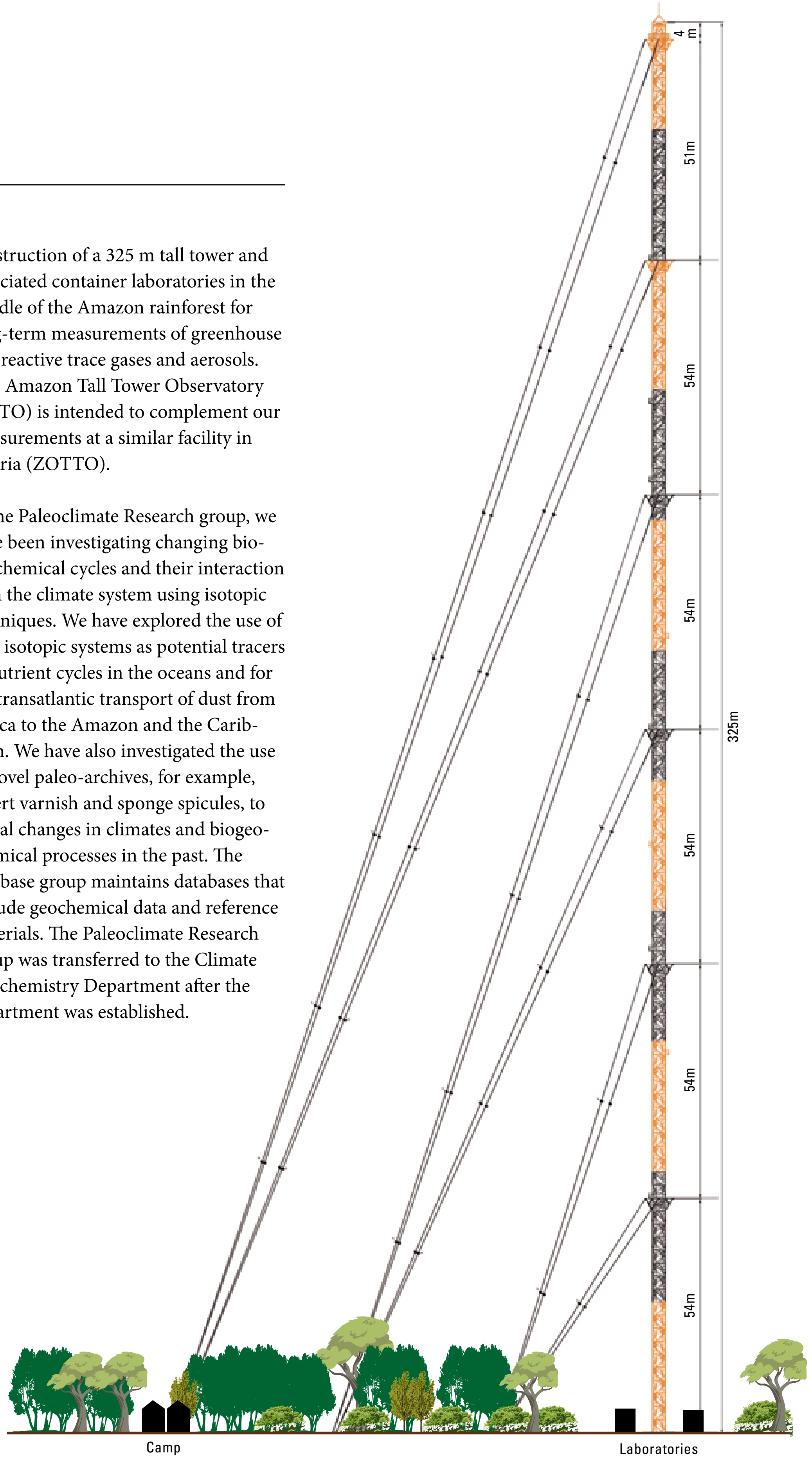
In recent years, our research has focused on the exchange of volatile chemical species between plants and soils and the atmosphere in tropical ecosystems, particularly the Amazon rainforest. Major objectives of this research are to understand the role biogenic volatile organic compound (BVOC) exchange plays in the carbon budget and in the production of atmospheric aerosols. Our research on BVOC exchange is complemented by investigations on the fluxes of trace gases such as dimethyl sulfide (DMS), NO, $NO_2$, and HONO from temperate and tropical sites, using micrometeorological techniques in combination with laboratory studies and remote sensing. We have also examined the exchange of COS between soils and the atmosphere and found that soil fluxes introduce serious complications for the use of COS as a tracer for biological carbon uptake.

A central research topic in the Biogeochemistry Department has been the origin of aerosol particles in the natural atmosphere, especially the pristine continental troposphere. In addition to primary biogenic particles, such as fungal spores, bacteria, and similar material, particles are produced via the oxidation of BVOC that leads to the formation of low volatility substances, which condense to form organic aerosol particles. Our recent work shows that the life cycle of these particles begins by nucleation in the upper troposphere, followed by downward transport and growth in the lower troposphere. In the near-pristine atmosphere, the number concentrations of aerosols and cloud condensation nuclei (CCN) are quite low, over both continents and oceans, resulting in a distinctive "clean" regime of cloud microphysical processes and rain formation mechanisms. Our aircraft studies over the Amazon show that this regime is dramatically perturbed by anthropogenic emissions, including large-scale deforestation fires and long-range transport of pollution, which lead to strong increases in the concentrations of aerosol and CCN. These emissions dramatically affect cloud properties and rainfall production, leading to redistribution of the transport of energy and chemical species in the atmosphere.

We have been studying the role fire plays in ecology, climate, and atmospheric chemistry in the Amazon and other regions. The Global Fire Monitoring Center (GFMC) serves as an interface between the scientific community and the global community of experts concerned with the social, health, and economic effects of vegetation fires.

We operate a station in Manaus, where we are conducting integrated studies on the biogeochemistry and ecology of the Central Amazon. We have completed construction of a 325 m tall tower and associated container laboratories in the middle of the Amazon rainforest for long-term measurements of greenhouse and reactive trace gases and aerosols. This Amazon Tall Tower Observatory (ATTO) is intended to complement our measurements at a similar facility in Siberia (ZOTTO).

In the Paleoclimate Research group, we have been investigating changing biogeochemical cycles and their interaction with the climate system using isotopic techniques. We have explored the use of new isotopic systems as potential tracers of nutrient cycles in the oceans and for the transatlantic transport of dust from Africa to the Amazon and the Caribbean. We have also investigated the use of novel paleo-archives, for example, desert varnish and sponge spicules, to reveal changes in climates and biogeochemical processes in the past. The database group maintains databases that include geochemical data and reference materials. The Paleoclimate Research group was transferred to the Climate Geochemistry Department after the department was established.



## MEINRAT O. ANDREAE

**19 May 1949**
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Study of mineralogy/geochemistry Karlsruhe and Göttingen University, doctorate in oceanography at Scripps Institute of Oceanography

**1978–1982**
Assistant Professor of Oceanography

**1982–1986**
Associate Professor

**1986–1987**
Professor of Oceanography Florida State University

**Since 1987**
Scientific Member of the Max Planck Society

**1987–2017**
Director at the Max Planck Institute for Chemistry

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# THE LIFE CYCLE OF AEROSOLS IN THE NATURAL ATMOSPHERE

**MEINRAT O. ANDREAE**

> **“To understand Global Change, we must find out how the Earth System functioned before human activities began to change it.”**

*Figure 1: Impressions from the ATTO research site.*

The climate effects of atmospheric aerosols remain the largest uncertainty in assessing present and future climate change. Model studies show that among the uncertainties related to aerosol climate forcing, the largest one pertains to the state of the atmosphere before humans introduced pollutants. For this reason, the source and fate of aerosol particles in the natural atmosphere have always been central research questions in the Biogeochemistry Department. Until 2014, we focused on the lowermost part of the atmosphere, the planetary boundary layer (PBL), as the dominant source region for atmospheric aerosols. Indeed, many aerosol types originate at Earth's surface: soil dust, seaspray, and primary biogenic particles such as fungal spores. Others are formed in the lower layers of the atmosphere, for example, sulfate aerosols from marine dimethyl sulfate, or secondary organic aerosols (SOA) from terpenes or other biogenic volatile organic compounds (BVOC).

Measurements collected during the German-Brazilian cooperative aircraft campaign ACRIDICON-CHUVA on the German High Altitude and Long Range Research Aircraft (HALO) in September 2014 over the Amazon Basin have profoundly changed this picture. The primary objectives of this campaign were to study tropical deep convective clouds over the Amazon rainforest and their interactions with atmospheric trace gases, aerosol particles, and atmospheric radiation. Measurements of aerosol particle concentrations were made in support of these objectives. Surprisingly, these measurements showed extremely high aerosol particle concentrations in the upper troposphere (UT) between 8 and 15 km altitude. The particle number concentrations (normalized to standard temperature and pressure) often exceeded those in the PBL by as much as three orders of magnitude.

We observed these aerosol enhancements consistently on all flights on which the UT was probed, using several aerosol metrics, including condensation nuclei (CN) and cloud condensation nuclei (CCN) number concentrations and chemical species mass concentrations. The UT particles differed in their chemical composition and size distribution from those in the PBL, ruling out the possibility that they could be combustion-derived pollution particles that had been brought up from below by convective transport in clouds. In fact, the air in the immediate outflow of deep convective clouds was depleted in aerosol particles as a result of scavenging by rain drops and ice crystals.

When we traced back the air that contained the strongly enhanced number concentrations of small particles (<90 nm diameter), we found that it came from regions in the UT that had experienced outflow from deep convection in the preceding 5-72 hours. We also found elevated concentrations of larger (>90 nm) particles in the UT, which consisted mostly of organic matter and nitrate and were very effective CCN. These particles tended to be in more aged air masses.

Our findings suggest a conceptual model, where new aerosol particles are produced in the UT from volatile organic compounds, for example, isoprene and terpenes, brought up by deep convection. Subsequently, downward mixing and transport of upper tropospheric aerosols can be a source of particles to the PBL, where they increase in size by the condensation of BVOC oxidation products.

This mechanism may be the answer to a long-standing puzzle about the origin of particles in the clean continental atmosphere: at locations where there are modest amounts of anthropogenic pollution and also abundant BVOC emissions, such as the boreal forest in Finland, aerosol production takes place in bursts where thousands of particles per cubic centimeter are produced within a few hours. Such events have never been observed at our remote sites in Amazonia and Siberia. Where do the particles that we observe in such places then come from? Based on our measurements collected on HALO, we propose that aerosol nucleation in the UT may be the dominant process supplying secondary aerosol particles to the pristine atmosphere. In this way, before the arrival of anthropogenic pollution, clouds may have been the dominant control on both the production and removal of atmospheric particles.

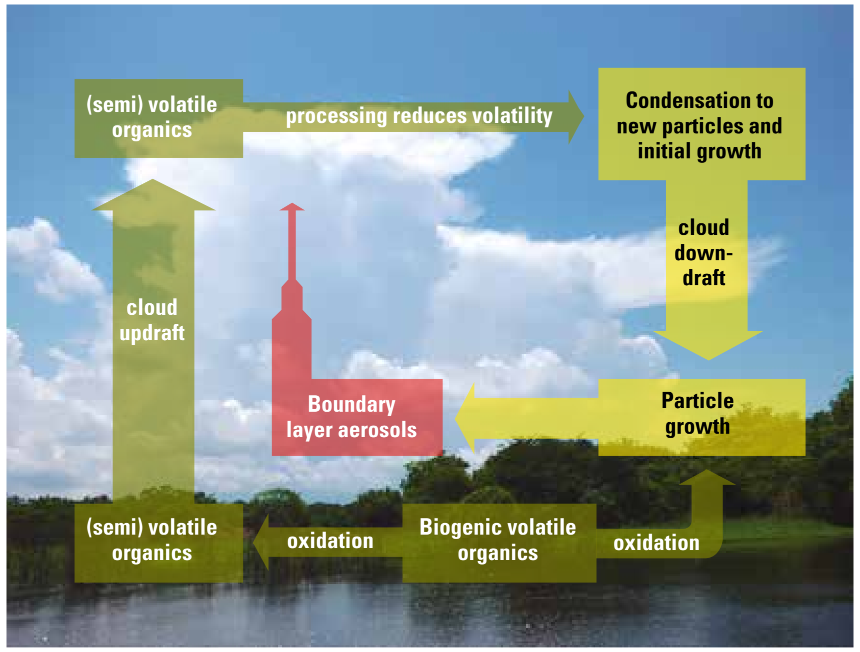

*Figure 2: Conceptual model of the aerosol life cycle over the Amazon Basin (background image by D. Rosenfeld).*

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# *AEROSOL ANALYSIS IN THE AMAZON RAINFOREST*

**CHRISTOPHER PÖHLKER**

> **“Atmospheric aerosols in the Amazon rainforest play a key role in hydrological and biogeochemical cycling in this unique and climate-relevant ecosystem.”**

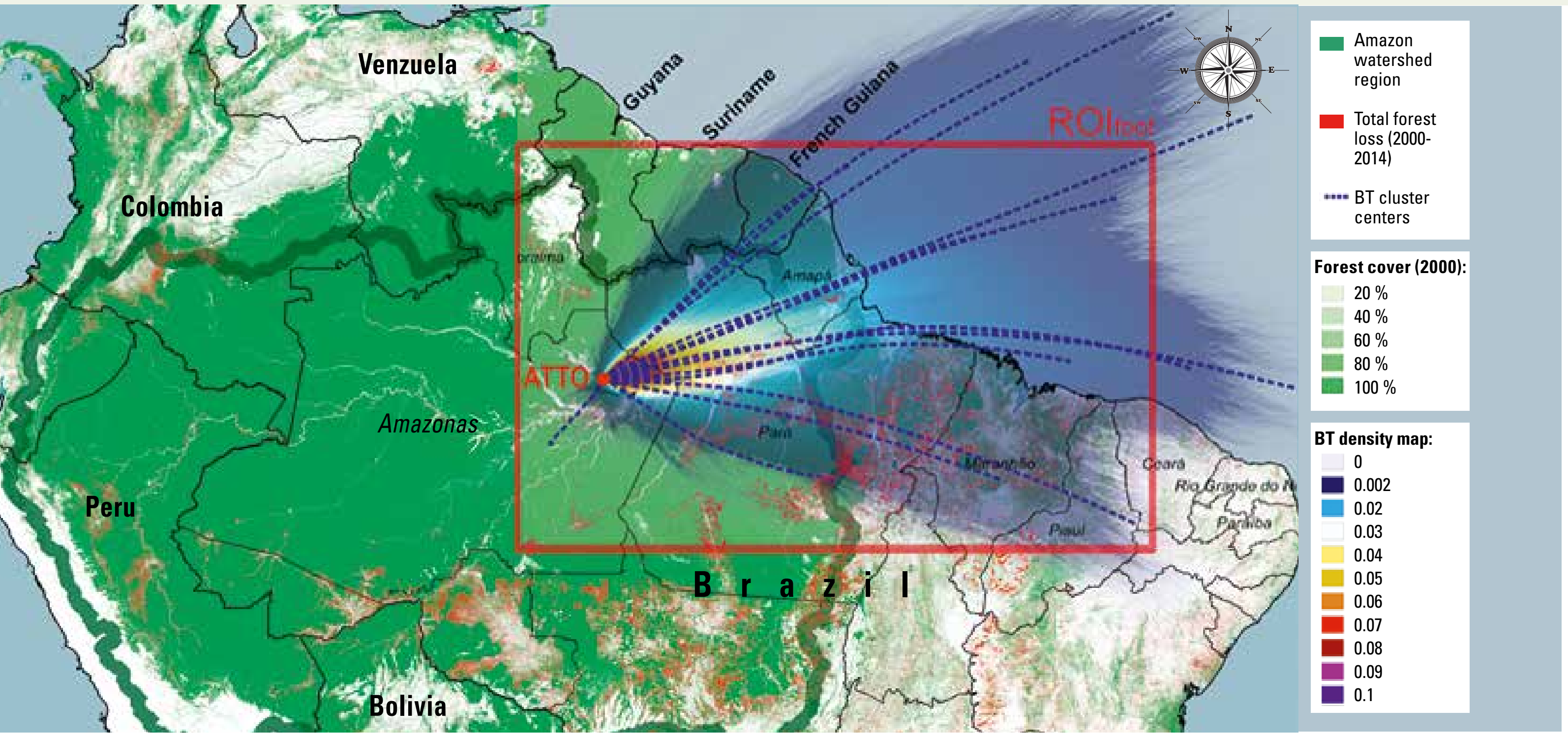

*Figure 1: Forested areas in the Amazon Basin with location of the ATTO site and its modelled backward trajectory (BT) footprint, showing the predominant wind directions.*

The Amazon rainforest is an important part of the Earth system; however climate change and land use change are increasingly disturbing this vulnerable ecosystem. In fact, dieback of the Amazon has been ranked as one of the potential tipping points in the global climate system. Furthermore, the Amazon is a unique location to study the human influence on the atmosphere, as it represents one of the few remaining continental places where episodes with a near-pristine atmosphere can still be found. The Amazon Tall Tower Observatory (ATTO) was established in the central Amazon Basin as a platform for in-depth and long-term observation of the Amazon's ecosystem functioning, integrity, and health. It is evolving into a research hub for atmospheric, climate, and ecological studies in the Amazon region.

The investigation of atmospheric aerosols has been a focus of the ATTO research, with the goal of understanding their role and interactions in hydrological and biogeochemical cycling in the Amazon. We seek to answer two core questions. First, what have been the central aerosol-related mechanisms in biosphere-atmosphere exchange under pristine and, thus, preindustrial conditions? Second, to what extent have anthropogenic activities, such as land use change and massive aerosol emissions, changed crucial processes in the Amazonian atmosphere, and what are the potential consequences of these changes to the Earth climate system? Along these lines, our research has been conducted in close collaboration with Brazilian and other international partners and has focused on a number of different facets of the aerosol population in the Amazonian atmosphere.

We analyzed the highly dynamic life cycle of aerosols, including their most relevant sources, their chemical and physical processing in the atmosphere, and their deposition into the rainforest ecosystem. Of major importance is the role of aerosol particles as cloud condensation nuclei (CCN) in cloud formation and, thus, hydrological cycling. Our recent in-depth investigations of aerosol and CCN properties during characteristic atmospheric states represent a solid basis for follow-up studies of cloud micro- and macrophysical properties. These studies are particularly relevant to understanding climate-relevant processes in near-pristine versus strongly polluted conditions. With respect to the extent of man-made pollution and its significance to rainforest health, we conducted a long-term analysis of aerosol optical properties, with particular focus on the abundance of combustion-derived aerosol particles. This analysis showed that in addition to the massive biomass burning-related emissions in the Amazon region, man-made as well as natural aerosols that are advected from Africa play a crucial role in the state of the Amazonian atmosphere. For example, a recent study details how Saharan dust deposited in the Amazon Basin fertilizes the rainforest ecosystem. A further focus of our studies is the morphology and composition of single aerosol particles, as well as their multiphase chemical and physical aging. For these studies, we apply sophisticated micro-spectroscopic techniques that provide high-resolution images of the particle's microarchitecture and insights into their physicochemical processing. The various aerosol studies conducted at the ATTO site are complemented by further measurements and samples collected on land, at sea by research vessels, and by aircraft at selected locations worldwide.

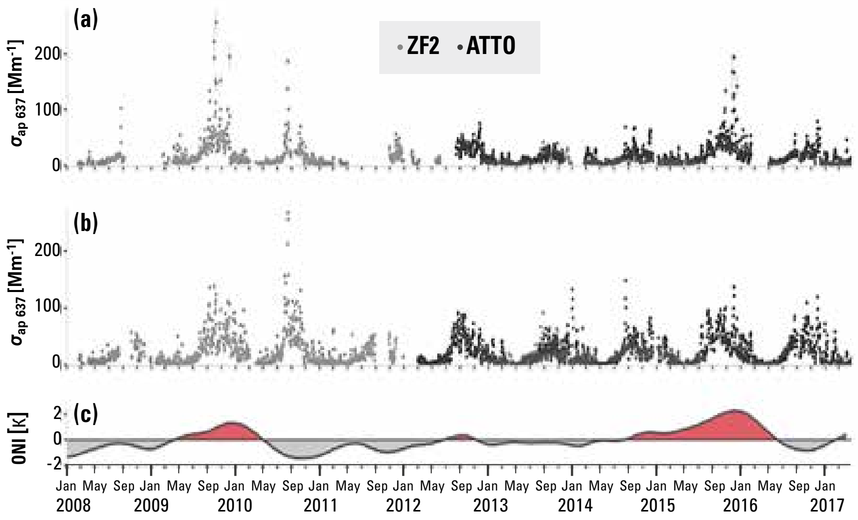

*Figure 2: Long-term time series of aerosol scattering (a) and absorption coefficients (b) in the ATTO region in relation to the Oceanic Nino Index (ONI), showing pronounced seasonality with clean wet seasons and polluted dry seasons as well as El Nino-related pollution peaks. Adapted from Saturno et al., 2017.*

Recently, a 325 m tall tower was erected at the ATTO site, and is currently being instrumented. This unique platform will permit us to extend the scope of aerosol and related observations so that researchers can better address pressing questions regarding future development of the Amazon biome in relation to climate change.

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# *FLUXES OF REACTIVE NITROGEN SPECIES AND OZONE*

**MATTHIAS SÖRGEL**

**“Linking concentration measurements to fluxes and biochemical processes.”**

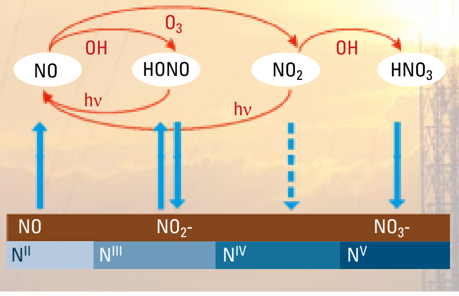


*Figure 1: Simplified scheme of daytime gas phase chemistry (red arrows) and fluxes (blue arrows) of oxidized reactive nitrogen (oxidation state given in lowest panel). The brown layer marks the soil layer and the main oxidized nitrogen compounds formed by microorganisms in soil.*

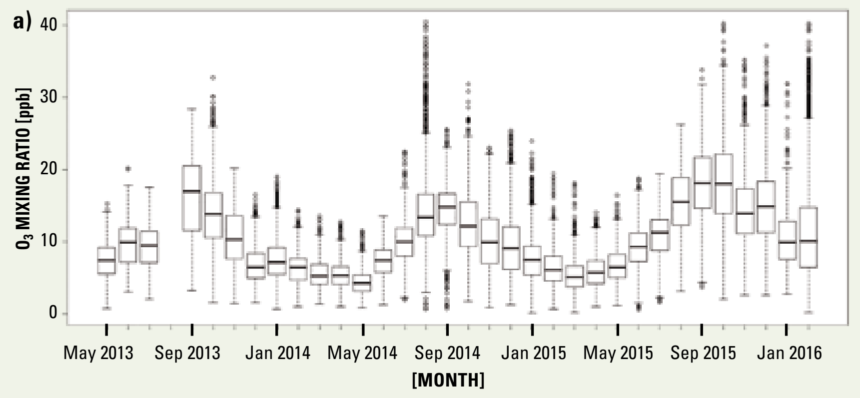
We measure nitrogen oxides and ozone ($O_3$) that are the key ingredients of atmospheric oxidation that sustains the atmospheric “self-cleansing capacity”. We measure the fluxes of these compounds between the atmosphere and the biosphere to quantify the exchange and study the processes (micrometeorological, chemical and biological) that drive the fluxes. Herby we also study the influence of turbulent mixing on chemical reactions in the lower troposphere.

Nitrogen oxides regulate atmospheric self-cleansing by initiating radical formation and regulating radical recycling. Ozone ($O_3$) photolysis is the main source of the hydroxyl radical (OH), the most important oxidizing agent in the atmosphere and therefore often named the “detergent of the atmosphere”. The sole tropospheric source of $O_3$ is the photolysis of nitrogen dioxide ($NO_2$). The back reaction of nitrogen monoxide (NO) with $O_3$ reforms $NO_2$, and thus this reaction scheme forms a so-called null cycle. Net $O_3$ production happens if NO is oxidized to $NO_2$ by pathways not involving $O_3$. This is the case for the important reactions converting peroxy radicals back to OH radicals by their reaction with NO. At high concentrations, nitrogen oxides can also terminate the radical formation by the reaction of $NO_2$ with OH and the subsequent deposition of the formed $HNO_3$. Another important oxidized form of nitrogen is nitrous acid (HONO), which photolyzes to OH radicals and NO, providing another important primary source of OH radicals.

The previous paragraph described atmospheric cycling of oxidized nitrogen species in the gas phase. Other processes, including fluxes into and out of the atmosphere from emission sources of nitrogen oxides and removal of $NO_2$, HONO, and $HNO_3$ by dry and wet deposition, also play a role (see scheme in Figure 1). Atmospheric turbulence drives the exchange of trace gases between the earth's surface and the atmosphere, as well as their mixing within the atmosphere. Therefore, our group not only focuses on the chemistry but also on atmospheric turbulence and micrometeorology. Our aim is to quantify the fluxes, describe the mixing, and provide a link between the processes observed at the surface (e.g., uptake by plant stomata, heterogeneous reaction on surfaces, microbial production, soil processes) and the concentrations observed in the atmosphere.

Our approach includes collecting profiles of $O_3$ and $NO_x$ in the remote Amazon rainforest at the Amazon Tall Tower Observatory (ATTO) site over seasonal to interannual time scales. These profiles will enable us to determine the variability of fluxes at ATTO at these longer time scales. For shorter periods direct flux measurements of $O_3$ and $NO_x$ by the eddy covariance technique could be realized to test the validity of the flux-gradient relationships. To study the processes that drive the exchange of oxidized nitrogen species and $O_3$, these field measurements are accompanied by studies using chambers (soil and plants) under controlled laboratory conditions. Furthermore, we collaborate with different modelling groups that run models on different scales (canopy scale to global scale) to compare modeled and measured data.

Figure 2a shows $O_3$ concentrations measured above the Amazonian rainforest at ATTO from May 2013 to February 2016. Figure 2b displays a laboratory experiment showing the influence of thin aqueous surface films (and their constituents) at leaf surfaces on nonstomatal $O_3$ deposition. Ozone concentrations at ATTO (Figure 2a) clearly show a distinct seasonal cycle, with lower values in the rainy season (~ 6-10 ppb) and higher values in the dryer season (up to 40 ppb). The peak values in the dry season are associated with pollution plumes from biomass burning and other pollution sources that often originate several hundred kilometers away. But it remains open whether the general annual cycle of $O_3$ in the atmosphere is driven more by the availability of chemical precursors (e.g., $NO_x$) or by changes in the stomatal and/or nonstomatal sink of $O_3$ in the canopy, which are the dominant removal pathways.



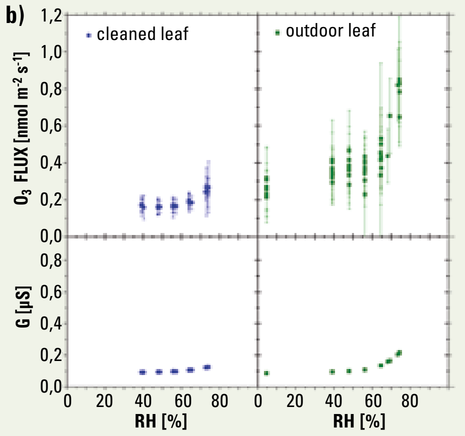


*Figure 2: a) Mixing ratios of $O_3$ measured at the ATTO site above the Amazonian rainforest canopy. The box (75 and 25 percentile) and whisker (90 and 10 percentile) plot contains all measured data (half hour means) for the 80 m height. b) Laboratory experiments on the contribution of the nonstomatal deposition of $O_3$ for leaves washed with distilled water (“cleaned”) and for leaves exposed to outdoor air (modified from Sun et al., 2016). The upper panel of b) shows the $O_3$ deposition flux with closed stomata and the lower panel the conductivity measured at the leaf surface.*

In order to better understand the processes involved in dry deposition (for deriving better parametrizations), we investigated the formation of liquid surface films on plant leaves and how they influence $O_3$ uptake (Figure 2b shows one example). We found that nonstomatal $O_3$ fluxes increase with rising relative humidity and surface water film formation. Different chemical constituents were found to increase the $O_3$ flux into the liquid films (Sun et al., 2016). These results may help to better parameterize nonstomatal deposition, which contributes up to 30 % of the total deposition in our laboratory studies and may be even larger in natural environments.

Having established a site in the Amazon rainforest where we rapidly collect continuous $NO_x$ and $O_3$ profiles over seasonal to interannual time scales, we are on track toward achieving our goals. We anticipated that our robust long-term continuous dataset will enable us to gain a better understanding of the biosphere-atmosphere exchange of ozone and nitrogen oxides. The results will be used to improve relevant models.

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# PROCESS-RELATED ENCLOSURE STUDIES WITH PLANTS AND SOILS TO UNDERSTAND BIOSPHERE-ATMOSPHERE EXCHANGE OF CARBONYL SULFIDE

**JÜRGEN KESSELMEIER**

> **“Understanding of plant/soil metabolism and exchange regulation by enzymatic and enclosure studies is indispensable for interpretation or modelling larger-scale processes.”**

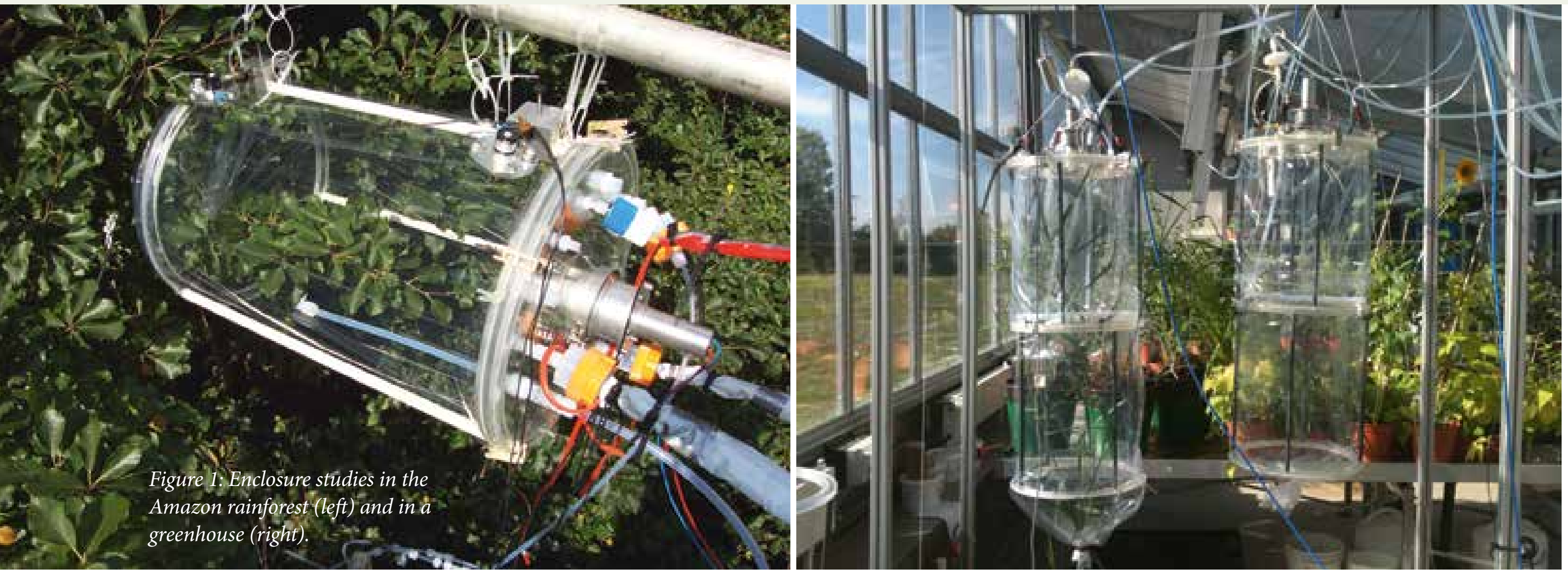

*Figure 1: Enclosure studies in the Amazon rainforest (left) and in a greenhouse (right).*

## INTRO

Estimating the exchange of trace gases between the biosphere and the atmosphere is only possible if we understand the basic biological processes (metabolism and exchange regulation) involved in the production and consumption and the release or uptake of the trace compounds relevant to atmospheric chemistry and physics. Special enclosure systems (cuvettes) adapted to research needs are the main tools used to investigate trace gas exchange between plants, soils, and the atmosphere. These fluxes may be bi-directional and may be related to intracellular metabolism or may be affected by surface reactions. A basic understanding of these processes is required to interpret measurements under field conditions.

The trace gas carbonyl sulfide (COS) is chemically stable in the troposphere and is transported up to the stratosphere. Since 1988, the exchange of COS between the biosphere and the atmosphere has been a target of our research group. Studies with higher plants, algae, lichens, and soils fostered our understanding of the role of the biosphere. In order to understand the role and contribution of soils to the overall COS exchange between forests and the atmosphere, our recent studies concentrated on the exchange processes with soils. This was of special interest in order to validate that COS can be used as a proxy for forest Gross Primary Productivity (GPP), a discussion initiated some years ago by our studies with different plant species, which was mainly based on the similarities of the uptake mechanisms for COS and $CO_2$.

## RESULTS

We used a new continuous integrated-cavity output spectroscopy analyzer and an automated soil chamber system to investigate the processes by which COS is exchanged between soils and the atmosphere under laboratory conditions. The COS exchange patterns were found to be highly dependent on soil moisture and ambient $CO_2$ concentration. Soil treated with the fungal inhibitor nystatin in the laboratory showed that fungi may be the dominant COS consumers in the soils. We found a clear tendency toward release of COS at higher soil pore $CO_2$ levels (up to several thousand ppm under natural conditions). The variability of the exchange was related to the microbial communities adapted to special conditions. Physical factors such as diffusivity that are governed by soil moisture also played a role.

Comparing the metabolic affinity of an enzyme to its substrate estimated as the Michaelis-Menten Value ($K_M$), we showed that competitive inhibition under increased $CO_2$ levels is unlikely to explain the decrease in COS uptake by the enzyme carbonic anhydrase and phosphoenolpyruvate carboxylase (PEPCO), but it might occur for ribulose-1,5-bisphosphate carboxylase (RubisCO) at higher $CO_2$ concentrations. An adjustment of the chamber air to different COS mixing ratios allowed us to separate COS production and consumption processes and to estimate compensation points for COS exchange. Under normal ambient conditions, COS uptake dominated at all soil moistures for forest soils, while production exceeded uptake at higher and very low soil moistures for agricultural soils, resulting in net emission. A strong dependency of the CPs for atmospheric COS from soil moisture was found over a wide range, on the order of 130 ppt to 1600 ppt of COS for the forest soils and 450 ppt to 5500 ppt for the agricultural soil. The lowest compensation points were found at about 20–25% water-filled pore space (WFPS), which implies maximum uptake in this soil moisture range, and limits or excludes COS emission under such conditions.

## OUTLOOK

Soils may play a substantial role in regional and global exchange of COS with the atmosphere. The largest gap in understanding is contribution of tropical and desert soils to this exchange. The use of COS as a proxy for GPP for forest is not possible without this knowledge.

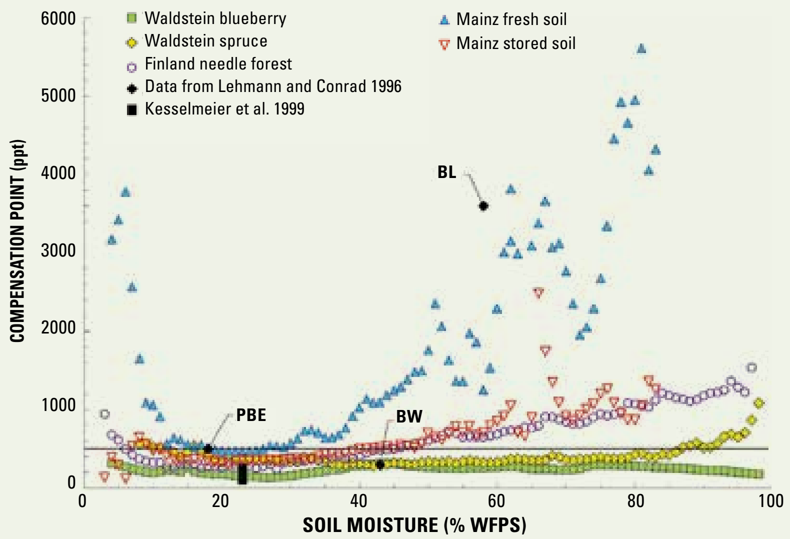

*Figure 2: Carbonyl sulfide (COS) compensation point mixing ratios plotted against soil water content. The continuous black line is the average tropospheric COS mixing ratio of the Northern Hemisphere. A compensation point below this line indicates potential uptake, above this line emission (Bunk, Dissertation 2017; Bunk et al., in preparation). Shapes with colors are our laboratory data. For comparison, older studies of three forest soils (Lehmann and Conrad, J. Atmos. Chem. 23: 193-207, 1996), one without small vegetation (PBE); one vegetated with Dryopteris assimilis, Mnium undulatum and Leucobryum glaucum (BW), and one vegetated with Allium ursinum (BL) are identified by the black shapes. The black bar at 23% WFPS represents compensation points measured for an agricultural soil at different temperatures (Kesselmeier et al., JGR 104, 9, 11,577–11,584, 1999).*

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# GLOBAL VEGETATION FIRES AND DEVELOPMENT OF PUBLIC POLICIES: PROGRESS IN BUILDING THE SCIENCE-POLICY INTERFACE (SPI)

**JOHANN G. GOLDAMMER**

> **"The mandate of the Global Fire Monitoring Center is to serve the science-policy interface by assisting in the development of science-based fire management policies and practices."**

*Figure 1: Science-based outreach work such as by the Central Asian Center has already resulted in the application of science-based principles in fire management, for example, the move from fire exclusion to integrated fire management by application of prescribed fire (Credit: FMRC-CAR).*

## INTRODUCTION

Since the late 1970s, the Fire Ecology Research Group, which was established at Freiburg University in 1979 and moved to the Biogeochemistry Department in 1990, has investigated the role and impacts of fire on natural, cultural, and industrial landscapes and societies in all vegetation zones. During the 1980s and 1990s, the research group observed that many fire regimes (i.e., frequency, intensity, size, season, pattern, and severity of fires) were changing rapidly as a consequence of changes in land-use and climate (Goldammer, 2013). In 1998, the Global Fire Monitoring Center (GFMC) was established within the Fire Ecology Research Group to assist in the development of science-based fire management policies and practices. At this science-policy interface (SPI), the GFMC addresses the human health and security problems resulting from the fire-caused alterations in global biogeochemical cycles and atmospheric composition (Goldammer 2013, Koutsias et al. 2015).

## RESULTS

In 2001, the GFMC established scientific fire research units and networks in various regions of the world and formed interdisciplinary research groups to address specific regional phenomena and problems of fire ecology and fire management. The publication of transdisciplinary syntheses for different regions and vegetation zones, including analyses of the multifaceted role vegetation fires play in the global system, received increasing interest by the community of practitioners and decision makers (Goldammer, 2013). In recent years, the request for science-based decision and management support by countries and international organizations overwhelmed the capacities of the GFMC. In order to decentralize and to specify the SPI work of the MPIC/GFMC at regional levels, the first four Regional Centers of Excellence were set up with the financial support of the Council of Europe through its Major Hazards Agreement, the Organization for Security and Cooperation in Europe (OSCE), and the German Government (through the Federal Ministry for Agriculture and Food). All centers were established at academic institutions:

- The Regional Fire Monitoring Center (RFMC) for Southeast Europe / South Caucasus Region (including some countries of the Middle East), based at the Faculty for Forestry in Skopje, the former Yugoslav Republic of Macedonia (2010)
- The Regional Eastern European Fire Monitoring Center (REEFMC), based at the National University of Life and Environmental Sciences in Kiev, Ukraine (2013)
- The Fire Management Resource Center – Central Asia Region (FMRC-CAR), based at the National University of Mongolia in Ulaanbaatar, Mongolia (2015)
- The Regional Fire Management Resource Center – South East Asia (RFMRC-SEA), based at the Faculty of Forestry of Bogor Agricultural University, Indonesia (2017)

The work of the GFMC and these four centers has already significantly influenced the development of national fire management policies (Goldammer 2016; Figure 1) and spurred regional cooperation in vegetation fire early warning, preparedness, and response, for example, in reducing the extent and the consequences of vegetation fire emissions on the environment and public health and security in Southeast Asia (Goldammer et al. 2017; Figure 2).

Furthermore, the Regional Fire Centers initiated a proposal to the signatory States of the Paris Climate Agreement and its implementation agenda to systematically apply the principles of Integrated Fire Management (IFM) (Anonymous, 2015).

## OUTLOOK

Additional Fire Monitoring and Fire Management Resource Centers are planned to open in late 2017 and 2018 in the Russian Federation and in Brazil and Chile in South America. With a total of six regional centers, the outreach work of the MPIC/GFMC will cover most of the regions of the world where science-based fire management policies and practices need to be developed and implemented.

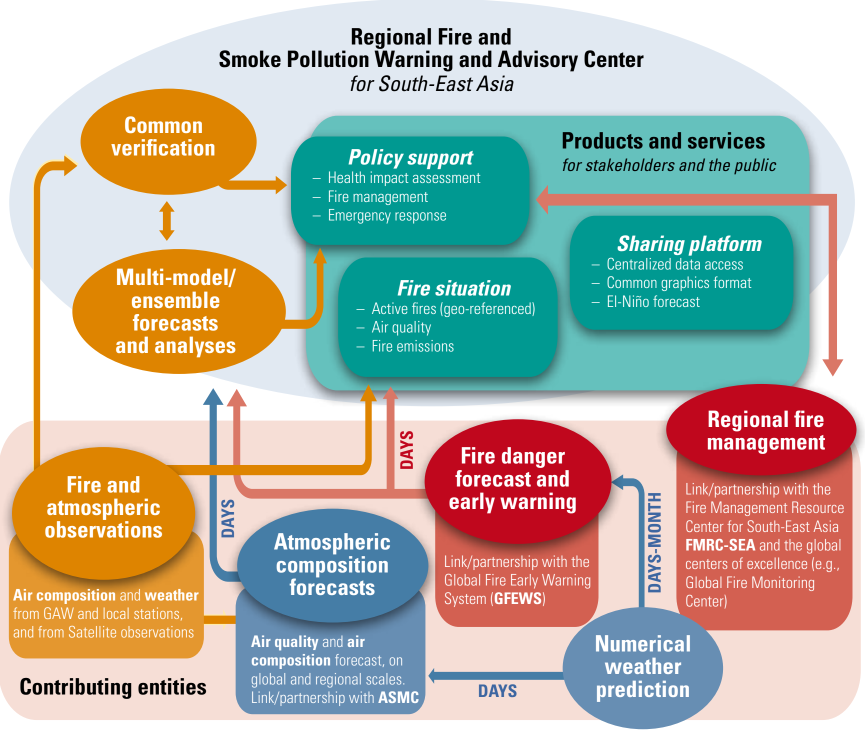

*Figure 2: Envisaged workflow between the proposed Regional Fire and Smoke Pollution Warning and Advisory Center for South East Asia and the Regional Fire Management Resource Center – South East Asia (FMRC-SEA), (Credit: Goldammer et al., 2017).*

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# *DATABASE PROJECTS WITHIN THE BIOGEOCHEMISTRY DEPARTMENT*

**BÄRBEL SARBAS**

**"Researchers need databases for managing, interpreting, and sharing data."**

*Figure 1: Plateau basalts at Snake River, Idaho.*

*Figure 2: The ATTO tower in the Amazon rainforest.*

The database group was started in the late 1990s in the former Geochemistry Department of the Max Planck Institute for Chemistry to build up and manage the open-access database GEOROC. This online database contains published chemical analyses (whole rocks as well as glasses, rock-forming minerals, and melt inclusions) of samples of volcanic rocks ranging in age from Archean to modern (Figure 1). Recently, we started adding data on plutonic rocks that come from of different geological settings worldwide. The extensive metadata include, among others, location name, latitude and longitude, geological setting, rock type, degree of alteration, and method of analysis/laboratory. Currently, the database contains about 1,075,000 analyses for about 460,000 samples published in more than 15,300 papers. Over the last several years, GEOROC has become an established and frequently used tool, not only in hard-rock geochemistry but also in paleoclimate, biogeochemical, and atmospheric research. For example, scientists studying the source of dust in the atmosphere use GEOROC to determine the possible source regions by comparing dust analyses with the composition of rocks in the database. GEOROC is used by scientists from more than 100 countries. The total number of users per months varies between 3,000 and 4,000. The number of publications that are based on data compilations from GEOROC and lead to new or revised interpretations of geological processes is steadily increasing. The database is among the Earth science databases recommended by Nature journals.

The ATTO database project was started in 2014 within the Biogeochemistry Department at the Max Planck Institute for Chemistry. Currently hosted on a server at the Gesellschaft für wissenschaftliche Datenverarbeitung in Göttingen (Society for scientific data processing, GWDG), this relational database's structure is similar to that of GEOROC. It contains results of measurements taken at various heights on the Amazon Tall Tower Observatory (ATTO) in the Brazilian rainforest (Figure 2). These measurements include concentrations of compounds such as $CO_2$, $CH_4$, CO, ozone, $N_2O$, $H_2O$, black carbon, and volatile organic compounds, and also meteorological data such as temperature, humidity, wind speed, and rainfall, and data such as particle scattering coefficient, particle number concentration, and particle number size distribution. Metadata include the name and geographical location of the tower, the height where measurements were done, the time stamp, the instrument or sensor used (with averaging interval, time resolution, calibrations, and response time of the instrument), information on the inlet used, as well as name and institution of the scientist. A flag system distinguishes data of various qualities such as processed data, raw data, and data showing some noise. To ensure that data are entered into the database consistently so that users can confidently evaluate and compare data, we apply a certain degree of standardization. In the case of the ATTO data, a defined time stamp (days since 30/12/1899) is crucial as well as consistent units and abbreviations. Thus, we developed a template for scientists to use when supplying data that distinguishes mandatory and optional information.

The main purpose of the ATTO database is to quickly exchange measurements between the working groups of the Max Planck Institutes for Chemistry, and for Biogeochemistry, and the Brazilian National Institute of Amazon Researches (INPA) in Manaus. Currently, it is only accessible to the scientists working within the ATTO project. The database does not yet have functional user administration that would permit other selected scientists to access the data. The web interface allows users to select data by various criteria such as measured item, quality of data, inlet height, and/or scientist name.

At the beginning of 2016, during a joint workshop of the two Max Planck Institutes Biodiversity Exploratories Information System (BEXIS 2) was suggested as an alternative database management system to store and extract the data collected at the ATTO sites. BEXIS 2 is open-source software developed at the University of Jena to meet the requirements of the biodiversity community, but it is generic enough to be used for other research fields. Compared to the ATTO database developed in Mainz, BEXIS 2 has better user administration but its search functionality is not as good. At the Earth System Research Partnership (ESRP) meeting 2017 in Jena, participants decided to maintain the ATTO database in Jena and use BEXIS 2 as the database management system.

Since June 2017, the database group is part of the Climate Geochemistry Department and will be involved in data archiving and data management demands.

# CLIMATE GEOCHEMISTRY

## CLIMATE GEOCHEMISTRY

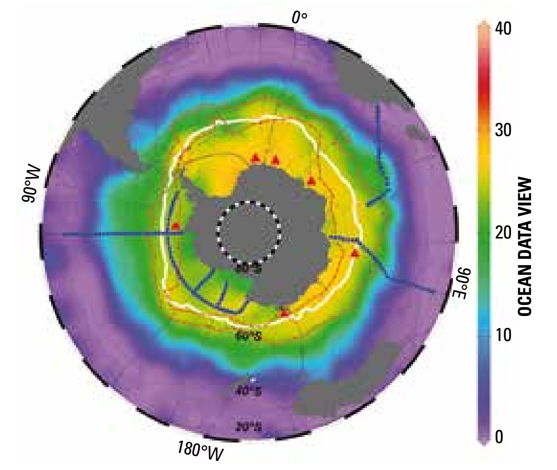
Past changes in climate, ocean-atmosphere interactions, the oceanic nutrient status, the ocean's heat transport, and atmospheric greenhouse gases.

# *CLIMATE GEOCHEMISTRY DEPARTMENT*

**THE CLIMATE GEOCHEMISTRY DEPARTMENT ADDRESSES CLIMATE-OCEAN-ATMOSPHERE PROCESSES AND LARGE-SCALE DYNAMICS IN THE GLOBAL BIOGEOCHEMICAL CYCLES AS REVEALED BY THE SEDIMENTARY AND FOSSIL RECORDS.**

Periods of interest include much of the Cenozoic, the past 65 million years, including the Pliocene thermal maximum some 3 million years ago, which is the youngest geologic analogue of a 400 ppm $CO_2$ world, the glacial cycles of the last 2.7 million years, and more recent intervals such as the Holocene including the Anthropocene.

This new department at MPIC has been built to focus on three key approaches that will improve our understanding of past environmental conditions on Earth. First, building on a previous focus of the director, we have acquired and developed archives of sediments, speleothems, and other materials, as well as the appropriate instrumentation, to enable us to conduct extremely high temporal resolution paleoenvironmental studies. Second, we have built state-of-the-art laboratories for geochemical and isotopic analysis of specific organic compounds and organic matter fractions (e.g., fossil-bound organic matter). In particular, we seek to apply these tools to the reconstruction of changes in the polar oceans, which play an important role in setting atmospheric $CO_2$ levels on the time scale of centuries to many thousands of years. Third, with regard to these paleoproxies and others, we will mount oceanographic cruises during all four seasons to provide a new level of understanding of paleoproxy environmental sensitivities, both those measured at MPIC and elsewhere. This effort will make use of a state-of-the-art small sailing vessel perfectly designed for this purpose (see next page).



*Southern Ocean nitrate concentration and the location of the oceanographic stations (blue dots) and sediment cores (red triangles) from ongoing work. Red dashed lines: Polar front and Southern Boundary of the Antarctic Circumpolar Current. White line: Winter sea ice extent.*

The first unifying theme in our work is well summarized by a piece of advice given by late Sir Nicolas Shackleton to an audience of paleoceanographers: "Whatever you do, do it in high resolution." The underlying message, I believe, is that much "noise" in geologic records is actually composed of meaningful environmental signals.

A central goal of our department is to use new approaches and techniques that do justice to the complexity of geologic records, in order to expose previously hidden signals. One major thrust of our research is to reconstruct millennial to subdecadal scale climatic changes in the tropics and mid-latitudes. Some of this work has been centered around remarkable, often laminated sediment archives such as the Cariaco Basin off the coast of Venezuela, Lake Challa in the foothills of the Kilimanjaro, the Arabian Sea, Lake Van in Turkey, the Dead Sea, Eifel Maar lakes, and speleothems in Asia and Central America, among others. Environmental change as recorded in these sediments has also been correlated with events in the evolution of ancient human societies.

Ongoing work takes advantage of new sediment cores from Lake Challa (International Continental Scientific Drilling Program drilling in spring 2016), which are annually laminated throughout the last 250,000 years and may provide major insights into African climate and ENSO for two complete glacial-interglacial cycles. Lake Challa is probably the best climate archive in Africa and will provide unprecedented records of rainfall variability in East Africa, one of the most vulnerable parts of the world. In Central Europe, together with Frank Sirocko of Mainz University, we successfully cored the varved Eiffel Maar lakes, which will provide insight to the past 600,000 years Central European and North Atlantic climate. Numerous other archives will also be tapped.

The second theme, the use of organic-based tools to reconstruct biogeochemical and carbon cycle changes in the ocean, also draws on team members' previous work. With regard to the measurements themselves, we have made major investments in instruments and facilities that are allowing for N isotopic measurements of coral-, diatom- and foraminifera-bound organic matter at unprecedented sensitivity. Moreover, we are also positioned to make major steps forward with C isotopic composition, and to take the next major analytical step to analyze specific compounds from within the fossil-bound organic matter pool. Our work in the polar oceans has so far focused on Pleistocene glacial cycles as well as the major intensification of Northern Hemisphere glaciation 2.7 million years ago. Moreover, we are also beginning work to understand the evolution of climate and atmospheric $CO_2$ over the entire 65 million years of the Cenozoic, including periods of much warmer conditions.

While our focus has so far been on the subarctic North Pacific and Southern Ocean, we are now beginning to apply the same isotopic tools (e.g. fossil-bound nitrogen isotopes) to sediment cores collected in the high-latitude North Atlantic. Moreover, we are also seeking to increase our spatial coverage of samples within individual polar regions. In particular, it will be critical to build a spatially complete paleoceanographic picture of the Southern Ocean, which has multiple zones that appear to change in complementary ways. To study the sedimentary history close to Antarctica, we are taking advantage of our close collaboration with the Alfred Wegener Institute (AWI) in Bremerhaven, which has the best cores from the region.

## *GERALD H. HAUG*

*SELECTED CAREER ACHIEVEMENTS*

*Haug, G. H., Ganopolski, A., Sigman, D. M., Rosell-Mele, A., Swann, G. E. A., Tiedemann, R., Jaccard S. L., Bollmann, J., Maslin, M. A., Leng, M. J., Eglinton, G.: North Pacific seasonality and the glaciation of North America 2.7 million years ago. Nature 433, 821-825 (2005).*

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*Haug, G. H., Tiedemann, R.: Effect of the formation of the Isthmus of Panama on Atlantic Ocean thermohaline circulation. Nature 393, 673-676 (1998).*

**14 APRIL 1968** Born in Karlsruhe, Germany

**1992** Diploma in Geology at the University of Karlsruhe

**1995** PhD in Geosciences at the University of Kiel

**1995–1996** Postdoctoral Research Associate at GEOMAR, Center for Marine Geosciences, Kiel, Germany

**1996–1997** Postdoctoral Research Associate in the Department of Oceanography at the University of British Columbia (UBC) in Vancouver, Canada

**1997–1998** Postdoctoral Guest Investigator at the Woods Hole Oceanographic Institution in Massachusetts, USA

**1998–2000** Research Assistant Professor at the University of Southern California in Los Angeles, USA

**2000–2002** 'Oberassistent' at the ETH Zürich, Switzerland

**2002** Habilitation in Earth Sciences at the ETH Zürich

**2003–2007** Professor at the German Research Centre for Geosciences (GFZ) in Potsdam and the University of Potsdam, Germany

**SINCE 2007** Ordinary Professor for 'Climate Geology' at the ETH Zürich

**SINCE 2015** Director at the Max Planck Institute for Chemistry and scientific member of the Max Planck Society

# *SEASONAL INVESTIGATIONS OF PALEOCEANOGRAPHIC OCEAN PROXIES WITH THE RV EUGEN SEIBOLD*

**GERALD H. HAUG**

**“Seasonality matters.”**

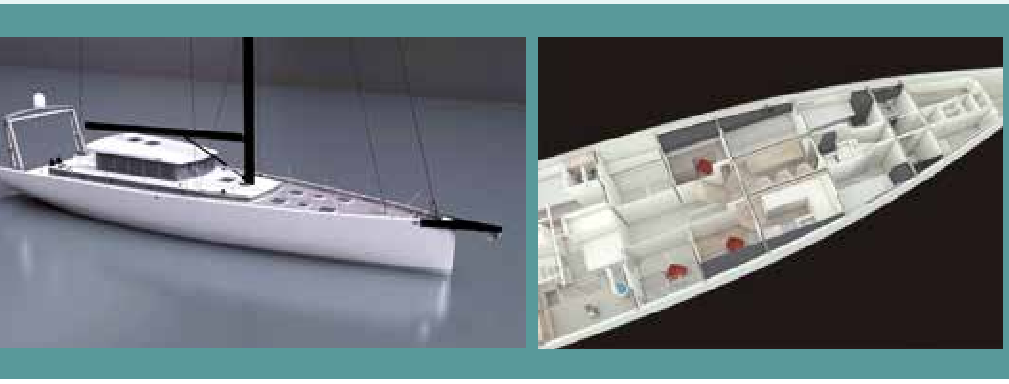

*Figure 1: Drawings of the custom designed 75′ research vessel RV Eugen Seibold. About half of the ship contains clean laboratories and work space. The cockpit can be fully closed. The boat will be simple and extremely durable, with a foremost focus on seaworthiness and safety under all conditions of extensive sampling campaigns. A high-end McArtney winch with a Dyneema rope will allow us to sample the ocean down to 2500 m water depth. The ship will sail in April 2018.*

The Werner Siemens-Foundation donated a relatively small and affordable (length: 22 m) but technologically advanced and seaworthy sail-powered vessel (*RV Eugen Seibold*) as an oceanographic sampling platform to the Max Planck Institute for Chemistry. Such a vessel represents an obvious and yet underexplored complement to the large diesel-powered research vessels. Given its design, it can travel safely across vast expanses of the global ocean, and provides an excellent platform for making measurements in, and collecting samples from, the upper ~500 m of the ocean water column (as deep as 2500 m). This vessel has great potential for facilitating studies of seasonally varying processes of the upper ocean. After the diurnal cycle, seasonality, both on land and in the ocean, can be thought of as the dominant driver of “climate” variability. For example, seasonal temperature changes dwarf all but the largest temperature changes known from Earth history. The role of seasonality is arguably even more fundamental for ocean biogeochemical cycles and the carbon cycle, as many organisms evolve to align their growth stages to the seasonal cycle. Yet, given the disconnect between the materials used for paleoceanographic proxy calibration (e.g., foraminifera and biomarkers from surface sediments) and the environmental measurements against which they are compared (most often mean annual averages based on a compilation of measurements from prior cruises), paleoproxy calibration very rarely considers seasonality to an appropriate degree. Our sampling on *RV Eugen Seibold* will permit direct comparison of paleoceanographic proxies to the organisms that produce them as they respond to in situ environmental conditions on a seasonal basis.

Most of the effort, intellectual energy, and financial resources devoted to paleoceanographic studies have gone into the application of diverse paleoceanographic proxies to deep-sea sediment cores, often yielding high-resolution reconstructions of past environmental change. As a participant in this process over two decades, I am convinced that there is an urgent need for a more thorough understanding of the geochemical and paleontological tools that we are applying. To a large degree, we have been limited by the availability of appropriate sample types acquired by ground-truthing efforts. However, when it comes to sampling and measuring the ocean, whether for the purpose of studying modern processes and conditions, or for seasonally resolved paleoproxy calibration, limited access to research vessels makes it difficult or impossible to collect data at the needed temporal and spatial scales. With regard to physical processes, the Argo float network has proven revolutionary, collecting spatially and temporally dense ocean temperature and salinity data globally, regardless of ocean conditions. The floats are progressively gaining new measurement capabilities, with new sensors being added. However, many environmental and biogeochemical parameters currently cannot be determined without direct ocean sampling of both water and particulate matter in the water, and these data are critical for understanding the links among physical, geochemical, and biological phenomena. More to the point, a research vessel is required to collect the physical samples (e.g., the foraminifera shells collected by net tows, phytoplankton collected by high volume pumping), in particular, that contain paleoceanographic proxies of temperature (from Mg/Ca in foraminifera to organic molecule based proxies such as $\mathrm{U}^{\mathrm{K}37'}$ and $\mathrm{TEX}_{86}$) and nutrients (e.g. nitrogen isotopes in foraminifera and diatoms). This will be the case for the foreseeable future.

Two broad approaches exist for sampling the open ocean, discrete sampling and continuous underway measurement, and *RV Eugen Seibold* is well suited to both. In particular, we propose to vastly improve reconstructions of climate and environmental change through time by studying important paleoceanographic proxies in the modern ocean, at seasonal resolution in a range of open ocean environments. Through monthly cruises over the course of approximately one year, each in four North Atlantic regions, upper ocean samples containing the proxy-carrying materials will be collected, analyzed, and compared to high-density, climate-, carbon-, and biogeochemistry-related observations from the same cruises. Discrepancies in reconstructions of past ocean temperatures and other environmental conditions using different proxies suggest that the proxies are sensitive to season and/or ocean depth when and where the proxy was produced. If those different sensitivities can be understood, the proxies will provide a more robust and more detailed view of the ocean in the past than has been achieved to date, leading to a new era in paleoceanographic discovery.

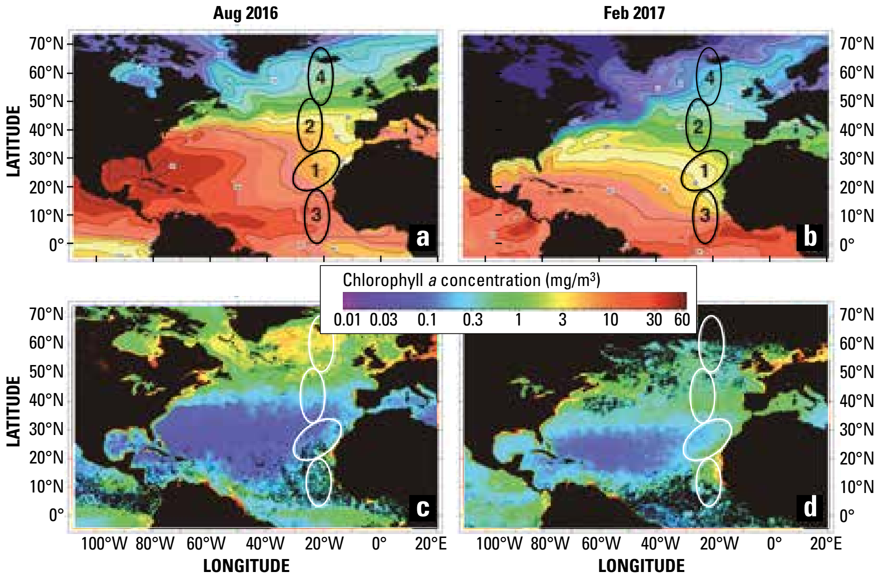

*Figure 2: Planned sampling regions from project years 1 to 4 (black/white ellipses, with number indicating year), overlain on North Atlantic sea surface temperature (a, b) and chlorophyll a (Chl-a) concentration (c, d) in August 2016 and (b, d) February 2017. Monthly Chl-a concentration (mg m*$^{-3}$*) from oceancolor.gsfc.nasa.gov at 9 km resolution. The cruises are designed to capture a broad range of oceanic regimes in the North Atlantic: Polar, temperate to subtropical, tropical, coastal upwelling, and equatorial upwelling. The ship will stay for one full annual cycle at each of the regimes indicated. For logistical reasons, we will center our activities in year 1 around the Canary Islands, in year 2 around the Azores, in year 3 around the Cape Verde islands, and in year 4 as far north as possible around Iceland, depending on weather and avoiding sea ice. The ship will sample continuously over the two to three week cruises between port calls.*

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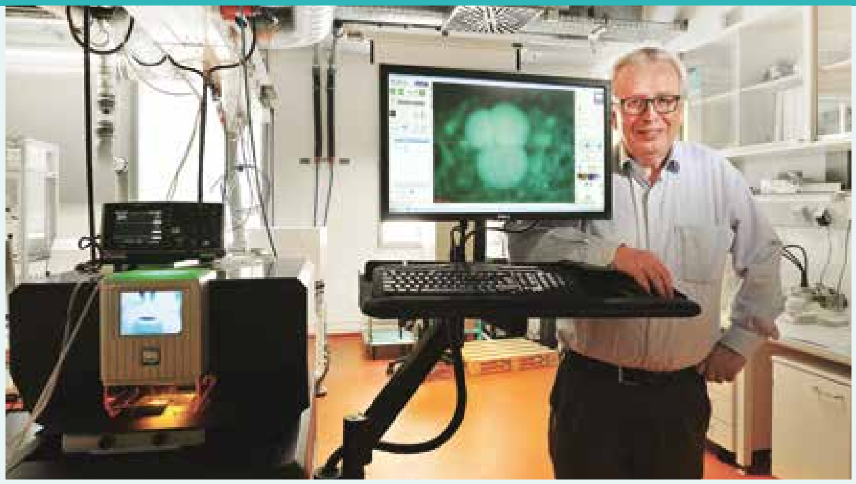
# *HIGHLY RESOLVED Mg/Ca DEPTH PROFILES OF FORAMINIFERS TO UNRAVEL THE CLIMATE OF THE PAST*

**KLAUS PETER JOCHUM**



> **“Femtosecond LA-ICP-MS measurements help to quantify previously hidden climate signals in paleoclimate archives.”**

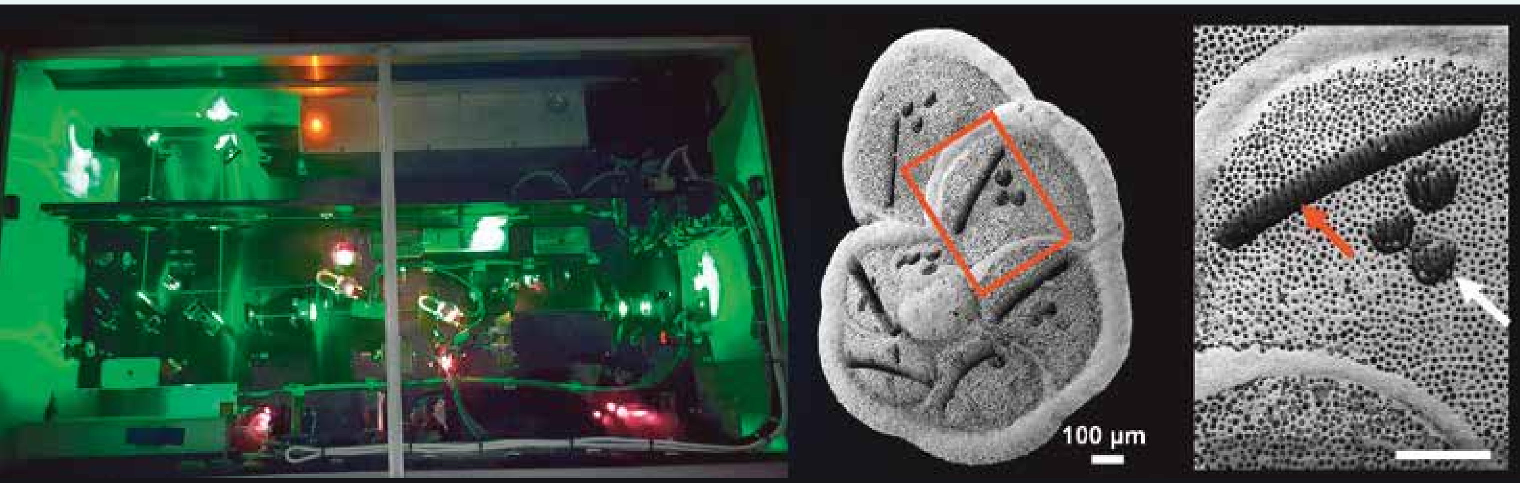


*Figure 1: Photograph of a femtosecond laser that is used for inductively coupled plasma (ICP) mass spectrometric measurements of Mg/Ca, Sr/Ca ratios, and trace element abundances in foraminifers with high spatial and depth resolution either by spot (white arrow) or line (red arrow) analysis.*

The paleoclimate research group uses glass sponges, ostracods, otoliths, corals, and foraminifers, cave deposits, and desert varnish to investigate past climates. Such studies are conducted in collaboration with several groups at the Max Planck Institute for Chemistry and other Max Planck Institutes, and with scientists at the Johannes Gutenberg University Mainz, as well as at other universities and research institutions in Germany and abroad.

Here, we highlight a promising new project that takes advantage of our facilities and expertise in spatially resolved geochemical measurements. Foraminifers are microorganisms whose calcium carbonate shells are sensitive recorders of climate and the marine environment. Of particular interest is the Mg/Ca signal, which can be used as a proxy for seawater temperature at the time the shell was formed. In contrast to most former studies that average the signal from many foraminifers, we investigate the variation of this elemental ratio in single specimens. We developed a microanalytical technique using femtosecond – laser ablation – inductively coupled plasma – mass spectrometry (fs-LA-ICP-MS) to enable precise and accurate analysis of the micrometer-scale layered calcite shell of foraminifers. This research is conducted in collaboration with the micropaleontology group at MPIC.

One of the great advantages of fs-LA-ICP-MS is that the measurements are nearly matrix-independent. To get highly resolved depth profiles through the shell, we chose low fluences of approximately 0.3 J cm$^{-2}$ and performed single-shot measurements using a pulse repetition rate of 1 Hz. These measurements yielded precise Mg/Ca ratios (ca. 5 %) by measuring $^{44}\text{Ca}^{++}$ and $^{25}\text{Mg}^{+}$ ions simultaneously. By analyzing consecutive laser pulses from the same ablation site (Figure 1), depth profiles were generated with a resolution of about 50 nm per pulse (Figure 2a). To recover Mg/Ca variation, we integrated the whole background-subtracted pulses and calibrated them with the carbonate microanalytical reference material MACS3 from the United States Geological Survey. To evaluate accuracy, we also analyzed international reference materials; our data agree within uncertainty limits with certified and compiled values.

We analyzed Mg/Ca variation in a specimen of the planktic foraminifer *Globorotalia menardii* from a sediment core collected in the Arabian Sea. We investigated seven chambers of different wall thicknesses, observing significant Mg/Ca differences among the chambers (Figure 2b). Published calibration curves were used to determine seawater temperature. The oldest chambers F-3 to F-6 (three to six chambers before the final chamber F) have a Mg/Ca of about 2 mmol mol$^{-1}$, consistent with a seawater temperature of about 18°C. In contrast, the Mg/Ca of the youngest chambers F and F-1 is much higher (about 5 mmol mol$^{-1}$), yielding a surface temperature of 28°C. These results indicate that the foraminifer individual (1) had built its shell when ascending from the sub-thermocline depth of ~150 m to the sea surface, (2) experienced a temporal change in seawater temperature caused by upwelling (cold) versus stratified (warm) conditions, or (3) both.

Femtosecond-LA-ICP-MS is also well suited for precisely determining Sr/Ca ratios with the same depth resolution as Mg/Ca by measuring $^{87}\text{Sr}^{++}$ and $^{43}\text{Ca}^{+}$ ions. These investigations, in combination with Mg/Ca measurements of whole specimens, are of special interest because they can be used to test whether the Sr/Ca ratio is temperature sensitive. Femtosecond-LA-ICP-MS can be used to determine the concentrations of many other elements as well, for example, B, Mn, Fe, Ba, and U using fast line scans (40 µm s$^{-1}$) and repeated analyses in the same line (Figure 1). Such analyses may provide further insights into the behavior and ecology of foraminifers, helping to provide an understanding of so far unexplained “vital effects”.

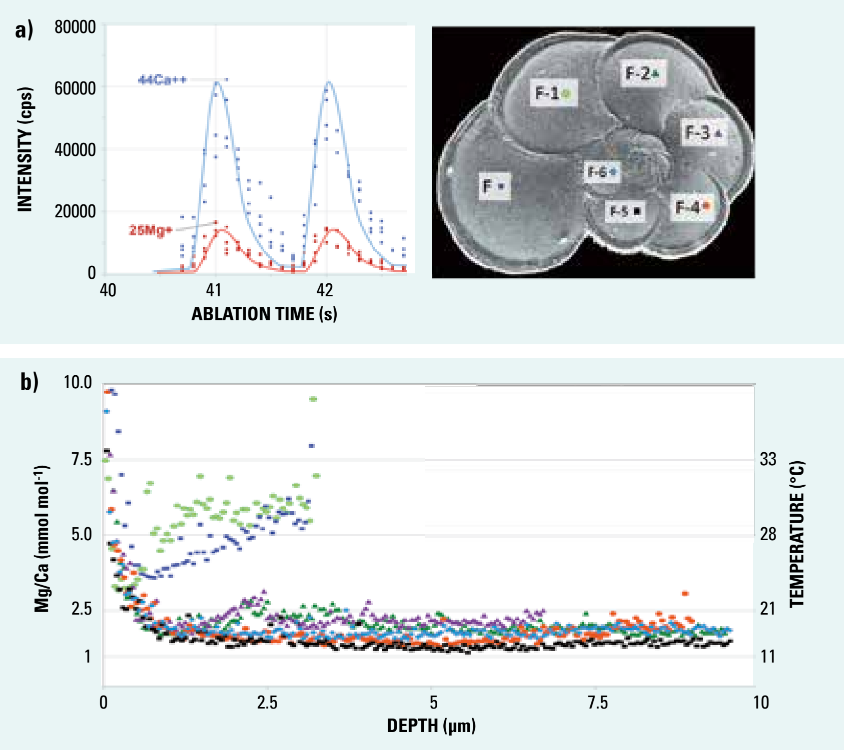


*Figure 2: Femtosecond (fs) LA-ICP-MS measurements of Globorotalia menardii from the Arabian Sea; (a) Time-resolved 44Ca$^{++}$ and 25Mg$^{+}$ signals of single laser shots; (b) Mg/Ca ratios differ significantly for the seven chambers.*

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# *MICROFOSSIL PROXY CALIBRATION IN PALEOCEANOGRAPHY AND PALEOCLIMATE*

**RALF SCHIEBEL**

> **"Knowing the ecology of microfossil species is pivotal for proxy calibration and reconstructing climates of the past."**

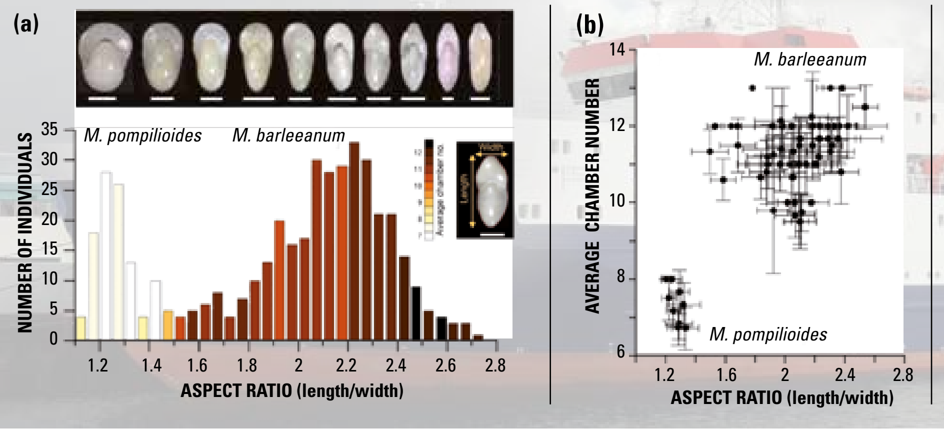

*Figure 1: (a) Aspect ratio (length/width; inset) of the Melonis specimens with two peaks centered around 2.2 (M. barleeanum) and 1.25 (M. pompilioides), respectively. The average chamber number ranges from 7 (white) to 13 (dark red) with varying aspect ratio. Top panel: Melonis morphotypes in frontal view with their aspect ratio roughly corresponding to the x-axis below. (b) Aspect ratios vs. chamber number. Scale bars are 200 µm. From Hasenfratz et al. (2017).*

Microfossils play a key role as proxy carriers in paleoceanography and climate reconstructions spanning the past 100 million years. Both benthic and planktic foraminifer shells provide sufficient amounts of calcite and organic matter for chemical and isotopic analyses (Mojtahid et al. 2015). Other microscopic organisms such as pteropods, ostracods, radiolarians, coccoliths, and diatoms provide additional information on past marine and aquatic environments (Satler et al. 2014; Rembeauville et al. 2016). Due to differential environmental prerequisites and preservation potentials, various calcareous and siliceous animal and plant remains are employed in a complementary approach to reconstruct, for example, temperature changes in the polar oceans and past oxygenation states of Eifel maars from laminated sediments.

Foraminifers and other fossil-generating organisms integrate environmental signals over varying time intervals and regional scales. In addition, biologic prerequisites and ecological demands vary between species and ontogenetic stages of the same species. We calibrate paleoproxies such as stable isotope ratios (e.g., $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$), and element ratios (e.g., Mg/Ca) at the species level and ontogenetic stage at the diurnal to seasonal scale.

As a next major step in this effort, the new research vessel *RV Eugen Seibold* will collect paleo-proxy samples and corresponding data on environmental conditions at the same times, sites, and depths. Plankton will be sampled at high temporal and spatial resolution using horizontal plankton nets. A new light (titanium frame) multinet has been developed in collaboration with the company HYDROBIOS (Kiel, Germany) to facilitate stratified sampling by *RV Seibold* and similar small vessels. Large sample volumes will facilitate analyses of the proxies that have very low concentrations in foraminifer shells, such as cadmium and nitrogen isotopes ($\delta^{15}N$), leading to an improved understanding of plankton ecology. The new data will also improve proxy calibration, making reconstructions of past ocean and climate change more accurate. The new textbook by Schiebel and Hemleben (2017) reviews the current state of knowledge of modern planktic foraminifers. The next major advances in this field may be achieved by the upcoming campaigns with *RV Seibold*. To complement the work aboard *RV Seibold*, we outfitted a new six-meter laboratory container for sampling at sea onboard other research vessels and ships of opportunity. With the new infrastructure and our long-lasting local, national, and international commitments, we are set up to take a leap forward in science.

In fall 2016, in collaboration with the international paleoceanography community, we organized and led expedition 58 of *RV Maria S. Merian* to the North Atlantic, which collected sediment cores, plankton, and water samples. Analysis of these materials are used to improve understanding of the Atlantic Meridional Overturning Circulation (AMOC) and its effect on climate.

In the lab, we are applying technologies such as femtosecond-laser ablation-inductively coupled plasma-mass spectrometry (K. P. Jochum, MPIC) and NanoSIMS (secondary ion mass spectrometry; P. Hoppe, MPIC) to analyze single chambers and individual calcite layers. These data provide high-resolution information on the physical and chemical properties of the past ocean. We are also conducting wet-chemical analyses of entire foraminifer shells for comparison with the high-resolution data generated by the mass spectrometers (Isotope Biogeochemistry, S. Galer, MPIC). In addition, using a new automated image analysis system, Mg/Ca in benthic foraminifers (*Melonis*) is being reevaluated at the species level (e.g., *M. barleeanum* and *M. pompilioides*) in an inter-calibration study (Hasenfratz et al. 2017; Figures 1 and 2).

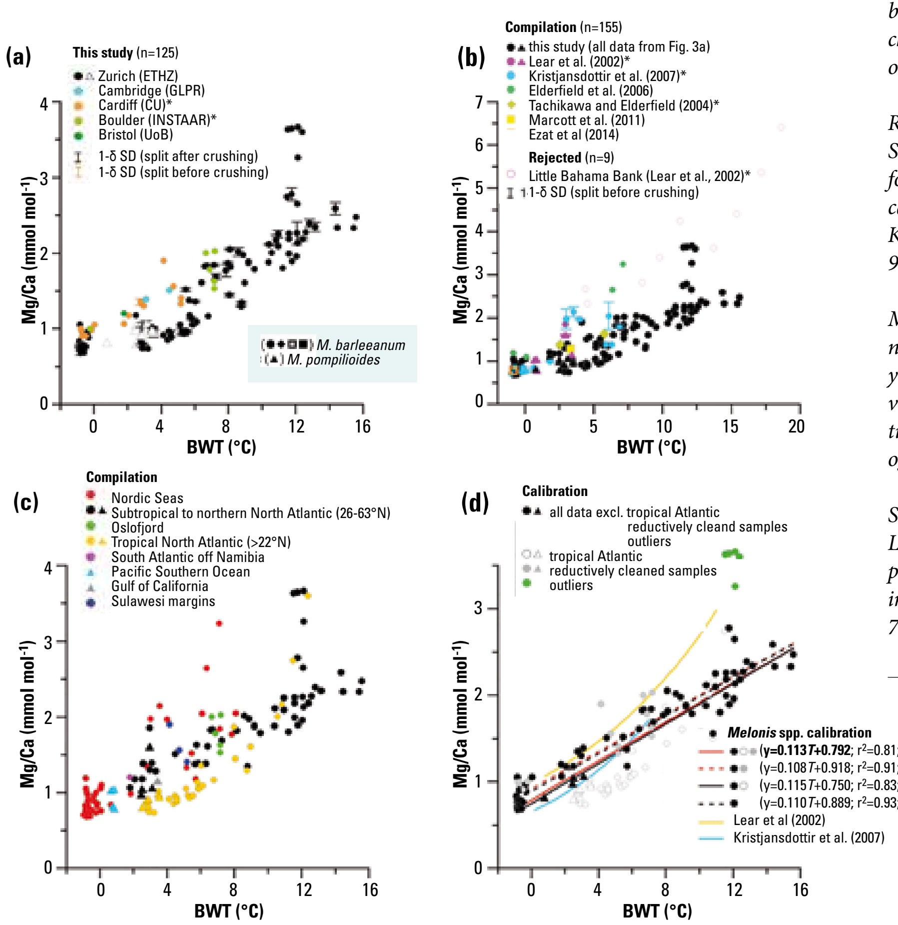

*Figure 2: Relationship between bottom water temperature (BWT) and Mg/Ca of Melonis. Reductively cleaned samples are corrected by factor 1.1. (a) Mg/Ca analyses from this study. (b) Compilation of new and published Melonis Mg/Ca. (c) Mg/Ca data sorted by region. (d) Differentiating between Mg/Ca data from the tropical Atlantic and other regions. Note different cleaning methods. Calibration curves only include new data new presented in this study. Excluded are data both form the tropical Atlantic (dashed red line) and reductively cleaned samples (solid black line). Calibration curves from literature are shown in yellow and blue. From Hasenfratz et al. (2017).*

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# *IMPORTANCE OF DUST FOR BIOGEOCHEMICAL CYCLES AND PALEOCLIMATE*

**STEPHEN GALER**

> **"Dust has a pivotal role in the whole Earth System so we must find out where and how emission takes place – identifying sources is best done using radiogenic isotope tracers."**

*Figure 1: Dust outbreak entering the eastern tropical Atlantic Ocean over the Canary and Cape Verde Islands (right), the Amazon rainforest (middle), a phytoplankton bloom off the Argentinian coast (left) - cause and effect? Picture credits: NASA; Shao, CC BY-SA 3.0.*

Our focus is on understanding present and past biogeochemical cycling of trace metals from sources to sinks using radiogenic isotopes and novel metal stable isotope systems.

Atmospheric dust plays both a positive and a negative role in the Earth System. On the negative side, human health is seriously impacted by dust, while pesticides and pathogens can hitch a ride on mineral dust across the Atlantic Ocean to the Caribbean, stressing coral reefs there. Positively, though, dust provides vital nutrients, such as iron, to parts of the ocean and rainforests impoverished in micronutrients to increase marine biological productivity and land fertility; both of these result in the potential draw-down of atmospheric $CO_2$.

The Southern Ocean is a key region rich in major nutrients but low in biological productivity due to micronutrient limitation. Here, dust blown in from South America provides the iron, zinc and other elements needed for phytoplankton – photosynthetic algae at the bottom of the food chain – to grow. Transferring organic matter to the deep ocean in this way lowers atmospheric $CO_2$ concentrations, cooling the Earth. Since we know that atmospheric dust loads in glacial times were around three times higher than today, dust inputs to key regions, such as the Southern Ocean, exert a strong positive feedback on climate, and may be a driving force for ice ages – a hypothesis championed by the late John Martin.

But, it is important to stress that while we know that atmospheric dust loads have changed dramatically over the last million years, whether the dust-emitting regions changed as well is largely unknown. Similarly, dust emission is often localized under specific meteorological conditions which are poorly understood. This means we need to be able to identify and distinguish small, localized dust sources.

We have been characterizing individual mineral dust sources, in order to track the inputs from dust emitting source to outputs, as archived in the sedimentary record. The tool that we are using is the radiogenic isotope compositions of lead, strontium and neodymium of the dust, which are elements primarily residing in the fine-grained clay fraction. The isotopic compositions of these elements are affected by long-lived radioactive decay, and vary according to the age of the continental crust from which the dust is ultimately derived. Thus, we can use this information as an isotope fingerprint of the provenance of the dust.

We have isotopically fingerprinted the principal regions emitting dust from Northern Africa, which are mainly in Northern Mali/Southern Algeria and in the Bodélé Depression in Chad, which has been dubbed the "dustiest place on Earth." This has been done by analyzing soil samples from North Africa, as well as aerosols collected at the Cape Verde Islands (Figure 2) and determining the origin of the dust using back-trajectory analysis and satellite imagery.

A particular feature seen in Figure 2 is a major isotopic spike on 9th February 2012, marking the onset of a large dust outbreak, starting in Northern Mali and migrating progressively to Western Mauritania.

Using radiogenic isotopes, we have also been looking at paleo-records of dust from sedimentary cores. One core off Western Africa shows that dust emission sources did change over time: during so-called African Humid Periods, the African monsoon penetrated much further north and many dust-emitting regions today – dry lake beds – were under water. Similarly, we can show that dust emission from South America to the all-important Southern Ocean switched in glacial periods to sources further south in Patagonia, consistent with paleo-environment modelling.

We are in exciting times in which we can use radiogenic isotope information to trace how localized dust sources changed in the past, in response to variations in aridity and wind patterns over time. Further, we can evaluate the role mineral dust has on the ocean biological pump and global climate feedbacks in the Earth System.

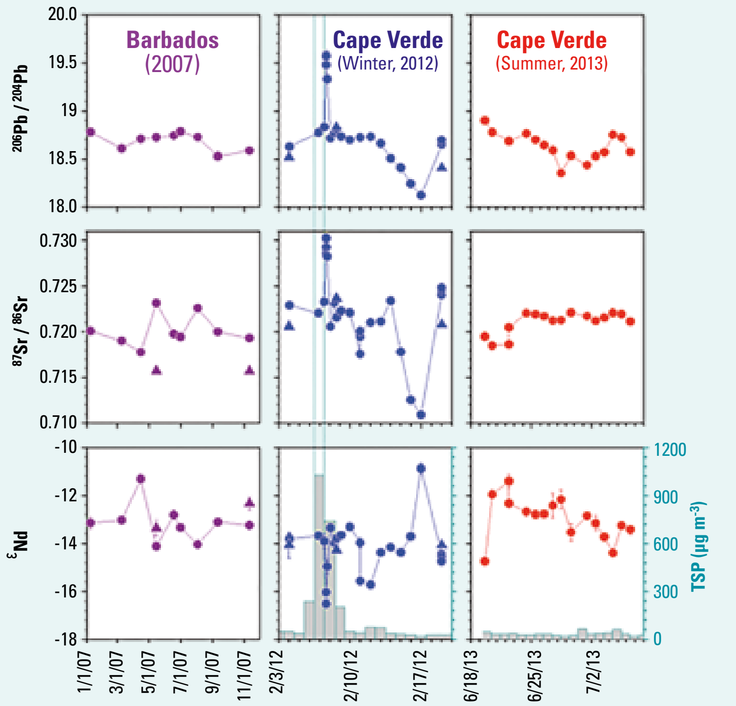

*Figure 2: Time series of radiogenic isotopes and dust concentration (TSP in μg $m^{-3}$) in the winter and summer months in 2012 -13 at the Cape Verde Islands and during 2007 at Barbados. This provides primary evidence that transatlantic dust transport does indeed take place as far as the Caribbean, and that the emitting sources are located in Northern Mali and not the Bodélé Depression in Chad.*

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# *THE ROLE OF THE SOUTHERN OCEAN IN GLACIAL-INTERGLACIAL CHANGES IN ATMOSPHERIC $CO_2$ CONCENTRATIONS*

**ALFREDO MARTINEZ-GARCIA**

**“Geochemical measurements can provide key insights on the mechanisms controlling atmospheric $CO_2$ changes over millions of years.”**

*Figure 1: Southern Ocean Icebergs. Credits: Alfredo Martinez-Garcia.*

The analysis of air bubbles trapped in Antarctic ice has revealed that atmospheric carbon dioxide concentrations have varied in step with atmospheric temperatures and sea level over the glacial/interglacial (G/IG) cycles of the last 800,000 years. In the context of the current anthropogenic increase in atmospheric $CO_2$ levels, understanding the causes of the G/IG atmospheric $CO_2$ cycles has emerged as a priority in Earth science research.

One important focus of the Organic Isotope Geochemistry research group has been the study of a series of biogeochemical processes occurring in the Southern Ocean and their role in driving atmospheric $CO_2$ changes through time. Despite the high concentration of the major nutrients nitrate and phosphate in the modern Southern Ocean, the scarcity of iron limits marine phytoplankton growth. This represents an important inefficiency in the modern global biological carbon pump because it represents a missed opportunity for marine organisms to grow and fix atmospheric $CO_2$. Hence, an increase in the efficiency of carbon sequestration in the ocean can be accomplished either by decreasing the physical cycling of $CO_2$-rich deep water through the surface of the Southern Ocean or by increasing the degree to which surface nutrients are consumed by marine organisms, for example, by increasing the supply of the limiting micronutrient iron. In 1990, John Martin suggested that during glacial times, an increase in the supply of iron-rich dust could have fertilized the Southern Ocean, stimulating marine phytoplankton productivity, increasing the rain of organic carbon into the deep ocean, and thus contributing to the reduction in atmospheric $CO_2$. However, testing the impact of iron supply on the efficiency of biological sequestration of carbon during ice ages remained elusive.

We have used a combination of novel geochemical techniques to test the iron hypothesis. In particular, we have pioneered (together with our colleague Daniel M. Sigman from Princeton University) the use of nitrogen isotope analysis of the organic matter bound within the calcite structure of planktonic foraminifera to study changes in the degree of nutrient consumption in the Southern Ocean. Combining this new technique with other geochemical measurements, we have shown that in the Subantarctic Atlantic, peak glacial times and millennial cold events are characterized by increases in dust/iron flux, phytoplankton productivity, and the degree of nitrate consumption. This combination is uniquely consistent with Subantarctic iron fertilization and represents strong support for the iron hypothesis (Martinez-Garcia et al., 2014). Our data suggest that the associated strengthening of the Southern Ocean's biological carbon pump can explain the lowering of around 40 ppm of $CO_2$ at the transition from mid-climate states to full ice age conditions as well as the millennial-scale $CO_2$ oscillations (Martinez-Garcia et al., 2014). More recent measurements of dust/productivity flux proxies and foraminifera-bound nitrogen isotopes from the Subantarctic Pacific suggest that ice age iron fertilization was not limited to the Subantarctic Atlantic (Lamy et al., 2014; Martinez-Garcia et al., unpublished). In addition, the analysis of the nitrogen isotopic composition of deep-sea corals has provided strong independent support for these findings, suggesting more efficient nutrient consumption in additional regions of the Subantarctic zone during the last ice age (Wang et al., 2017).

In addition, we have studied sediment cores and corals located further south, in the Antarctic zone of the Southern Ocean. These samples indicate that nutrient consumption also increased in areas where productivity decreased during ice ages (Studer et al. 2015; Wang et al 2017). These observations suggest that during glacial times, the physical cycling of $CO_2$-rich deep waters through the Antarctic zone decreased dramatically, and represent another mechanism for increasing the efficiency of carbon sequestration. Consistent with these findings, the analysis of redox-sensitive trace metals suggests a decrease in deep-ocean oxygenation during ice ages and millennial cold events (Jaccard et al., 2016), as well as during periods of pronounced $CO_2$ decrease during the penultimate interglacial (Hayes et al., 2014), providing independent evidence for enhanced deep ocean carbon sequestration during those periods. Thus, the datasets generated during the past years indicate that the combination of enhanced organic carbon export by iron fertilization and decreased deep ocean ventilation in the Southern Ocean can explain most of the G-IG atmospheric $CO_2$ change observed during ice ages.

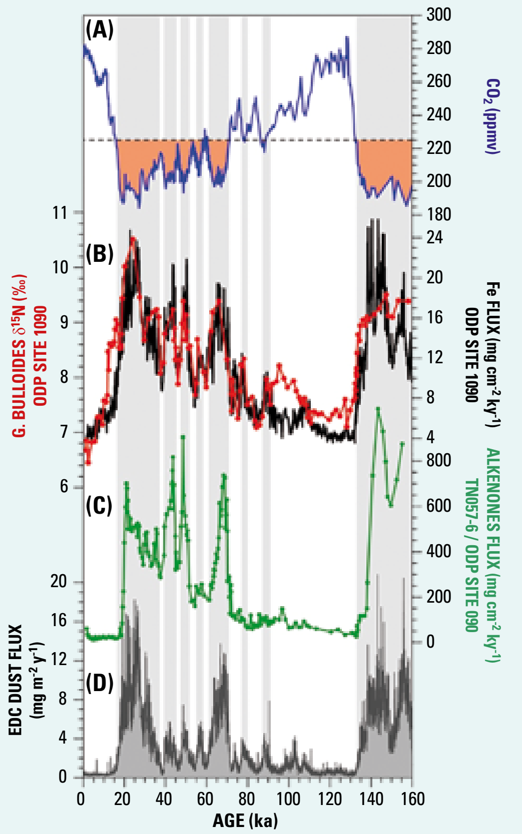

*Figure 2: Example of findings resulting from combining foraminifera-bound N isotopes, biomarkers, and high resolution XRF elemental scanning, used to test the “iron hypothesis” (Martinez-Garcia et al., 2014). The red symbols show foraminifera-bound $\delta^{15}N$ measurements, which indicate the degree of nitrate consumption. The black line shows dust-derived iron flux. The green line shows the flux of alkenones, and indicator of marine productivity. The blue and gray lines show the evolution of atmospheric $CO_2$ levels and dust deposition reconstructed from Antarctic ice cores. Contingent on our current interpretation, these coupled changes can only be explained by iron fertilization of Southern Ocean phytoplankton during the ice ages.*

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*Wang, X. T., Sigman, D. M., Prokopenko, M. G., Adkins, J. F., Robinson, L. F., Hines, S. K., Chai, J., Studer, A. S., Martinez-Garcia, A., Chen, T., Haug, G. H.: Deep-sea coral evidence for lower Southern Ocean surface nitrate concentrations during the last ice age. PNAS, Vol. 114, 13, 3352-3357 (2017).*

# THE ENVIRONMENTAL ISOTOPE SIGNAL CAPTURED IN (SKELETAL) CARBONATES

**HUBERT VONHOF**

“Focus of our group is the application of stable isotope techniques to better understand climate-driven environmental changes.”

*Figure 1: Impressions from the East African Rift System: Turkana Basin (left) and the adjacent Suguta Basin (middle and right).*

## INTRODUCTION

Our group investigates carbonate fossils and rock with the objective to reconstruct paleo-environmental conditions, both in the marine realm and on land. Our main tool in these investigations is stable isotope geochemistry.

The group started in February 2016, with our initial efforts focused on setting up the laboratories at MPIC to support our projects. We acquired state-of-the-art stable isotope instrumentation for the analysis of water- and carbonate-based stable isotope ratios. We developed analytical protocols for the analysis of very small single-specimen planktic foraminifers (in collaboration with the group of Ralf Schiebel) and for the isotope analysis of microscopic quantities of water in the fluid inclusions of speleothems and biogenic carbonates. With this instrumentation, we are pursuing the following projects.

## TRACING PALEO-FLUIDS THROUGH FLUID INCLUSION ISOTOPE ANALYSIS

Previous work in my group has shown the potential of isotope analysis of water in the fluid inclusions of stalagmites to reconstruct isotopic changes in rainfall. Such information gives direct hydroclimate information and can also be valuable for testing isotope-enabled climate model results. Using this approach, we recently began a project that uses stalagmites collected from several caves in Brazilian Amazonia to reconstruct at high stratigraphic precision the changing isotopic composition of rainfall over the Amazon Basin from the Last Glacial Maximum to the present. We also recently began a collaborative project on several well-known Chinese speleothem records.

A related study around this theme focuses on the isotopic composition of water captured in deep-sea coral skeletal aragonite. Deep-sea corals are important paleoceanographic archives, but their skeletal carbonate isotopic composition is notoriously difficult to relate to environmental conditions. Our isotopic measurements of the water trapped in the corals indicate a significant contribution of metabolic water to the organism's internal water pool. In ongoing work, we seek to relate the data to the different calcification models that have been proposed for deep-sea coral species.

## CLIMATE-DRIVEN FAUNAL DYNAMICS ON THE INDONESIAN ARCHIPELAGO

A further field of interest is the application of isotope techniques to bone and tooth enamel to better understand climate-driven changes in the diet and behavior of fossil mammalian faunas of the Indonesian archipelago. This biodiversity hotspot undergoes dramatic environmental change over glacial-interglacial transitions. During the glacials, significantly drier conditions affect the vegetation composition in the area. In recent work, we were able to document, through analysis of tooth enamel carbon and oxygen isotope ratios, that the herbivores react to such changes by switching from grazing in glacials to browsing in interglacials. In collaboration with the group of Steve Galer, we are currently exploring additional isotope systems to get a better picture of changing diet and mobility of Indonesian fossil faunas over glacial-interglacial transitions. The crown jewels of this project are samples of bone material of some of the most iconic hominin specimens found in the area more than a century ago by Eugene Dubois.

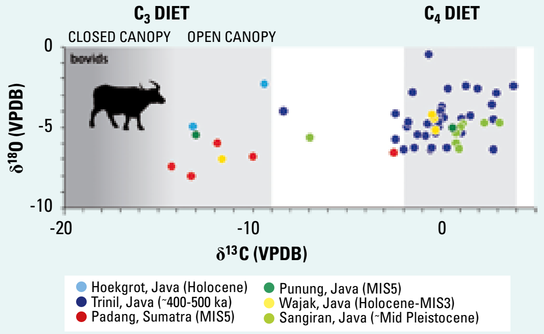

*Figure 2: Carbon and Oxygen isotope ratios of tooth enamel structural carbonate of fossil bovids (cows) from the Indonesian archipelago (Janssen et al., 2016, Quaternary Science Reviews). The carbon isotope data show that the bovids span the entire range from a grazing life style (C$_4$ diet) to browsing (C$_3$ diet). Generally the specimens that lived in interglacials plot in the C$_3$ range, while those plotting in the C$_4$ range are thought to have lived in glacial conditions. We believe that this pattern reflects the dramatic changeover in vegetation in Sundaland on Glacial-Interglacial time scales.*

## HYDROCLIMATE OF THE EAST AFRICAN RIFT SYSTEM

Building on collaborations within the Hominin Sites and Paleolakes Drilling Project (HSPDP), we are investigating the changing Quaternary hydroclimate of the East African Rift System (EARS). In these projects, we are measuring the strontium isotope ratios of the skeletal carbonate of fossil lake fauna to reconstruct changing run-off patterns to the lake. The lacustrine Sr isotope system in the EARS lakes is remarkably suitable to reconstructing longer-term (orbitally forced) changes to regional run-off patterns because the system is chemically conservative and, therefore, inherently insensitive to sub-decadal climate “noise” in the long-term signal. We recently used this proxy system to demonstrate that the spatial rainfall patterns around the termination of the African Humid Period changed slowly and in pace with the insolation cycle, in contrast to the rapid drops in lake level that occurred in the EARS roughly five thousand years ago.

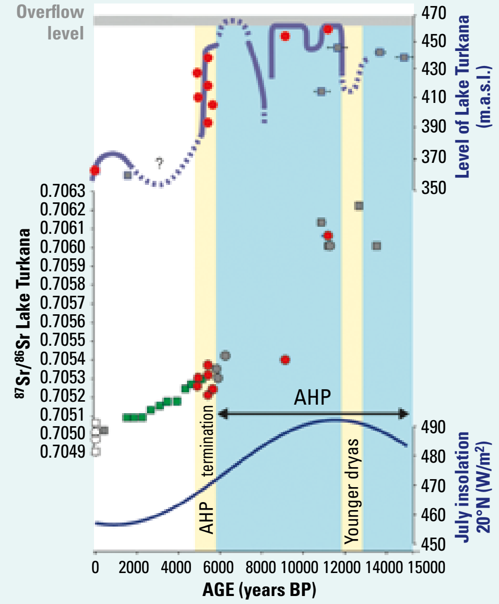

*Figure 3: Sr isotope evolution of Lake Turkana water over the past 15 thousand years, based on lacustrine fossils (center panel) compared to lake level reconstruction (Garcin et al., 2012, Earth and Planetary Science Letters) and solar insolation over the same time interval. The Sr isotope data are generally in-phase with insolation and do not show an abrupt change at the end of the African Humid Period (AHP). This suggests that rainfall patterns shifted slowly in the larger Turkana catchment, and that the rapid lake level drop was a threshold reaction of the hydrological system to slow insolation forcing. Figure adapted from van der Lubbe et al. (2017).*

Our work so far has focused on the Turkana Basin, an area that contains rich hominin fossil faunas. Our Sr isotope work enables the detection of Milankovitch cycles in the lacustrine sedimentary sequences and serves as an important tool for correlating hominin-bearing sedimentary sequences over long distances within the basin.

We are expanding our work in the region, targeting the lacustrine Sr isotope record of neighboring basins to search for hydrological connections to the Turkana Basin that are expected during the wet phases of the Quaternary.

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*Millo, C., Strikis, N. M., Vonhof, H. B., Deininger, M., da Cruz, F. W., Wang, X.,. Lawrence Edwards, R.: Last glacial and Holocene stable isotope record of fossil dripwater from subtropical Brazil based on analysis of fluid inclusions in stalagmites. Chemical Geology (2017).*

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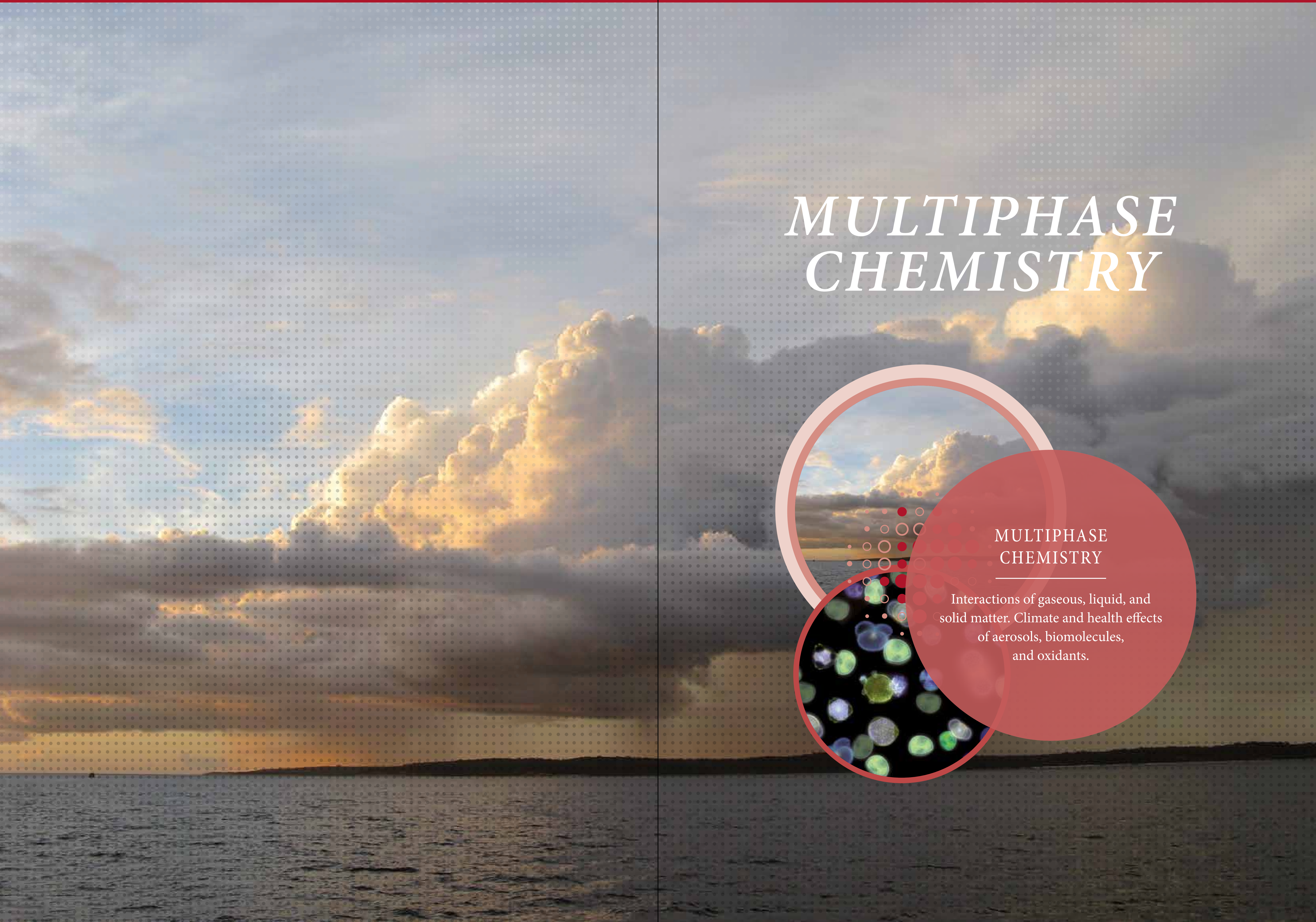
*van der Lubbe, H. J. L., Krause-Nehring, J., Junginger, A., Garcin, Y., Joordens, J. C. A., Davies, G. R.,. Vonhof, H. B.: Gradual or abrupt? Changes in water source of Lake Turkana (Kenya) during the African Humid Period inferred from Sr isotope ratios. Quaternary Science Reviews, 174, 1-12. d (2017).*



# MULTIPHASE CHEMISTRY

## MULTIPHASE CHEMISTRY

Interactions of gaseous, liquid, and solid matter. Climate and health effects of aerosols, biomolecules, and oxidants.

# *MULTIPHASE CHEMISTRY DEPARTMENT*

**Multiphase chemistry deals with reactions, transport, and transitions between different phases of matter such as gases, liquids, and solids. These processes are essential for the Earth system, climate, life, and public health. Prominent examples are the formation of clouds, rain, and snow or the respiration of humans, animals, and plants.**

From a chemical perspective, life and the metabolism of living organisms can be regarded as multiphase processes that transform and exchange gases such as oxygen, nitrogen, and carbon dioxide; liquids such as water, blood, and lymph; and solid or semi-solid substances such as bone, skin, and cellular membranes. The global biogeochemical cycling of chemical elements and compounds, which constitute the metabolism of planet Earth, also involves multiphase chemical reactions, mass transport, and phase transitions within and between the atmosphere, biosphere, hydrosphere, and pedosphere.

The overarching aim of the Multiphase Chemistry Department is to elucidate the role of multiphase processes that are essential in the interplay of air pollution, climate, and public health in the Anthropocene, that is, in the present era of globally pervasive human influence on Earth. Key issues are: (1) the sources and properties of natural and anthropogenic aerosols and their effects on clouds and precipitation; and (2) the chemical mechanisms, environmental causes, and therapeutic treatment of inflammatory and allergic reactions.

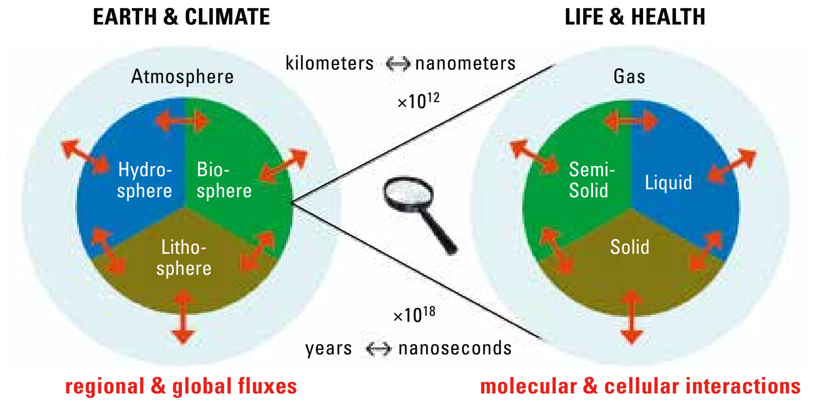


*Figure 1: Chemical reactions, mass transport and phase transitions of gases, liquids and solids influencing the Earth system, climate, life, and public health (adapted from Pöschl & Shiraiwa 2015).*

To explore and resolve these issues, we combine physical, chemical, and biomedical techniques in laboratory experiments, field measurements, and model studies at the interface of Earth and life science. We develop and apply advanced experimental and theoretical methods, including aerosol measurement techniques; chromatography, spectroscopy, and microscopy; bioassays and DNA analyses; kinetic process models; and regional to global atmospheric models.

The main areas of research in the Multiphase Chemistry Department are broadly reflected by the group structure as follows: Aerosol, Cloud, and Surface Interactions (*H. Su et al.*), Biomolecular Analyses and Interactions (*J. Fröhlich et al.*), Inflammatory Processes (*K. Lucas et al.*), Microbial Communities and Processes (*B. Weber et al.*), Organic Aerosols and Oxidants (*M. Shiraiwa et al., moved to UC Irvine in 2016*), Organic Pollutants and Exposure (*G. Lammel et al.*), and Multiscale Interactions and Integration (*U. Pöschl et al.*), with project teams on protein chemistry (*C. Kampf et al.*, moved to JGU Mainz in 2016), radical chemistry (*H. Tong et al.*), and cloud condensation nuclei (*M. Pöhlker et al.*). The Minerva group on Aerosols and Regional Air Quality (*Y. Cheng et al.*) is also closely associated with the department. Moreover, an additional research group on “Aerosol Analysis and Microscopy” (*C. Pöhlker et al.*) was taken up into the Multiphase Chemistry Department when the Biogeochemistry Department expired in 2017.

Common themes across the different research areas and groups include bioaerosols, proteins, and allergens; cloud condensation and ice nuclei; reactive oxygen and nitrogen species; chemical reactions in epithelial lining fluid; and the contrast between pristine rainforest and polluted megacity air.

The focal points and highlights of recent and ongoing research activities are detailed in the following group and project reports. They comprise insights into the biogenic sources of nitrous acid; the rapid formation of sulfate in aerosol water during severe haze events in China; the size dependence of nanoparticle phase transitions; the phase state and transformation of organic aerosols and pollutants; the ice nucleating ability of bioparticles and water-soluble macromolecules; the nitration and oligomerization of allergenic proteins; chemical exposure response relations between reactive oxygen species and ambient fine particulate matter; and the response of pattern recognition receptors and immunological signaling pathways to pro- and anti-inflammatory agents.

## *ULRICH PÖSCHL*

**9 OCTOBER 1969** Born in Klagenfurt, Austria

**1988–1995** Diploma and doctoral studies in chemistry at the Technical University of Graz

**1996–1997** Schrödinger fellow and postdoctoral researcher at the Massachusetts Institute of Technology

**1997–1998** Research scientist at the Max Planck Institute for Chemistry

**1999–2005** Research group leader and habilitation in chemistry at the Technical University of Munich

**2005–2012** Research group leader at the Max Planck Institute for Chemistry and lecturer at the University of Mainz

**SINCE 2012** Director at the Max Planck Institute for Chemistry, Scientific Member of the Max Planck Society, and professor at the Johannes Gutenberg University of Mainz

*SELECTED CAREER ACHIEVEMENTS*

*Pöschl, U., Shiraiwa, M.: Multiphase Chemistry at the Atmosphere–Biosphere Interface: Influencing Climate and Public Health in the Anthropocene, Chemical Reviews 115, 4440–4475 (2015).*

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*Pöschl, U.: Atmospheric aerosols: composition, transformation, climate and health effects, Angewandte Chemie International Edition, 44, 7520-7540 (2005).*

# *AEROSOL, CLOUD & SURFACE INTERACTIONS*

**HANG SU**

> **“We investigate the properties and interactions of aerosols and clouds, atmosphere-surface exchange processes, and their effects on the Earth system and climate.”**

*Figure 1: Aircraft measurements of CCN over the North China Plain.*

### FAST DETERMINATION OF CCN ACTIVITY

To understand and quantify aerosol-cloud interactions and their impact on climate, it is important to characterize the ability of atmospheric aerosol particles to serve as cloud condensation nuclei (CCN). The CCN activity of aerosol particles depends on the water vapor supersaturation to which they are exposed, and measurements at multiple supersaturation levels are usually time-consuming and limit the temporal resolution of laboratory experiments and field observations. We developed a new approach that exploits the supersaturation profile across the flow tube of a continuous-flow thermal-gradient CCN counter to simultaneously cover an entire range of supersaturation from zero up to a prescribed maximum value. The practical applicability of the new approach is demonstrated by taking CCN measurements of laboratory-generated and ambient aerosol particles. Due to its fast response and technical simplicity, the new approach may be well suited for aircraft and long-term measurements. Because CCN activity is closely related to the mass fraction of organic matter and inorganic salts in aerosol particles, CCN measurements based on the new approach can also serve as a complementary sensor for fast detection/estimation of aerosol chemical composition.

### SURFACE SOURCES OF HONO AT A REMOTE COASTAL SITE

Up to ~50% of the primary OH radical production in the lower troposphere is attributed to the photolysis of nitrous acid (HONO), and field observations suggest a large missing source of HONO. In earlier experimental and modeling studies, we showed that atmosphere-surface exchange of HONO may be the missing source. During the CYPHEX campaign in summer 2014, we investigated HONO concentrations and sources at a remote coastal site on the Mediterranean island of Cyprus. The observed average HONO volume mixing ratio was 35 pptv with a HONO/NOx ratio of 0.33, which is considerably higher than reported for most rural and urban regions. Budget analyses revealed large unidentified sources for both HONO and NO. Under humid conditions, the source strengths of HONO and NO exhibited a close linear correlation, suggesting a common source that can be attributed to emissions from microbial communities at the land surface and possibly also at the sea surface.

### FLUORESCENCE DETECTION & SPECTROSCOPY OF ATMOSPHERIC BIOAEROSOLS

Atmospheric bioaerosols including airborne bacteria, fungal spores, pollen and viruses etc., can affect human health and may influence the formation and evolution of clouds through their ice nucleating ability. Fluorescence-based methods are commonly used to detect bioaerosols. By using a commercial instrument (wideband integrated bioaerosol spectrometer, WIBS-4A) in polluted air of a Chinese megacity region, we found that the concentration of fluorescent aerosol particles (FAPs, 1–15 µm) in this environment was much higher than reported for forested and rural regions. The fraction of FAPs was positively correlated with the black carbon mass fraction, suggesting a substantial contribution of combustion-related particles to the fluorescent aerosols. To distinguish primary biological particles from other fluorescent aerosol particles, we developed a new spectrometer that simultaneously measures the aerodynamic size and fluorescence spectra of single particles. First results obtained with laboratory-generated aerosols show that the new instrument is able to measure characteristic spectra. Further studies performed in close collaboration with the Minerva group of Yafang Cheng provided new insights into the thermodynamic properties of nanoparticles and the influence of nitrogen chemistry in aerosol water on extreme haze pollution events in China.

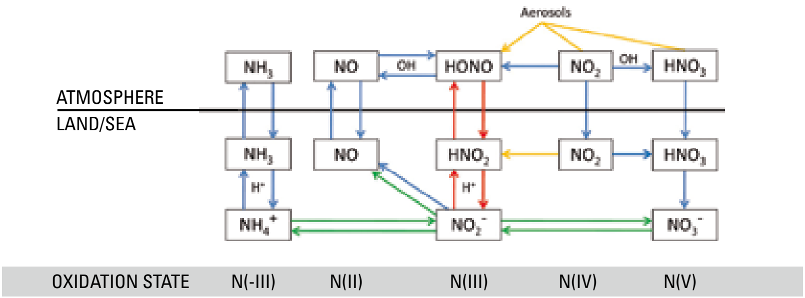

*Figure 2: Coupling of HONO and other reactive nitrogen species in the atmosphere with biogenic nitrite and related species at the land or sea surface. Red arrows represent the multiphase processes linking gaseous HONO and nitrite (acid-base reaction and phase partitioning); green arrows represent biological processes; orange arrows represent heterogeneous chemical reactions converting $NO_2$ and $HNO_3$ into HONO; blue arrows represent other related physico-chemical processes in the nitrogen cycle (adapted from Su et al. 2011).*

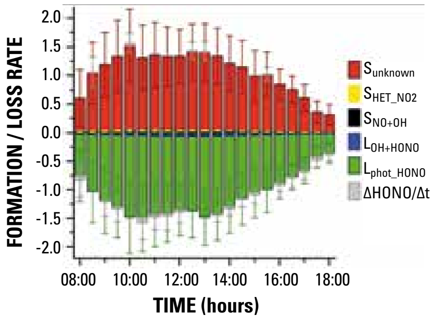

*Figure 3: HONO budget during the CYPHEX campaign. $S_{NO+OH}$ (black) stands for the formation rate of HONO via the reaction of NO and OH, $S_{Het\_NO_2}$ (yellow) is the formation rate for the heterogeneous reaction of $NO_2$, $L_{phot\_HONO}$ (green) and $L_{OH+HONO}$ (blue) are the loss rates via photolysis and the reaction with OH, and $S_{unknown}$ (red) is the unknown source. Error bars indicate standard deviation of diel mean (Meusel et al., 2016).*

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*Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Science Advances, 2, 10.1126/sciadv.1601530 (2016).*

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*Yu, X., Wang, Z., Zhang, M., Kuhn, U., Xie, Z., Cheng, Y., Pöschl, U., Su, H.: Ambient measurement of fluorescent aerosol particles with a WIBS in the Yangtze River Delta of China: potential impacts of combustion-related aerosol particles, Atmos. Chem. Phys., 16, 11337-11348 (2016).*

# *BIOMOLECULAR ANALYSES & INTERACTIONS*

**JANINE FRÖHLICH**

**"We aim to understand the interactions of biomolecules and biological aerosol particles with air pollutants, climate, and public health."**

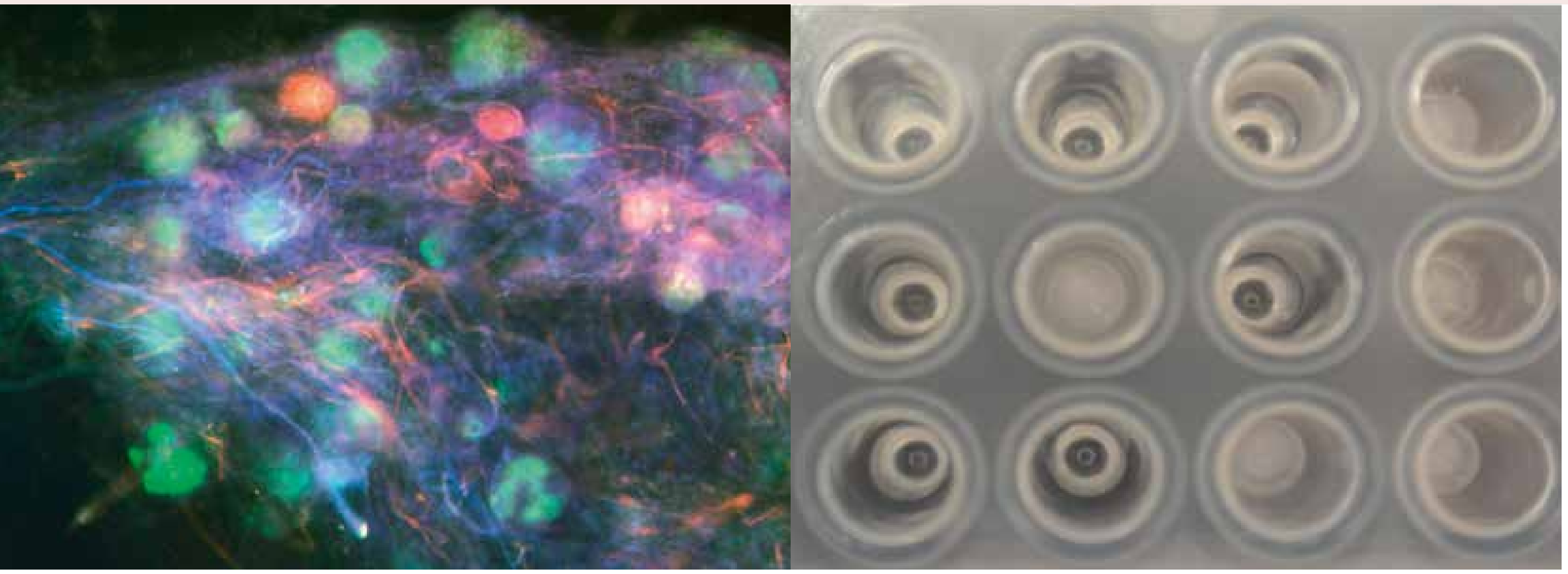

*Figure 1: Fluorescence microscopy image of spores and mycelium of the ice nucleation active soil fungus Mortierella alpina (left); frozen and unfrozen samples in droplet-freezing assay MINA (right).*

Biological aerosol particles and biomolecules play a vital role in the Earth system, particularly in the interactions between atmosphere, biosphere, climate, and public health. They are emitted directly from the biosphere into the atmosphere and comprise living and dead organisms, dispersal units, various fragments or excretions. Airborne bacteria, fungal spores, pollen, and other bioparticles are essential for the spread and reproduction of many organisms, and they can cause or enhance human, animal, and plant diseases. Moreover, they can serve as nuclei for ice crystals or cloud droplets, thus triggering the formation of clouds and precipitation and influencing the hydrological cycle and climate. However, the sources, abundance, composition, and effects of biological aerosols are not yet well characterized and constitute a large gap in the scientific understanding of the interaction and co-evolution of climate, life, and health in the Earth system.

A focus of our research is to understand the ability of biological particles to serve as ice nuclei (IN). We develop and apply multi-well plate droplet-freezing assays (Mono- and Twin-Plate Ice Nucleation Assay, MINA, TINA) to investigate the IN activity of biological samples in immersion freezing. We isolated and identified several species of soil and airborne fungi that were not previously known as IN-active. We found that the IN activity in these species is related to the presence of nanometer-sized ice-nucleating macromolecules (INM) such as proteins and polysaccharides. Cell-free INM may be more numerous and potentially more important for cloud glaciation than intact spores or hyphae. Associated with soil dust particles, these INM may impact cloud glaciation indirectly, also indicating a higher contribution and importance of biological, in particular fungal, IN than previously assumed.

In collaboration with the Max Planck Institute for Polymer Research we investigated the interaction of bacterial ice nuclei with water on the molecular level using interface-specific sum frequency generation (SFG) spectroscopy. We found that the ice-nucleating protein promotes the formation of ice by arranging water molecules into alternating stripes of higher and lower order molecules and by efficient removal of the latent heat of the phase transition from the nucleation site.

Another key topic is allergenic bioparticles and proteins. To identify and quantify allergenic species in air filter samples of fine and coarse particulate matter, we apply quantitative polymerase chain reaction (qPCR). For a five year sampling period, we found highly allergenic ragweed both during and outside the local pollination season that can be explained by long-range transport from southern Europe. We found higher concentrations in coarse particulate matter, but ragweed DNA was also detected in the fine particle fraction, suggesting the presence of small allergenic particle fragments that can reach the lower airways.

Pollen can also release allergenic proteins under humid conditions, and the proteins can interact with gaseous and particulate air pollutants, which may enhance the allergenic potential. To elucidate the abundance and transformation of airborne allergenic proteins, we analyze environmental samples and perform process studies and laboratory experiments under controlled conditions. In particular, we investigate the chemical reactions and physical interactions of the birch pollen allergen Bet v1 with traffic-related air pollutants (ozone, nitrogen oxides, soot, and related particulate matter). Currently, we are studying the chemical kinetics of Bet v1 nitration and oligomerization reactions, and we intend to explore if and how the co-location of allergens and adjuvants on the surface of inhalable ambient particles may promote allergic sensitization.

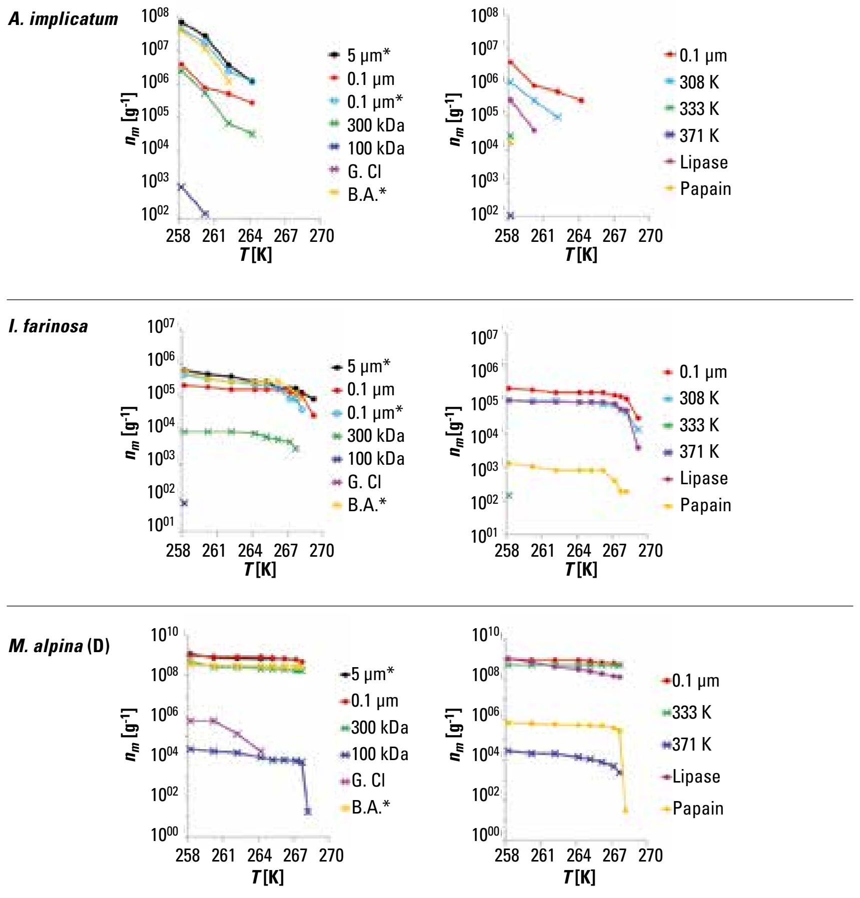

*Figure 2: Ice nucleation spectra of the fungi Acremonium implicatum, Isaria farinosa, and Mortierella alpina after filtration, chemical, heat, and enzyme treatments.*

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# *INFLAMMATORY PROCESSES*

**KURT LUCAS**

> "Understanding the chemical mechanisms of inflammatory processes will open up new perspectives for the treatment of diseases."

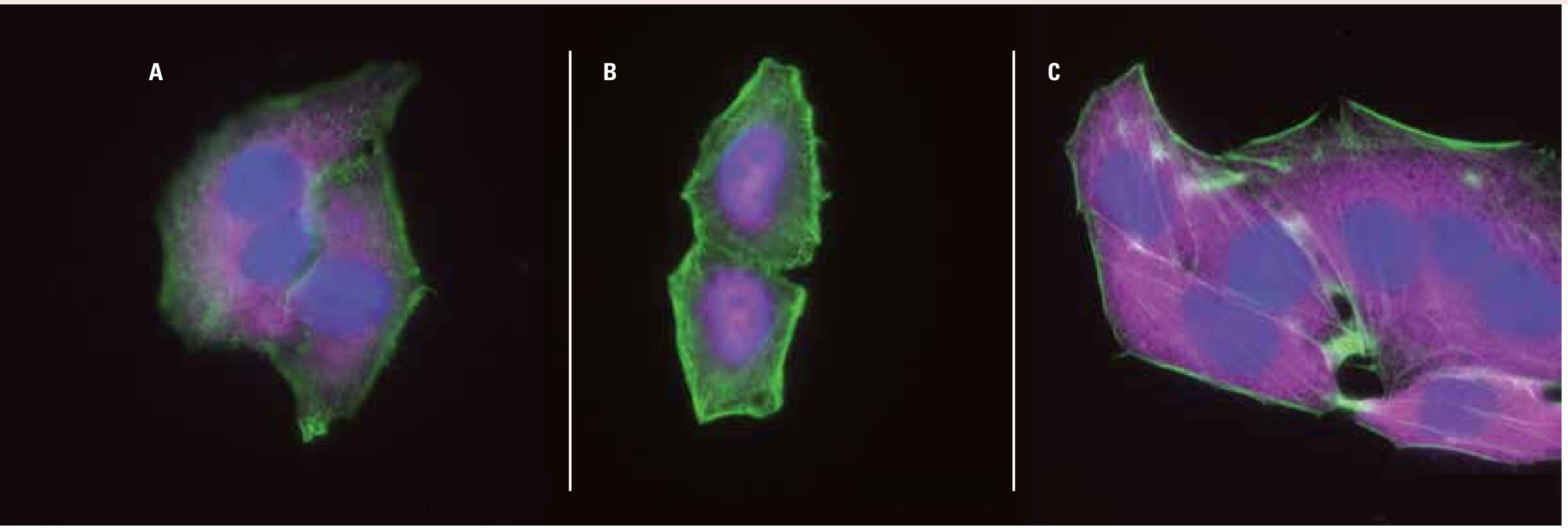

*Figure 1: Translocation of transcription factor NF-κB. A: untreated HeLa-TLR4 cells. B: LPS-stimulated HeLa-TLR4 cells. C: LPS-stimulated HeLa-TLR4 cells pre-treated with cinnamon-extract. Green: cytoskeleton, blue: nucleus, magenta: transcription factor NF-κB (p65 unit) (Credit: Jan Neumann).*

Inflammatory processes are essential for the functioning of the human immune system, but the underlying chemical mechanisms are not yet fully understood. Our studies are focused on pro- and anti-inflammatory effects resulting from the interactions of pattern recognition receptors with environmental contaminants and physiological or therapeutic agents. In particular, we investigate the effects of reactive oxygen and nitrogen species (ROS/RNS), air particulate matter, plant compounds, and molecular hydrogen. With partners from the Institute of Molecular Biology and the Medical Center of the Johannes Gutenberg University Mainz, we established the Mainz Program of Chemical Allergology to elucidate the causes and explore new perspectives for the treatment of allergic and chronic inflammatory diseases.

A key target of our investigations is the Toll-like receptor 4 (TLR4), which recognizes pathogen-associated and damage-associated molecular patterns (PAMPs/DAMPs) such as bacterial lipopolysaccharides (LPS) and a range of other substances including lipds and proteins. Stimulation of the TLR4 can trigger complex intra-cellular signaling pathways, leading to the activation of the transcription factor NF-κB, which regulates the production and release of pro-inflammatory cytokines and ROS/RNS. To study and elucidate these processes, we apply a wide range of cell culture experiments (HeLa-TLR4 reporter cell lines; THP-1 monocytes; macrophages, dendritic cells, and T cells from human donors), luminescence and immunoassays (ELISA, FACS, bead-based multiplex assays), and microscopic techniques (fluorescence, confocal, and super-resolution microscopy; Figure 1).

Amylase/Trypsin Inhibitors (ATIs) are pro-inflammatory and allergenic proteins that can stimulate TLR4, activate NF-κB, and promote chronic inflammation. To investigate the influence of chemical modification by ROS/RNS, we nitrated ATIs by different reagents (peroxynitrite, $O_3/NO_2$, TNM) and found that the nitration does not affect the recognition of ATIs and pro-inflammatory response of HeLa-TLR4 dual reporter cells. Immature dendritic cells, on the other hand, were found to express more maturation markers and release more pro-allergic cytokines when challenged with nitrated ATIs compared to native ATIs. Moreover, matured human dendritic cells pre-treated with nitrated ATIs and co-cultured with T helper cells (syngenic CD4+ T cells) lead to a significantly higher T cell proliferation rate in comparison to native ATIs (Figure 2). Our results indicate that nitration enhances the allergenic potential of ATIs and may promote allergic sensitization against these proteins, which is consistent with earlier studies of nitrated and native birch pollen allergens. Further investigations with grass pollen and other environmental allergens are in preparation. Combined biomedical experiments and proteomic analyses of ambient air filter samples shall reveal if and to what extent protein nitration and related chemical modifications of environmental allergens may indeed explain how air pollution can contribute to the observed increase of allergic diseases as suggested by epidemiological studies.

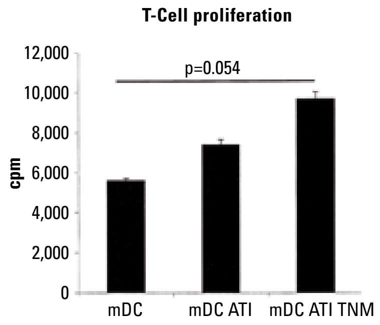

*Figure 2: Enhanced proliferation of T helper cells co-cultured with mature dendritic cells (mDC) stimulatetd with Amylase/Trypsin Inhibitors (ATI) in native form or nitrated with tetranitromethane (TNM). Radioactive signal of cell division rate (in counts per minute, cpm) from radioactive nucleoside, 3H-thymidine, incorporated into new strands of chromosomal DNA during cell division.*

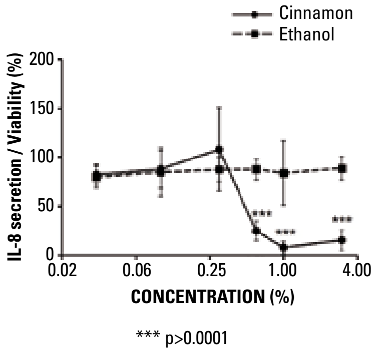

*Figure 3: Dose-dependent anti-inflammatory effect of cinnamon-extract in THP-1 monocytes pre-incubated with cinnamon extract or ethanol (extract solvent blank) for 2h followed by stimulation of TLR4 activity with 50 ng ml$^{-1}$ LPS-EB for 4h. Data are displayed as IL-8 secretion divided by viability normalized to control.*

To elucidate the molecular processes leading to inflammation and allergy, and to explore promising therapeutic approaches, we also work with anti-inflammatory agents such as cinnamon extract (C. verum) and molecular hydrogen ($H_2$). As illustrated in Figure 1, treatment with cinnamon extract can prevent the translocation of NF-kB into the nucleus of TLR-4 reporter cells. Accordingly, the extract also exhibits an anti-inflammatory effect in THP-1 monocytes with a dose dependency shown in Figure 3. By chromatographic fractionation of the extract, we found several chemical compounds that can decrease the inflammatory response of HeLa-TLR4 reporter cells (transcription activity of IL-8 promoter) in synergistic combinations. Further investigations shall provide insight into the chemical mechanisms by which these substances interfere with the immunological signalling pathways. Ongoing collaborative experimental and modeling studies shall also provide mechanistic insights into anti-inflammatory effects of molecular hydrogen, which are well documented but not yet well understood.

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# *MICROBIAL COMMUNITIES & PROCESSES*

**BETTINA WEBER**

> **“We explore and quantify how microbial surface communities interact with the atmosphere, climate, and global change.”**

*Figure 1: Left: Biological soil crust research; (a) field impression (Succulent Karoo, South Africa), (b) biocrust wetness probe, (c) gas flux measurements. Right: ATTO research; (d) tree with microclimate sensors, (e) moss cushion on tree bark, (f+g) moss cusions in mesh basket for studies under local environmental conditions.*

Microbial and cryptogamic surface communities constitute the most compact and oldest forms of terrestrial ecosystems. They comprise photoautotrophic cyanobacteria, algae, lichens, and bryophytes, which grow together with heterotrophic fungi, bacteria, and archaea in varying proportions. Mostly inconspicuous, these organisms and communities grow on the stems, bark, and even leaves of trees; they cover rocks; and they grow on soil, forming so-called biological soil crusts (biocrusts) as well as lichen and moss carpets.

Biocrusts occur mostly on dryland soils but also in other environments where vascular plant growth is limited. In an earlier study, we obtained a first estimate of current global biocrust distribution, covering an overall area of ~15.4 million km$^2$, which corresponds to ~11% of the global terrestrial surface (Elbert et al., 2012). These cover values are likely to be substantially reduced during the next years and decades, as biocrusts have been shown to react quite sensitively upon increased temperatures and altered precipitation regimes (Weber et al., 2016a). Such a reduction may have drastic impacts on the affected ecosystems, because biocrusts deliver multiple key ecosystem services (Rodríguez-Caballero et al., 2017). Biocrusts affect global nutrient cycling, they alter soil surface albedo and the water regime, fertilize desert soils, facilitate vascular plant growth, stabilize dryland soils, and effectively reduce the atmospheric emissions and transport of sand and dust (including hazardous dust stroms). These and related issues concerning biocrusts are detailed and discussed in a recently published volume of the book series “Ecological Studies” (Weber et al., 2016a).

Biocrusts are passively controlled by their water status, being physiologically inactive under dry conditions and re-activated by humidity. Thus, accurate knowledge of the water status is essential for assessing the overall physiological activity of biocrusts, but suitable measurement devices have not been available until recently. We developed a novel biocrust wetness probe that reliably measures the water content of biocrusts (Weber et al., 2016b). It uses a weak alternating current to determine the electrical conductivity of the sample and an automated calibration routine to derive the corresponding water content. Production of the device has been licensed to a commercial instrument manufacturer (UP GmbH, Ibbenbüren, Germany). We have also adapted the sensor for epiphytic surface communities.

As earlier studies had indicated major amounts of $N_2$ fixation by cryptogamic surface covers, we investigated whether internal N cycling processes cause the formation and release of gaseous N compounds. Our measurements revealed that substantial amounts of the reactive trace gases nitric oxide (NO) and nitrous acid (HONO) are emitted to the atmosphere. According to our calculations, biocrusts release 1.7 Tg per year of reactive nitrogen, corresponding to ~20% of global nitrogen oxide emissions from soils beneath natural vegetation (Weber et al., 2015). For the greenhouse gas nitrous oxide ($N_2O$), our investigations suggest a global release of 0.32-0.59 Tg a$^{-1}$ from cryptogamic covers on all substrates, accounting for 4-9% of the global $N_2O$ budget from natural terrestrial sources (Lenhart et al., 2015). The latter values have also been corroborated by an alternative approach using a process-based lichen and bryophyte productivity model (Porada et al., 2017).

At the Amazon Tall Tower Observatory (ATTO), located 150 km northeast of Manaus, Brazil, we are investigating the interaction of microbial and cryptogamic surface communities with the Amazonian rainforest ecosystem and their exchange processes with the atmosphere. In particular, we are focusing on the emission of bioaerosols and the exchange of reactive trace gases and greenhouse gases across the canopy. We have instrumented a tree to measure stem profiles of temperature, light intensity, and water content within these communities to assess their activity. We are measuring aerosol particles and trace gas concentrations and gradients, and we are mapping the cryptogamic covers on ground and plant surfaces around ATTO for quantitative assessment and upscaling of the emissions.

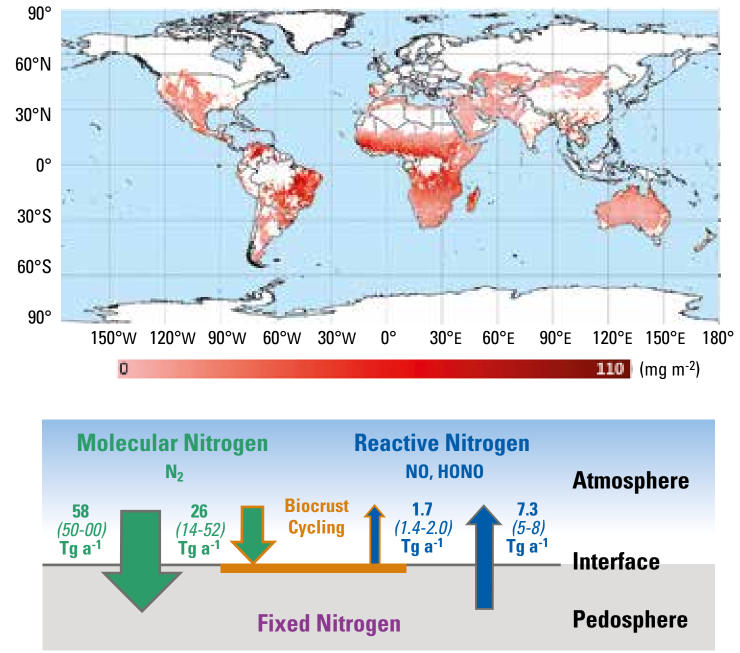

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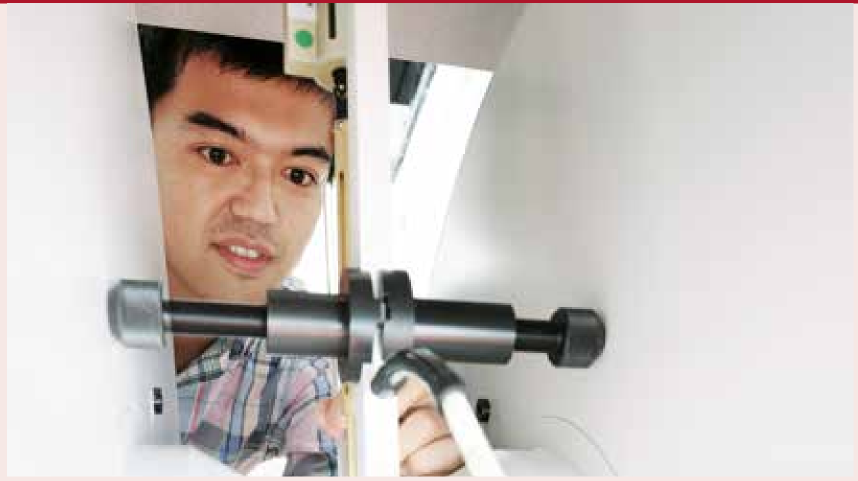
*Figure 2: Top: Global map of annual emissions of reactive N gases (HONO and NO) from biological soil crusts in desert and steppe regions.*
*Bottom: Relevance of biocrust N fluxes as part of the global terrestrial biological nitrogen fluxes.*

# *ORGANIC AEROSOLS & OXIDANTS*

**MANABU SHIRAIWA**



**“Elucidate the multiphase chemistry of organic aerosols and reactive oxygen species at the atmosphere-biosphere interface.”**

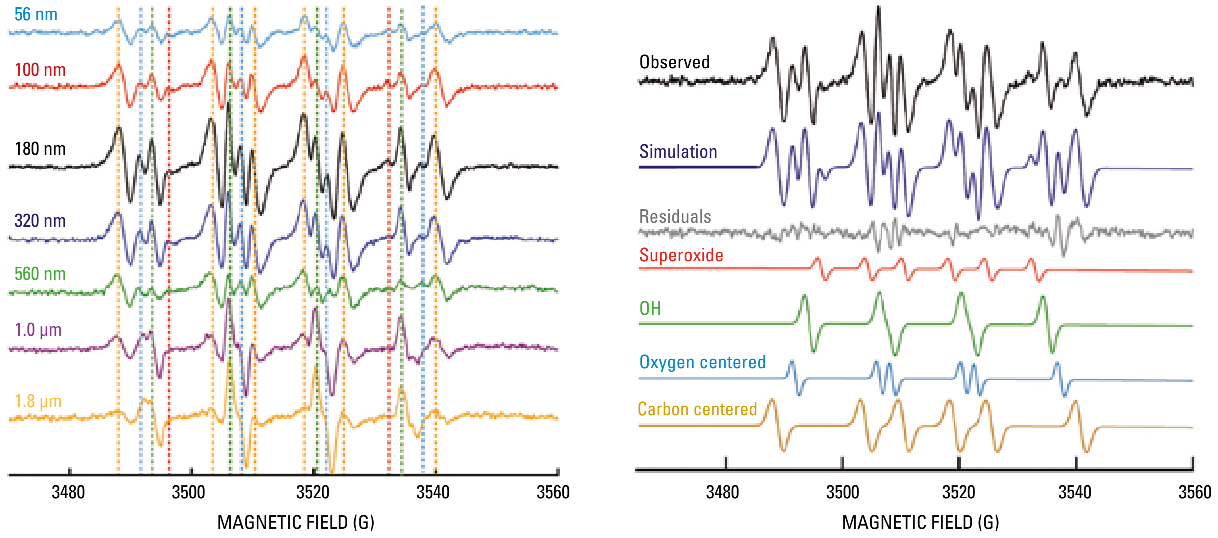


*Figure 1: Electron paramagnetic resonance (EPR) spectra of ambient aerosol impactor samples (Mainz, Germany; 26–27 June 2015) with lower cut-off diameters in the range of 56 nm to 1.8 µm extracted in water mixed with the spin-trapping agent BMPO (5-tert-Butoxycarbonyl-5-methyl-1-pyrroline-N-oxide). Dashed lines indicate the position of each peak for different types of trapped radicals of $O_2$- (red), OH (green), carbon-centered (orange), and oxygen-centered organic radicals (light blue) (Arangio et al., 2016).*

Organic aerosols are ubiquitous in the atmosphere, influencing air quality, climate, and public health. The interactions of organic aerosol particles with atmospheric oxidants can affect the abundance of trace gases and significantly alter physical and chemical properties of aerosols such as toxicity, reactivity, ice and cloud condensation nucleation abilities, and radiative properties. To describe multiphase processes in aerosols and clouds, we developed a kinetic multi-layer model for aerosol surface and bulk chemistry and gas-particle interactions that treats explicitly all steps of mass transport and chemical reaction of semi-volatile species partitioning between gas phase, particle surface, and particle bulk. Applying the kinetic model to experimental data, we demonstrated how moisture-induced phase changes can affect the gas uptake and chemical transformation of organic matter. We also elucidated the role of reactive oxygen intermediates in atmospheric aerosol chemistry.

Secondary organic aerosols (SOA) are a large source of uncertainty in our current understanding of climate change and air pollution. The phase state of SOA is important for quantifying their effects on climate and air quality, but their global distribution is poorly characterized. Based on the molecular corridor approach, we developed a method to estimate glass transition temperatures based on the molar mass and molecular O:C ratio of SOA components. We used the global chemistry climate model EMAC with the organic aerosol module ORACLE to predict the phase state of atmospheric SOA. For the planetary boundary layer, global simulations indicate that SOA are mostly liquid in tropical and polar air with high relative humidity, semi-solid in the mid-latitudes, and solid over dry land. We find that in the middle and upper troposphere, SOA should be mostly in a glassy solid phase state. Thus, slow diffusion of water, oxidants, and organic molecules could kinetically limit gas–particle interactions of SOA in the free and upper troposphere, promote ice nucleation, and facilitate long-range transport of reactive and toxic organic pollutants embedded in SOA.

Air pollution can cause adverse health effects such as asthma and other respiratory diseases, but the underlying chemical processes are not well characterized.

Reactive oxygen species (ROS) play a central role in the adverse health effects of air pollution, as they can cause oxidative stress. We found that ambient and laboratory-generated SOA form substantial amounts of OH radicals upon interaction with liquid water, which can be explained by the decomposition of organic hydroperoxides. Inhalation and deposition of SOA particles may lead to substantial release of OH radicals in the human respiratory tract. We derived chemical exposure-response relations between ambient concentrations of air pollutants and the production rates and concentrations of ROS in the epithelial lining fluid of the human respiratory tract. In highly polluted environments, fine particulate matter (PM2.5) containing redox-active transition metals, quinones, and SOA can increase ROS concentrations in the lung to levels characteristic of respiratory diseases. Chemical exposure-response relations provide a quantitative basis for assessing the relative importance of specific air pollutants in different regions of the world, showing that aerosol-induced epithelial ROS levels in polluted mega-city air can be several orders of magnitude higher than in pristine rainforest air.

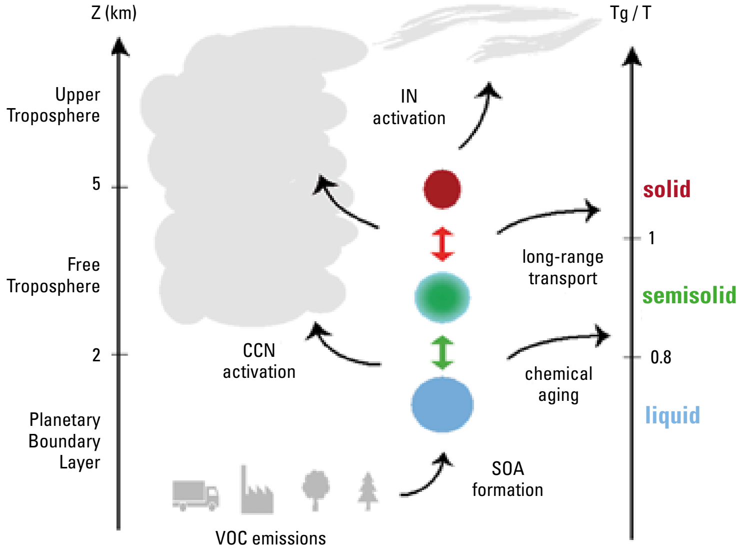


*Figure 2: Schematic of evolution of SOA phase state as a function of altitude and temperature, which has significant implications for activation to cloud droplets and ice crystals, chemical aging and long-range transport (Shiraiwa et al., 2017).*

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# *ORGANIC POLLUTANTS & EXPOSURE*

**GERHARD LAMMEL**

> **“Understanding the exposure of the environment and humans to organic pollutants that cycle between atmosphere and surface compartments.”**

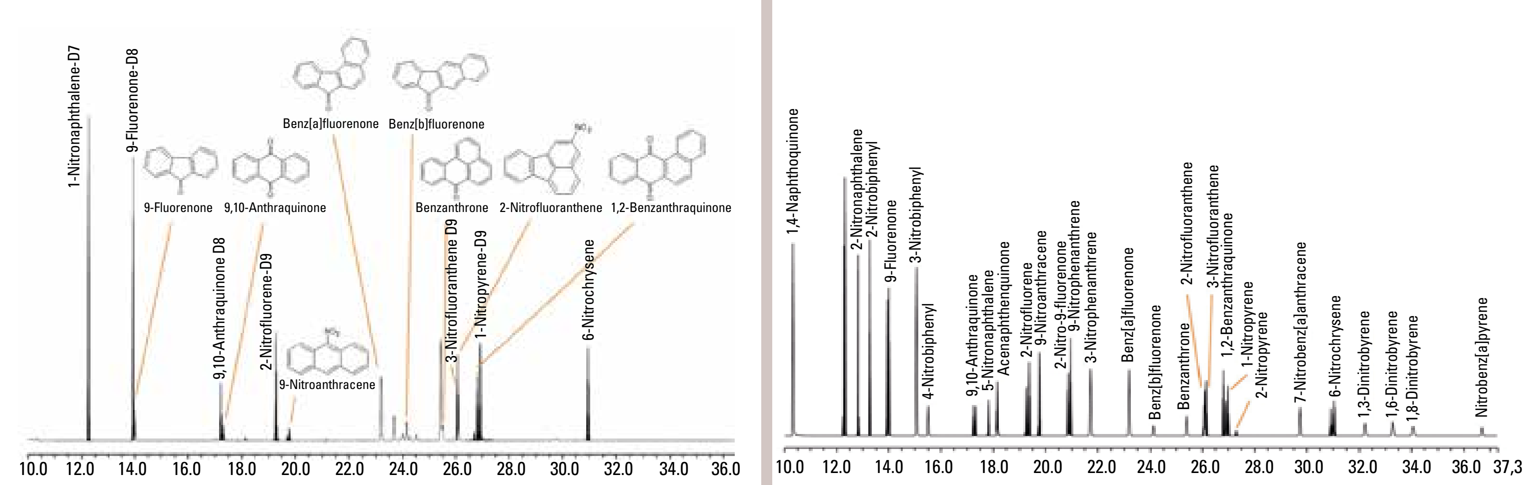

*Figure 1: Gas-chromatograms of an extract of a size-segregated filter sample of polluted air (left) and of a standard mixture of nitrated and oxygenated polycyclic aromatic hydrocarbons (right).*

Humankind has introduced over 30,000 anthropogenic substances into the environment, including unintended by-products, many of which pose a hazard to human health and ecosystems. The cycling of long-lived (persistent) organic pollutants in the Earth system is particularly complex. In atmospheric aerosols, most of these pollutants are semivolatile, and partition between the gaseous and particulate phases. Upon deposition onto soil, vegetation, and sea surfaces, they may re-volatilize to the atmosphere (so-called multihopping). Long after peak emission, such secondary sources may overrun the primary sources, which are usually concentrated in the highly populated areas. The total environmental residence time of these persistent organic pollutants typically exceeds the atmospheric residence time by several orders of magnitude. The latter depends strongly on partitioning in the aerosol.

Our research group studied air-surface exchange by conducting field experiments in the Great Hungarian Plain and in the Eastern Mediterranean, regions that have been receiving significant airborne pollutants from afar. Persistent organic pollutants have been emitted for decades, with peak emissions of pesticides and polychlorinated biphenyls (PCBs) mostly in the 1970s and brominated flame retardants and polycyclic aromatic hydrocarbons (PAHs) more recently. While historically the Great Hungarian Plain has been receiving pollutants mostly from adjacent Central and Western Europe, the Eastern Mediterranean has been receiving them mostly from Central and Eastern Europe. We found that in summer, when re-volatilization is strongest, these receptor areas actually turn into secondary source areas, and air pollution there may be even sustained from surface emissions during nighttime.

Long-lived toxic substances can also be formed photochemically in plumes of fossil fuel or biomass burning emissions. Nitrated and oxygenated PAHs are almost unavoidably formed as by-products of all kinds of combustion, from the reactions of parent PAHs with radicals, ozone, and nitrogen oxides. Mutagenicity generally increases with nitration of PAHs. Little is known about even the most abundant species of these substance classes in air, soils, and surface waters, their multiphase chemistry, and long-range transport potential. Phase partitioning can now be satisfyingly predicted and, hence, the long-range transport potential assessed using a thermodynamic model (i.e., a poly-parameter linear free energy relationship). Our observations of 2-nitrofluoranthene, a nitrated 4-ring PAH, in remote marine air suggest that this is a ubiquitous, globally distributed air pollutant.

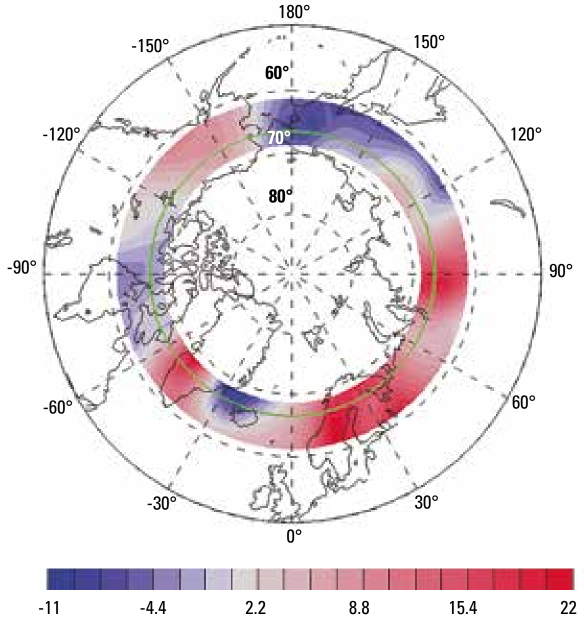

*Figure 2: Rates of pollutant import (red) into and export (blue) out of the Arctic. Average of DDT net mass flux close to the polar circle (60°-70°N) from 1970 to 1999 (ng m$^{-2}$ s$^{-1}$).*

By numerical modeling, we also studied the long-term trends of transports to and exposure of the Arctic to persistent organic pollutants, PCBs, and the pesticide DDT for the 20th century and under a climate change scenario for the 21st century based on the distribution of emissions since the start of industrial production around 1950. Our model simulations suggest that the monitored downward trend of DDT in the Arctic will reverse around the year 2075 when more DDT will arrive in the Arctic. Climate change will amplify this effect. On the other hand, the model suggests that PCBs will not increase due to stronger northward atmospheric flow across the Arctic Circle, although the rate at which the flows weaken will level off.

These results help to explain why the concentration of persistent pollutants in the atmosphere above Svalbard correlates with the so-called Arctic Oscillation, a regular pressure oscillation of the atmosphere, whereas this is not the case above Greenland. Pollutant flows from Europe, which correlate positively with the Arctic Oscillation, maintain the concentrations above Svalbard. The pollutant concentrations above Greenland, however, are determined by flows over the Canadian Archipelago, where air currents are in a reverse relation with this atmosphere oscillation.

Human exposure through inhalation can be assessed when referring to the bioavailable fraction of atmospheric pollutant concentrations. The bioavailability and effects of nitro- and oxy-PAHs will be studied using simulated lung lining fluids and bioassays.

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# *MULTISCALE INTERACTIONS & INTEGRATION*

**ULRICH PÖSCHL**

**“Multiphase processes on molecular to global scales play a vital role in the co-evolution of climate, life, and health in the Earth system and in the Anthropocene.”**

*Figure1: (a) HALO research aircraft during the EMERGE campaign investigating trace gas and aerosol emissions from European megacities. (b) Ragged Point Observatory in Barbados where we collected long-term observations of aerosol-cloud interactions in marine air.*

Chemical reactions, mass transport, and phase transitions between gaseous, liquid, and solid matter in the Earth system bridge a wide range of spatial and temporal scales. The Anthropocene, i.e., the present era of globally pervasive human influence on planet Earth is characterized by a widespread increase of air pollutants like ozone, nitrogen oxides, and combustion- or traffic-related aerosol particles. These pollutants can have a strong influence on atmospheric chemistry and physics, climate, and public health, but their actual impact remains to be fully unraveled and quantified.

The effects of aerosols on clouds and precipitation are among the largest uncertainties in the scientific understanding of climate change. This is partly due to a lack of information about how the properties and interactions of aerosols and clouds in polluted air differ from that of pristine air equivalent to pre-industrial background conditions. To gather such information, we conduct ground-based and airborne measurements of aerosol and cloud condensation nuclei (CCN) in remote regions with low influence of anthropogenic pollution as well as in moderately and heavily polluted regions. For this purpose, we develop and deploy sophisticated and robust sampling and measurement devices that resolve aerosol particle size distribution, composition and mixing state, hygroscopicity, and CCN activity of aerosols with high precision over a wide dynamic range.

Our long-term, ground-based observations at the Amazon Tall Tower Observatory (ATTO) in the Amazonian rainforest in Brazil and at the Ragged Point Observatory on the Atlantic coast of Barbados reveal characteristic features and differences between rainforest (“green ocean”) and marine (“blue ocean”) air. In particular, we determine the properties and sources of pristine rainforest and marine aerosols (primary biological, secondary organic, sea spray), and we quantify the influence of regional and long-range transported anthropogenic and natural contaminants (biomass burning, desert dust). In addition, we use the research aircraft HALO to obtain altitude profiles of aerosol and convective cloud properties from Earth’s surface to the upper troposphere during intensive campaigns over the Amazon rainforest (ACRIDICON-CHUVA) and over polluted megacities in Europe and Asia (EMERGE). While continuing the long-term ground-based observations and preparing further HALO aircraft campaigns, we are working on the analysis and interpretation of the comprehensive data sets using a novel parameterization of CCN efficiency spectra, microphysical cloud process models, large-scale atmospheric models, and satellite data in collaboration with local and international partners.

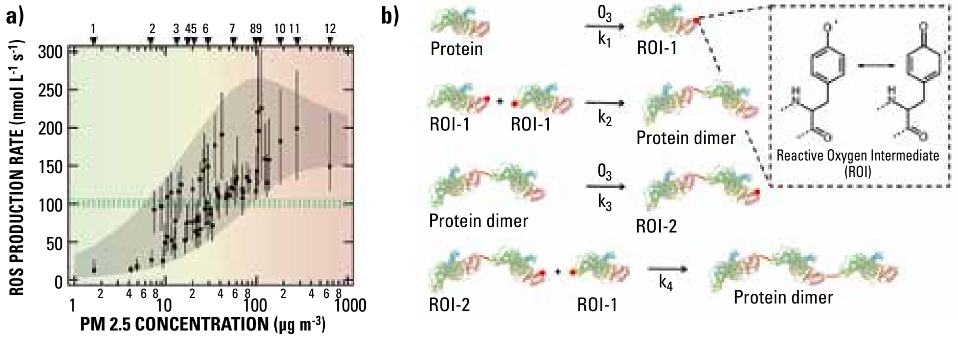

*Figure 2: (a) Chemical exposure-response relation between reactive oxygen species (ROS) in epithelial lining fluid and ambient fine particulate matter (PM2.5) calculated for different locations and aerosol compositions (Lakey et al. 2016). (b) Reaction pathways of protein oligomerization involving tyrosyl radicals as reactive oxygen intermediates (ROI; Kampf et al. 2015).*

A major public health concern is the observed and ongoing increase of allergic diseases. In earlier studies, we found that chemical modifications of allergenic proteins upon exposure to air pollutants may promote allergic sensitization and reactions. Thus, we perform experimental and modeling studies to elucidate the chemical mechanism and kinetics of protein oxidation, nitration, and oligomerization by environmental pollutants, physiological agents, and reactive intermediates ($O_3/NO_2$, peroxynitrite, tyrosyl radicals). Moreover, we investigate how atmospheric oxidants and aerosols can induce oxidative stress by raising the levels of reactive oxygen and nitrogen species (ROS/RNS) in the epithelial lining fluid (ELF) of human airways. Recent and ongoing investigations provide first quantitative estimates of chemical exposure-response relations, nonlinear interactions, and the relative importance of redox-active particulate matter, ozone, and nitrogen oxides. Further studies combining physicochemical and biomedical experiments with numerical model simulations will corroborate the preliminary exposure-response relations and incorporate biological feedback mechanisms.

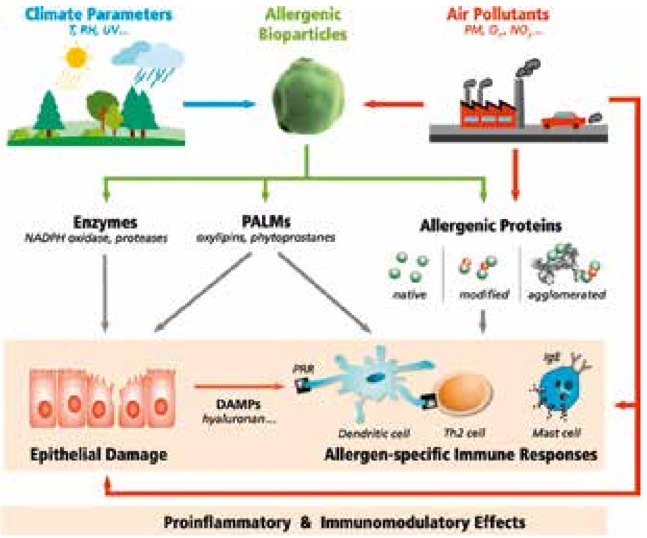

*Figure 3: Pathways through which climate parameters and air pollutants can influence the release, potency, and effects of allergens and adjuvants relevant for allergic sensitization and responses: temperature (T), relative humidity (RH), ultraviolet (UV) radiation, particulate matter (PM), ozone and nitrogen oxides ($O_3$, NOx), reduced nicotinamide adenine dinucleotide phosphate (NADPH) oxidase, pollen-associated lipid mediators (PALMs), damage-associated molecular patterns (DAMPs), pattern recognition receptors (PRR), type 2 T helper (Th2) cells, immunoglobulin E (IgE), allergenic proteins (green dots), and chemical modifications (red dots). (Reinmuth-Selzle et al., ES&T 2017).*

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# PARTICLE CHEMISTRY

## PARTICLE CHEMISTRY

Properties and transformation of natural and anthropogenic aerosol particles in the atmosphere, smog, cloud formation, formation of ice in the atmosphere. Meteorite and star dust.

# *PARTICLE CHEMISTRY DEPARTMENT*

## BACKGROUND

In 2001 the Particle Chemistry Department (PCD) was established jointly between the Johannes Gutenberg University of Mainz (JGU) and the MPI for Chemistry (MPIC). The director is Prof. Stephan Borrmann, who holds a "C4" professor position at the JGU Institute for Atmospheric Physics (IPA) and a formal part-time ("Direktor im Nebenamt") appointment at MPIC. The department consists of five groups: (1) Aerosol and Cloud Physics (Ralf Weigel), (2) Instrumental Aerosol Analytics (Frank Drewnick), (3) Aerosol and Cloud Chemistry (PD Johannes Schneider), (4) Atmospheric Hydrometeors (PD Miklós Szakáll and Karoline Diehl), and (5) Nano- and Microparticle Research (NAMIP, PD Peter Hoppe). The laboratories and offices of groups 1 and 4 are on the JGU/IPA premises; the others are at MPIC.

## RESEARCH FOCUS

The subjects of Particle Chemistry Department's research activities are physical and chemical processes of atmospheric aerosols, clouds, large hydrometeors, pollution and its sources, as well as particulate matter of extraterrestrial origin. The experimental activities are centered on ground based, mobile, and aircraft-borne field measurements, sophisticated instrument development, and also include laboratory studies.

## EXPERIMENTAL FOCUS

The department operates several large facilities, including the Mainz Vertical Wind Tunnel  (see report by M. Szakáll and K. Diehl), the Mobile Laboratory for Atmospheric research (Mola, see report by F. Drewnick), and the NanoSIMS laboratory of the NAMIP group (see report by P. Hoppe). Six mobile state-of-the-art aerosol mass spectrometers are available for field research. Four of these instruments are certified for implementation – and have been operated – on different European research aircraft, including IAGOS-CARIBIC, the Russian M-55 "Geophysica", the research aircraft DLR HALO, the AWI Polar P6 (see report by J. Schneider), DLR Falcon, and the British BAe 146 FAAM. In addition, for conducting aircraft-borne atmospheric research, there are ten in situ instruments dedicated to cloud and aerosol microphysics in the upper troposphere/lower stratosphere (see reports by R. Weigel, S. Borrmann). Several of the instruments are in-house developments, such as the Aircraft-based Laser ABlation Aerosol MAss spectrometer (ALABAMA), the HALO-HOLO holographic imaging probe (for ground- and ship-based, aircraft, helicopter application), and ERICA (the ERc Instrument for Chemical composition of Aerosols).

The development of ERICA began in 2013 supported by S. Borrmann's European Research Council (ERC) Advanced Research Grant. The instrument was in-house assembled by the workshop facilities at MPIC and IPA-JGU. This unique prototype combines laser desorption/ionization with flash vaporization/electron impact ionization mass spectrometry to measure the chemical composition of aerosols with sizes between 60 nm and several micrometers in particular at high altitudes. Development of this highly complex, fully automated instrument was completed in 2016, and its inaugural flight was on the M-55 "Geophysica" during the StratoClim testcampaign in Kalamata, Greece (July/August 2016). During this first deployment, ERICA delivered useful data up to 20 km altitude. In July/August 2017, eight successful mission flights were conducted for StratoClim from Kathmandu, Nepal (see report by S. Borrmann).

During the reporting period, all of the aircraft instruments from PCD, as well as MoLa were in high demand for many national and international high-profile field projects (e.g., DACCIWA from Lomé in Togo), AIRTOSS-ICE, several projects in the Arctic (see report by J. Schneider), HALO missions (ML-Cirrus, ACRIDICON, EMeRGe), StratoClim, DIAPASON (see report by F. Drewnick), BIOCOMBUST, industry related projects, and others.

## TEACHING AND EDUCATION

The PCD was established to form a common structure for both the University and MPIC. As a result, in addition to research, the education of "Diplom", bachelors, masters, and Ph.D. students also is at the core of PCD's mission. From 2014 to 2017 twelve Ph.D. theses were completed, as well as seven diploma, one masters, and three bachelor theses. Currently, nine Ph.D. projects are in progress. Since 2001, the department has supervised a total of 52 Ph.D., 40 "Diplom", one masters, and six bachelors theses (of these 99 graduates 46 are female). In addition, M. Szakáll successfully completed his formal "Habilitation" (i.e., the postdoctoral lecturer qualification, PD) at JGU in 2015. Several members of the department, including PD J. Schneider, PD M. Szakáll, R. Weigel, and S. Borrmann, are engaged in the mandatory teaching within the bachelors and masters curricula (in Meteorology) at IPA during each semester, and the Mola facility (F. Drewnick) participates in the practical courses.

## *STEPHAN BORRMANN*

**18 JANUARY 1959** Born in Mainz, Germany

**1977–1984** Study of Physics and Biology Johannes Gutenberg University Mainz

**1985–1986** Adjunct Research Instructor at the Naval Postgraduate School in Monterey/CA/USA

**1991** PhD in Physics

**1991–1993** Postdoctoral Fellow of the Advanced Study Program (University Corporation of Atmospheric Research, UCAR) at the National Center for Atmospheric Research (NCAR) in Boulder/CO/USA

**1999** German Habilitation in Meteorology

**1998–2000** Head of the Aerosol Research Group at the Institute for Chemistry and Dynamics of the Geosphere at the Research Center Jülich Ltd.

**since 2000** Professor Johannes Gutenberg University Mainz and Scientific Member of the Max Planck Society

**since 2001** Director (part-time) at the Max Planck Institute for Chemistry

### *SELECTED CAREER ACHIEVEMENTS*

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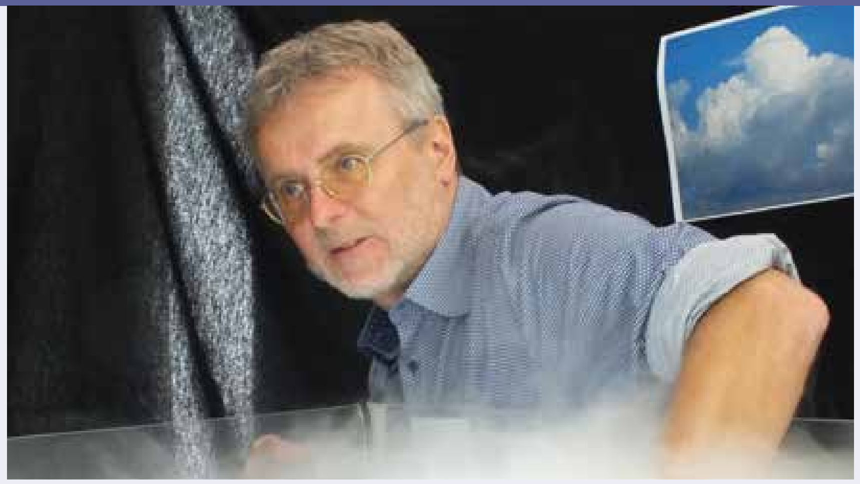
# THE ASIAN MONSOON ANTICYCLONE – FIRST AIRBORNE IN SITU MEASUREMENTS ON PHYSICS AND CHEMISTRY OF AEROSOLS AND CLOUDS

**STEPHAN BORRMANN**



> **“Designing a scientific instrument is our mind’s effort to organize a small piece of nature within some confinement, such that nature unveils a tiny bit about itself.“**

*Figure 1: (a): Integration of ERICA into the aircraft in Kalamata (24.8.2016) for the first test flight. (b): Laboratory setup of ERICA. (c): Takeoff M-55 “Geophysica“ from Kalamata, Greece, on 31.8.2016 (Credit: R. Weigel). (d): ambient aerosol sampling inlet for ERICA (Credit: Th. Böttger); (e): COPAS I and II units (see Report by Ralf Weigel) inside wheel compartment of Geophysica. (f): Three cloud probes; CIP – Cloud Imaging Probe, PIP – Precipitation Imaging Probe, Holography Instrument (lower canister) (all other photos: S. Borrmann).*

## THE ASIAN MONSOON ANTICYCLONE (AMA) AND STRATOCLIM

The AMA is an important component of the global atmospheric circulation system extending from East Asia to the Middle East between mid-June and the end of October in an altitude band from 12 to 20 km. As a fairly closed rotating air mass, it is reminiscent of the polar vortex, albeit with a strong upward transport (probably dominated by convection) of tropospheric source gases and aerosols into the upper troposphere and lower stratosphere (UT/LS). Measurements obtained from the CALIPSO space borne Lidar led to discovery of an aerosol layer (the Asian Tropopause Aerosol Layer; ATAL) between 15 and 16.5 km altitude within the AMA. During the EU StratoClim project, for the first time detailed, systematic in situ experiments were performed inside the AMA and the ATAL that measured their hitherto largely unknown physical and chemical characteristics. Dedicated to physical and chemical measurements of clouds and aerosols nine of the 25 instruments on board of the Russian high altitude research aircraft M-55 “Geophysica” were provided by the Particle Chemistry Department/JGU groups. All our nine instruments performed nearly flawlessly during the eight research flights from Kathmandu, Nepal, in July/August 2017, which constitutes a significant experimental success.

## CHEMICAL COMPOSITION OF THE AEROSOL

The aerosol particle mass spectrometer ERICA (ERc Instrument for the Chemical composition of Aerosols, an in-house development funded by the ERC Advanced Research grant of S. Borrmann) was among the four, at our department newly developed instruments that were deployed for the first time during the EU StratoClim project (see Figure 1). ERICA samples ambient submicron aerosol particles and immediately converts the particulate matter into ions by means of laser ablation or by flash vaporization/electron impact ionization. The mass spectra of the ions containing the information on the particle chemical composition were recorded in situ and online. During the research flights from Kathmandu, approximately 160,000 single particle mass spectra were acquired at all altitudes up to 20 km. For the first time, both polarities – cations and anions – could be simultaneously recorded for each aerosol particle in the stratosphere. Figure 2 shows examples of such mass spectra (e.g., meteoric dust, organic particles, soot). The flash vaporization/electron impact ionization Aerosol Mass Spectrometer (AMS) component of ERICA also recorded spectra during each flight. The increase of the sulfate aerosol toward higher altitudes becomes evident in the data. Detailed analyses of the ERICA measurements will yield the chemical structure and composition of the ATAL. This will be supported by a posteriori laboratory analyses of particles that were captured at high altitude on boron plates and electron microscope grids by the MPIC/JGU HAPACO (High Altitude PArticle COllector) impaction device (Ebert et al., 2016).

## CIRRUS AND CONVECTIVE OUTFLOW

Because the convective upward transport inside the AMA carries gases, precursors, and aerosols aloft, three research flights were dedicated to measuring the outflow of convective clouds. Here, our four cloud particle instruments recorded particle size distributions from nanometers to millimeters (see Figure 3). In addition, the in-house-developed holographic instrument recorded the first ever holograms of high-altitude cirrus and convective anvil outflows for imaging the particle and crystal habits (Right panel insert of Figure 3). Some of the sampled cloud segments contained high levels of CO, which shows that the high reaching convective clouds uplift polluted boundary layer air parcels to high altitudes. Our department’s continuous efforts and resources will be devoted to the detailed analyses of this extensive and unique StratoClim dataset and particle samples in the years to come.

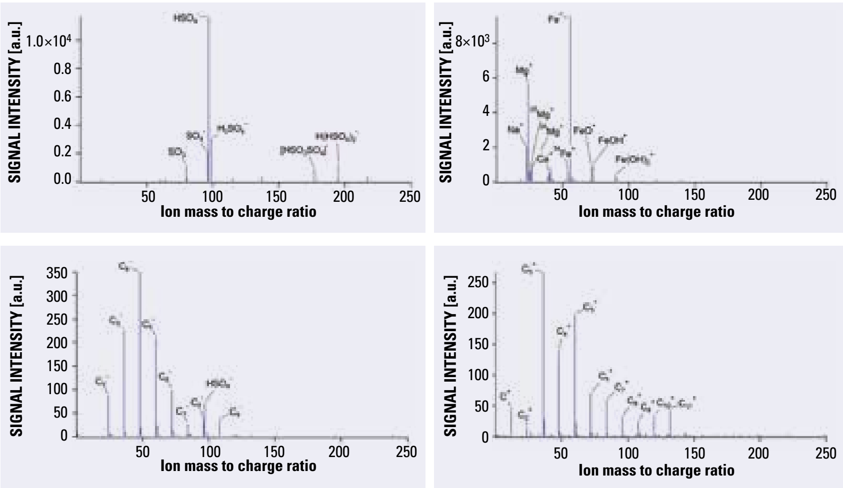


*Figure 2: Upper panels: Single particle mass spectra of meteoric dust particle with sulfuric acid coating recorded by ERICA during the flight on 31.7.17 (Kathmandu, Nepal) at 19,593 m altitude. Lower panels: Soot particle mass spectra from the same flight and 5321 m altitude.*

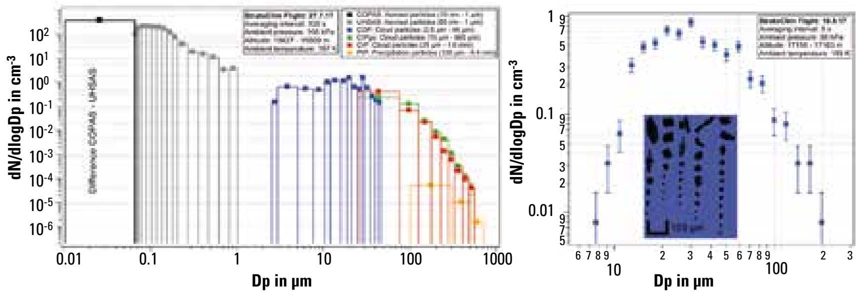


*Figure 3: Aerosol and cloud particle size distributions in the Asian Monsoon Anticyclone over India and Nepal from seven MPIC/JGU instruments on the M-55 “Geophysica.” Left panel: COPAS – COndensation PArticle counting System; UHSAS – Ultra High Sensitivity Aerosol Spectrometer; CDP – Cloud Droplet Probe; CIP – Cloud Imaging Probe; CIPgs – Cloud Imaging Probe gray scale; PIP – Precipitation Imaging Probe. Except COPAS the instruments are from Droplet Measuring Technologies Inc. (Boulder, Co, USA) with MPIC modifications. Right Panel: Subvisual cirrus size distribution over India. Insert: Holographic image reconstructions of ice particle shapes and habits.*

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# *VERTICAL DISTRIBUTION OF SUB-MICROMETER SIZED AEROSOLS IN THE UT/LS OF THE ASIAN MONSOON REGION*

**RALF WEIGEL**

**“We seek to answer questions related to sources and transport pathways of aerosol and gaseous materials in the Asian monsoon anticyclone region and their subsequent global distribution.“**

*Figure 1: The Russian M-55 Geophysica during take-off from Kalamata airport, Greece, August 2016.*

**AEROSOL AND CLOUD PHYSICS**

In the 15th year of continued participation in M-55 *Geophysica* (Figure 1) research flights, the 4-channel COPAS (COndensation PArticle counting System; see Figure 1 in the report by S. Borrmann) was deployed to investigate sub-micrometer aerosol-related properties in the upper troposphere/lower stratosphere (UT/LS). Three of the four channels detect and count particles with diameters $d_{p50}$ larger than 6 nm, 10 nm, and 15 nm, respectively, where $d_{p50}$ denotes the 50% detection efficiency “cut-off” levels. The fourth COPAS channel (with $d_{p50} = 10$ nm) counts aerosol particles after their exposure to heat (250°C), providing information on the non-volatile (nv) particle fraction (e.g., soot, mineral dust, metallic aerosols; cf. Weigel et al., 2014). The upper size detection limit is roughly 1 µm for all channels. For example, Figure 2 gives particle data as ambient mixing ratio $n_{10}$ in units of particle numbers per milligram of air (mg$^{-1}$) for size diameters between 10 nm and the upper detection limit. Since 2010, a dual-stage impactor system has also been part of the COPAS instrumentation, enabling collection of up to 12 samples of submicron particulate matter during each flight. A posteriori offline determination of single particle physico-chemical properties is performed in the laboratory by using scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (Ebert et al. 2016; Schütze et al. 2017).

StratoClim was a two-tier field mission, one part of which was conducted over the Mediterranean (start from Kalamata, Greece, August/September 2016). The second part of the mission took place during the monsoon season over the Indian subcontinent (start from Kathmandu, Nepal, July/August 2017) as detailed in the report by S. Borrmann. During StratoClim, three measurement flights were conducted at mid-latitudes and eight flights were over Nepal, India, and Bangladesh (cf. Figure 2 left panel), each with a duration of three to four hours. Due to the working liquid used (a chlorofluorocarbon, FC-43), the COPAS detection is limited to altitudes between approximately 11 km and 20 km. However, in total, up to nearly 10 hours and 27 hours of observational COPAS data were obtained at mid-latitudes and over Nepal, respectively. COPAS operates fully automatically on board the M-55 *Geophysica* while exposed to the ambient conditions that occur at up to 20 km altitude: atmospheric pressures down to 70 hPa and air temperatures of +40° to -90°C. During three flights (Mediterranean) and during seven out of eight flights (Nepal), at several altitudes between 380 K and 440 K potential temperature (Θ), in total, 60 individual aerosol impactor samples were collected that are currently under analysis (see e.g., Ebert et al., 2016; Schütze et al., 2017).

Figure 2 (right panel) shows the vertical profiles of the particle mixing ratios obtained from selected flights over the Mediterranean and from Nepal, with the altitude indicated at the ordinate in terms of potential temperature (Θ in Kelvin). The COPAS data are juxtaposed with earlier findings by Brock et al. (1995), and with results obtained from COPAS at mid-latitudes and the tropics. The most striking observation is the difference in the mixing ratios between Greece and Nepal. At mid-latitudes, the values range at, or slightly above, the mixing ratios typical for that region. Over Nepal, the abundance of sub-micrometer aerosol particles is excessive until reaching a potential temperature altitude of 420 K. Up to these altitudes, the results generally exceed all mixing ratios from earlier in situ measurements by at least one order of magnitude (cf. $\Theta \approx 360$ K, i.e. below the tropopause), if not even more than that (as is the case for $370\ \mathrm{K} < \Theta < 380\ \mathrm{K}$, i.e. at tropopause level). These high amounts of aerosols could in part be due to localized new particle formation (NPF). The prevailing abundance of aerosols at higher altitudes ($380\ \mathrm{K} < \Theta < 425\ \mathrm{K}$) illustrates how effective the monsoon-driven vertical transport of aerosol (or precursor gases) proceeds across the tropopause. At the highest altitude levels (corresponding to $\Theta > 430$ K), particle mixing ratios decline to values that compare to the earlier findings. Detected mixing ratios $n_{10}$nv (not shown) exhibit a maximum at the tropopause ($\Theta \approx 370$ K). The fraction of non-volatile particle number $n_{10}$nv and total number $n_{10}$, however, has its maximum (roughly 70 %) further above at $\Theta \approx 400$ K. Considering the entire vertical range, this fraction is most variable with values down to 15 %. To which extent various processes, such as NPF occurring in clear air, or inside cloud anvils, or convective upward transport of precursor gases for NPF, contribute to the observed enhanced mixing ratios still is unknown, and we hope to find answers from our future analyses on the StratoClim data. Also we hope to infer the chemical composition of the freshly nucleated and grown particles from the mass spectrometric analyses described in the report by S. Borrmann.

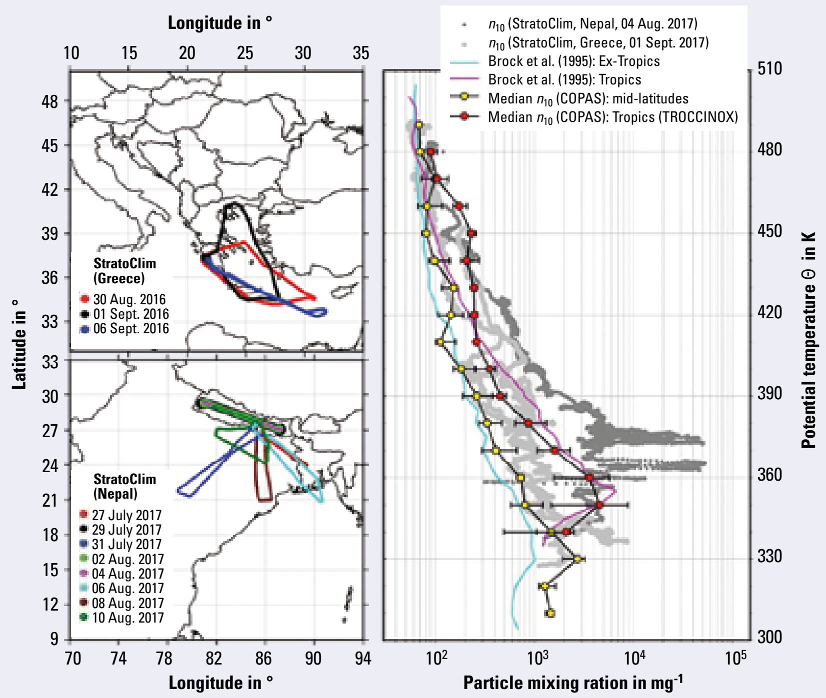

*Figure 2: Tracks of flights performed during the StratoClim missions over the Mediterranean and in the Asian Monsoon region, respectively (left panel). Vertical profiles of sub-µm sized aerosol particles from selected single flights at mid latitudes (Greece) compared to those from the Asian Monsoon region (Nepal) together with earlier findings.*

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# URBAN AEROSOLS IN EUROPEAN CITIES: SOURCES AND DYNAMICS IN ROME AND PARIS

**FRANK DREWNICK**

> **“To improve and predict air quality in complex environments such as urban agglomerations, understanding of sources, dynamics, and processing of ambient aerosols is required.”**

*Figure 1: Ambient aerosol measurements in Paris and Rome using MPIC’s mobile aerosol research laboratory MoLa and a field measurement container (Credits: Fachinger, Drewnick, Struckmeier).*

Unlike in urban agglomerations of developing countries, the air quality in European cities has significantly improved over the last decades. Here, the burden of gaseous pollutants, such as nitrogen oxides, carbon monoxide, and sulfur oxides, decreased by 40–70% within the last 15 years. During the same period, particulate matter concentrations ($PM_{10}$ and $PM_{2.5}$) were reduced by 25% and those of black carbon by 10%. Despite these achievements, roughly half a million lives are lost each year in Europe as a consequence of degraded air quality, especially due to particulate matter pollution.

To allow improved prediction and further reduction of urban particulate matter loadings, better knowledge of strength, distribution, and temporal behavior of PM sources as well as of the related transport, transformation, and deposition processes is needed. To better understand the complex urban aerosol system, we undertook a series of intensive field campaigns in different seasons and at different locations (i.e., city center and periphery) in two European cities, namely Paris and Rome (Figure 1). Highly time-resolved measurements of trace gas concentrations and of aerosol concentrations, size distributions, and composition were performed over several weeks at each location using the institute’s mobile aerosol research laboratory (MoLa) and a measurement container.

In these field studies, no strong and systematic differences in aerosol loadings were observed between city centers and related peripheries. Pollutant levels at both locations were mainly associated with air mass origin and local meteorology such as solar radiation intensity, precipitation, boundary layer height, and atmospheric stability. In other words, the city centers were not found to be generally more polluted compared to the outskirts.

Multiple aerosol sources were identified in the urban environments. Several of them showed distinct diurnal variations, with clearly different levels in the city center and the periphery, or with pronounced differences between seasons. Biomass combustion-related organic aerosol, for example, from the burning of agricultural residues, was mainly found in the outskirts of the cities and concentrations strongly depended on the occurrence of associated activities. Cooking-related organic aerosol was predominantly detected in the city center and had a distinct diurnal pattern, reflecting lunch and dinner cooking activities. Pollutants associated with traffic also showed clear diurnal patterns with surprisingly little difference between the different locations.

Significant differences between seasons were observed for the secondary organic aerosol. During the colder seasons (with less solar radiation), only relatively aged secondary organic aerosol was found, while during the warmer seasons, additionally a type of freshly oxidized organic aerosol was identified, likely resulting from rapid oxidation of precursor gases from the metropolitan region. Also new particle formation was observed in the early afternoon during the warmer seasons only, occurring more frequently in the city center compared to the outskirts (Figure 2).

In addition to pollution that originates in the city itself, advection of particulate matter contributes to the local aerosol burden. Saharan dust advection events were the source of strong increases of coarse particle concentrations observed in Rome, with sometimes more than doubled $PM_{10}$ concentrations. Furthermore, aged aerosol with high sulfate, nitrate, and oxidized organics concentrations transported from Central and Eastern Europe to the Paris region caused strongly increased aerosol loadings in this city. On average, however, the fractional contributions of “home-made” and “advected” aerosols are of similar magnitude (“home-made” aerosols range from ca. 20–70% of the particulate matter, depending on, for example, meteorological conditions). This means that local activities typically do not dominate urban aerosol loadings within these two modern European cities. However, an important difference between Paris and Rome is their geographical locations: while in Paris, clean Atlantic air masses often result in low particulate matter levels, in Rome, Central and Eastern European air masses often alternate with Saharan outflow. Thus, in order to further improve air quality in such major urban agglomerations more than local efforts are required.

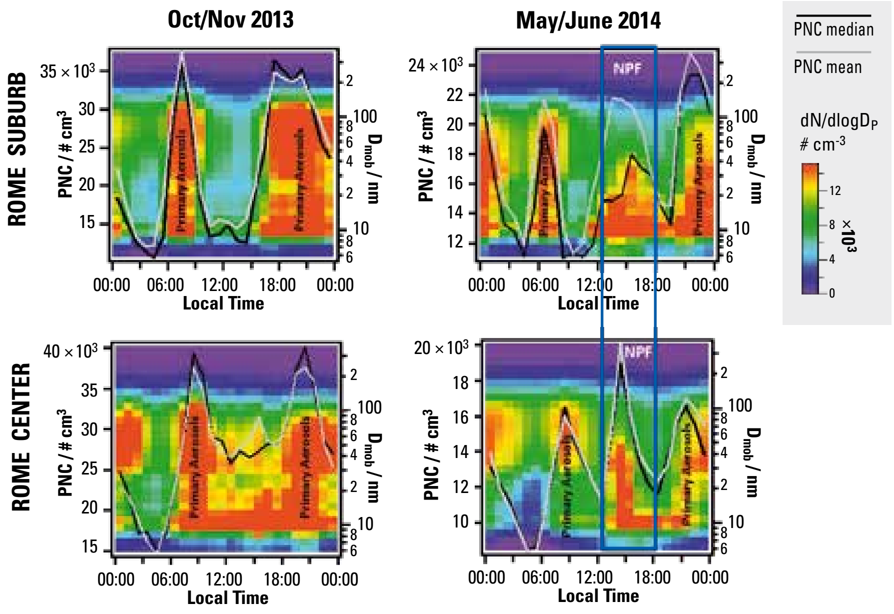

*Figure 2: Average diurnal particle number concentrations (PNC) and particle size distributions in Rome at different locations (top/bottom) and in different seasons (left/right), showing new particle formation (NPF) in the early afternoon in the warmer season.*

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# *AEROSOLS IN THE ARCTIC TROPOSPHERE: COMPOSITION, SOURCES, AND IMPACT ON CLOUD FORMATION*

**JOHANNES SCHNEIDER**

Credit: H. Bozem

> **"The Arctic lower atmosphere is warming significantly faster than the global average. Clouds and aerosol particles play an important role in this 'Arctic amplification' phenomenon."**

*Figure 1: Research aircraft Polar 5 and Polar 6, owned by the Alfred Wegener Institute (AWI), at Inuvik (Canada) during the mission "RACEPAC" in spring 2014 (Credit: Johannes Schneider).*

The Arctic has become focus of scientific interest as a result of measurements showing that lower tropospheric temperatures rose a factor of two faster than the global mean in the past 25 years, a phenomenon called "Arctic amplification". Between 1972 and today, the annual minimum sea ice extent has declined by about 40%. As a result, economic interest in the Arctic region has steadily increased. For example, by navigating the Northeast Passage, shipping routes from Europe to Asia will be shortened by roughly five thousand kilometers. Associated with growing commercial ship traffic are enhanced emissions, especially of particles (e.g., black carbon, metallic particles, primary organics) and particle precursor gases (e.g., sulfur dioxide, volatile organic compounds). Deposition of these particles onto snow and ice reduces the albedo, accelerating melting.

In order to assess the rise in atmospheric particulates resulting from increases in shipping, it is important to establish a baseline of emissions from currently known natural and anthropogenic inner-Arctic and extra-Arctic sources. An important extra-Arctic source of particles that impacts the Arctic are those originating from vegetation fires in the boreal forests of Siberia and Canada. The transport pathways for these particles are not yet fully understood. One reason is that the polar regions are partly isolated from lower latitudes by thermal stratification, because isentropic surfaces slope upward at higher altitudes. This phenomenon is known as the "Polar Dome," which at times prevents direct atmospheric transport from lower latitudes into the Arctic. One of the major inner-Arctic particle sources is thought to be the ocean, especially after sea ice melting in spring, when biological activity releases aerosol precursors from the ocean into the marine boundary layer.

The aerosol and cloud chemistry group operates state-of-the-art aerosol mass spectrometers to investigate the chemical composition of atmospheric aerosol particles. These instruments can be operated on research aircraft, allowing the study of aerosol properties at higher altitudes and over larger areas than ground-based measurements. We recently investigated transport and sources of aerosol particles as well as their chemical properties in Greenland, the Canadian Arctic, and Svalbard (POLARCAT, 2008; VERDI, 2012; RACEPAC, 2014; NETCARE, 2014; ACLOUD, 2017).

In general, concentrations of aerosol particles in the Arctic are low, especially in the lower altitudes, supporting the "Polar Dome" concept. However, above the Polar Dome, we found air masses with elevated particle concentrations. We analyzed the origins of these air masses using meteorological transport models, and they indicate transport from vegetation fires in Siberia and Canada. These high particle concentrations above the Polar Dome have been observed frequently, for example, during the POLARCAT mission out of Kangerlussuaq, Greenland, in summer 2008 (Schmale et al., 2011), but also during RACEPAC mission from Inuvik, Canada, in spring 2014.

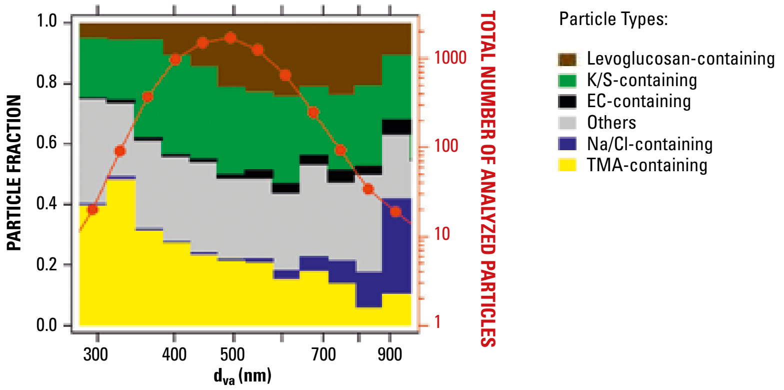

*Figure 2: Size-resolved single particle analysis of Arctic aerosol particles. The TMA (trimethylamine)-containing particles represent a biological marine inner-Arctic particle source, whereas the levoglucosan-containing particles indicate influence from biomass burning and long-range transport.*

In summer 2014 (mission NETCARE), we detected two important inner-Arctic marine biogenic sources of particles: methanesulfonic acid (MSA, Willis et al., 2016, 2017) and trimethylamine (TMA, Köllner et al., 2017), both of which are emitted through biological activity after the melting of the sea ice in summer. Such particles are highly water soluble, and thus is it very likely that they contribute to cloud formation. During the same mission, very small particle activation diameters were observed (Leaitch et al., 2016), indicating these Arctic biogenic particles can significantly aid in cloud formation. In a study during summer 2017 (ACLOUD, Svalbard), we investigated the impact of aerosol particles on cloud formation in more detail by sampling cloud particles using a counterflow virtual impactor. After sampling, this device evaporates the cloud water from the particles such that the cloud residual particles containing the original cloud condensation nucleus remains for analysis in the aerosol mass spectrometer. Particles of natural, biological origin (most likely from the ocean) were found in the cloud residuals, confirming the assumption that these particles possess a high cloud activation ability.

Future missions are planned to study the changing Arctic atmosphere, using the Alfred Wegener Institute´s (AWI) research aircraft Polar 5 and Polar 6, as well as HALO.

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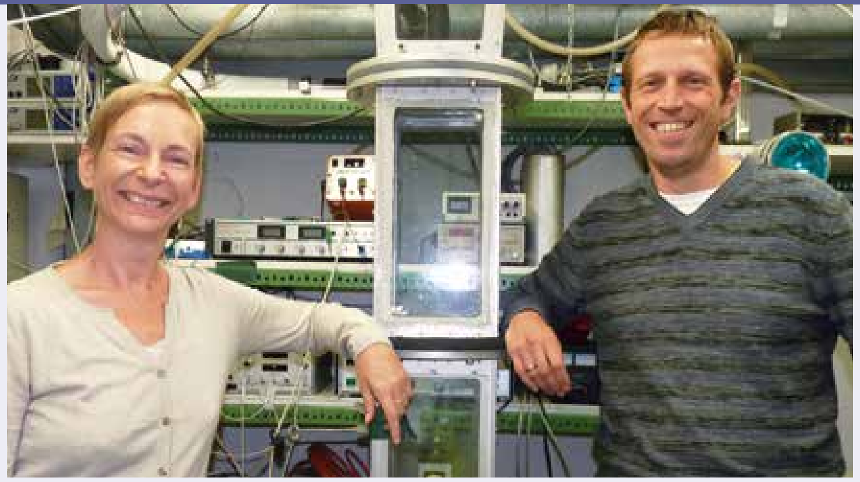
# LABORATORY AND NUMERICAL INVESTIGATION OF ICE NUCLEATION IN MIXED PHASE CLOUDS

**MIKLÓS SZAKÁLL AND KAROLINE DIEHL**



> **“The synergetic studies of laboratory and field measurements and numerical cloud modeling offer a crucial and unique possibility for understanding heterogeneous ice nucleation of different types of aerosols.”**

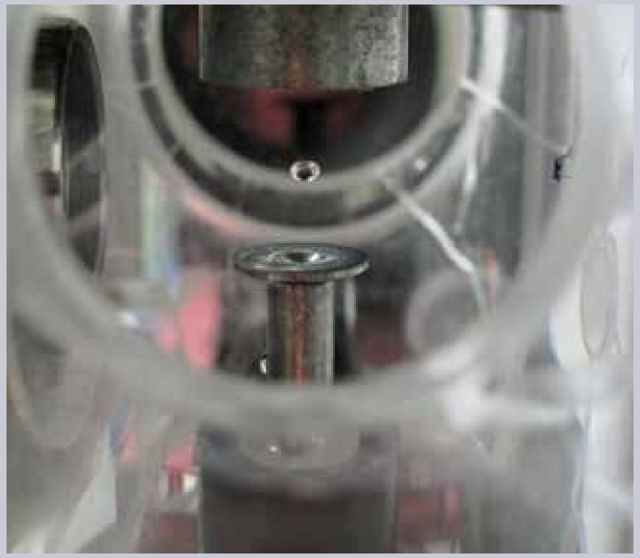


*Figure 1: A free floating 2 mm water droplet in the ultrasound wave field of the Mainz Acoustic Levitator. Credit: Amelie Mayer, JGU.*

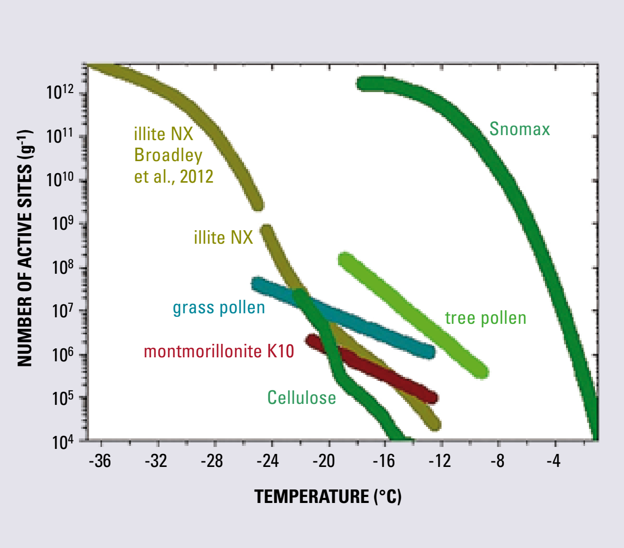


*Figure 2: Number of active sites per gram of ice nucleating particle material as function of temperature for several ice nucleating substances measured in the Mainz Acoustic Levitator and the Mainz Vertical Wind Tunnel. The parameterization of Broadley et al. (2012) for illite NX is also shown.*

## BACKGROUND

Mixed-phase clouds play a central role in generating precipitation, particularly in mid-latitudes. Hydrometeors – precipitation particles such as raindrops, graupel, and hailstones – are involved in a large number of microphysical processes during their lifetime inside clouds, the most important of which is ice nucleation. Our research group studies the heterogeneous nucleation of ice on various types of aerosol particles, including mineral dusts and biological particles, within the framework of the German DFG funded and coordinated research project INUIT (Ice Nuclei Research Unit). Our studies include laboratory investigations of immersion and contact freezing. Based on these and other experimental results from the INUIT consortium, process-related parameterizations are derived and incorporated into cloud models. Field measurements collected by Johannes Schneider’s group in the Particle Chemistry Department complement the laboratory and numerical studies conducted within INUIT.

## LABORATORY STUDIES

Immersion and contact freezing are considered the most important ice nucleation processes in mixed-phase clouds. Experimental studies have been carried out in the Mainz vertical wind tunnel laboratory in order to characterize these nucleation processes for different ice nucleating particles (INP) such as illite, feldspar, montmorillonite, cellulose, and bacteria.

Immersion freezing was investigated with two different experimental techniques, both attaining contact-free levitation of liquid droplets and cooling of the surrounding air down to about -28 °C. First, in the Mainz Acoustic Levitator (situated inside the walk-in cold room of our laboratory; see Figure 1), we investigated drops with diameters of 2 mm. Second, in the vertical air stream of the Mainz vertical wind tunnel, droplets with diameter of 700 µm were floated so that free atmospheric flow conditions were simulated. By repeating the experiments on many individual droplets, we determined the fraction of supercooled droplets that contain the INP and that do freeze. In this way, ice nucleation active sites (INAS) densities were derived (Figure 2) as function of temperature. The obtained INAS densities allowed direct intercomparisons among different measurement techniques within the INUIT community and a complete characterization of the efficiencies of the ice nucleating particles over wide ranges of temperature and INP particle concentrations. These parameters served as input for subsequent cloud modeling calculations.

The Mainz vertical wind tunnel is a unique platform for conducting contact freezing experiments. Supercooled water droplets were steadily floated in the vertical air stream while INP were injected into the tunnel upstream of their stationary position in the flow. As soon as a particle collides with the supercooled droplet, freezing is or is not initiated. From the time dependence of the freezing process the contact freezing probability of the droplets can be determined, if the collision rate is known. Further, from this quantity, immersion and contact freezing efficiencies for different types of aerosol particles can be directly compared. Our comparative studies on immersion and contact freezing experiments in the wind tunnel revealed that contact freezing under the given circumstances is the most effective ice nucleation mechanism.

## MODEL SIMULATIONS

Parameterizations of heterogeneous freezing for several INP types were included in a sectional microphysical scheme that describes all processes occurring during cloud and precipitation development. We used this scheme in two cloud models of different complexity: an adiabatic air parcel model and a 3D cloud model. Idealized convective clouds were investigated to demonstrate the impact aerosol particle concentrations and types as well as the active freezing modes have on ice formation and the initiation of precipitation.

The results indicate that immersion freezing with mineral dust particles is the most important process in convective clouds, although contact freezing is active at higher temperatures. However, contact freezing is limited by the availability of interstitial particles in the cloud. Biological particles show high ice nucleating efficiencies, but current understanding suggests that their amounts in atmospheric clouds are small in comparison to mineral dust. Precipitation initiated in convective clouds is modified via the formation of large ice particles that may be supported by direct freezing of large drops, by growth of pristine ice particles by riming, and by nucleation of large drops by collisions with pristine ice particles. The modification of precipitation depends on the active freezing modes, the fractions of active INP, and the chemical composition of the internal mixtures in the drops.

After the INUIT Research Unit ends in 2018, we will continue the experiments on large atmospheric ice particles (i.e., hail, graupel, and snow) as the Mainz vertical wind tunnel is the only facility of its kind in the world. We will primarily focus on major microphysical parameters, such as hydrometeor density and fall speed, and the role their melting plays in precipitation generation.

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# *NANO- AND MICROANALYTICAL STUDIES OF MATTER FROM SPACE AND EARTH*

**PETER HOPPE**

> **“Studying isotopic and mineralogical fingerprints of natural and synthetic materials: A tool to trace chemical and physical processes in space and on Earth.”**

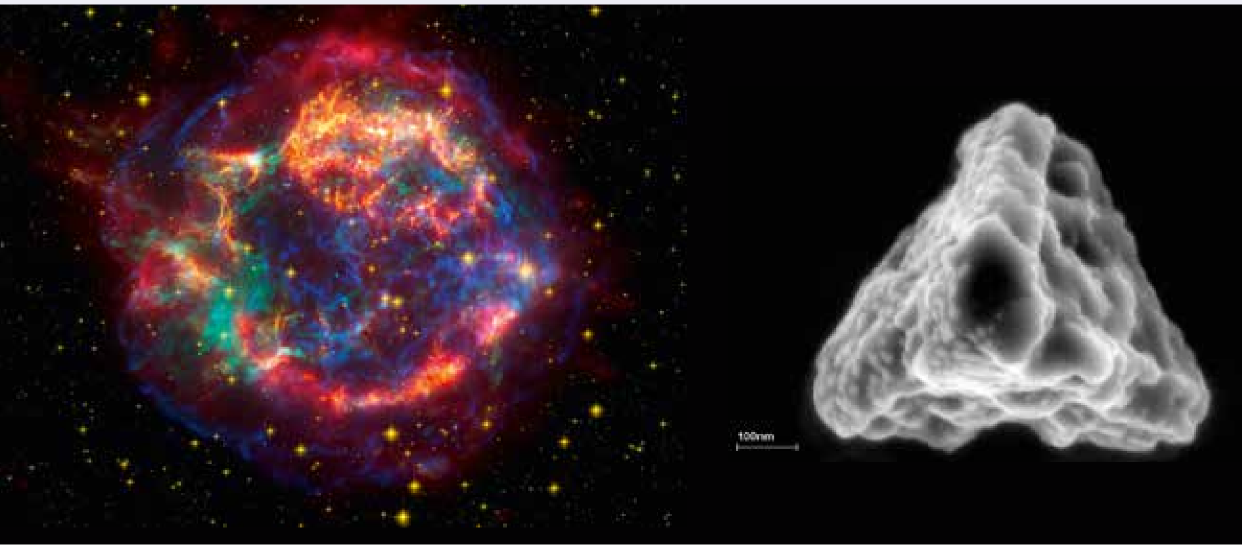

*Figure 1: (Left) Ejecta of supernova Cassiopeia A (Courtesy NASA/JPL-Caltech). (Right) Presolar SiC grain from the Murchison meteorite.*

## BACKGROUND

Dust plays an important role in space and on Earth. It is found around evolved stars, in interstellar and interplanetary space, in planetary materials, and in different places on Earth. Dust carries specific isotopic and mineralogical signatures that can be used to trace chemical and physical processes at the sites of dust formation or processing. To address this issue we studied a variety of extraterrestrial and synthetic materials as well as microfossils with different nano- and microanalytical analysis techniques, namely, nano secondary ion mass spectrometry (NanoSIMS), resonance ionization mass spectrometry (RIMS, in cooperation with the University of Chicago), and electron microscopy (SEM/EDX, TEM).

## RESULTS

*(i) Extraterrestrial Dust:* By studying isotopic compositions of stardust, so-called presolar grains, which are older than our solar system and which are found in small quantities in primitive meteorites, it is possible to get detailed insights into stellar nucleosynthesis and dust formation and to identify the types of parent stars. We developed a high-resolution ion imaging technique for our NanoSIMS ion probe that permits identification of presolar grains with sizes <150 nm in situ in meteoritic thin sections. Application of this technique showed that previous estimates of presolar grain abundances are at least a factor of two (by mass) too low (Figure 2; Hoppe et al., 2017) and that dust grains from supernova explosions are more abundant (~20 %) among presolar grains than inferred previously (Hoppe et al., 2015). From our studies it can be inferred that several percent of the interstellar dust in the interstellar cloud predating our solar system was stardust, making it an important initial ingredient in solar system formation. We identified a SiC supernova grain with an extremely high $^{12}C/^{13}C$ ratio of >20,000 (compared to ~90 on Earth), which is the highest ratio ever found in presolar grains. This ratio and Fe and Ni isotope data, as well as the polytypes of SiC supernova grains, provided important constraints for supernova models. Furthermore, we used abundances of presolar grains in different components of primitive meteorites to constrain thermal and aqueous alteration processes in the solar nebula and planetary bodies (Leitner et al., 2016).

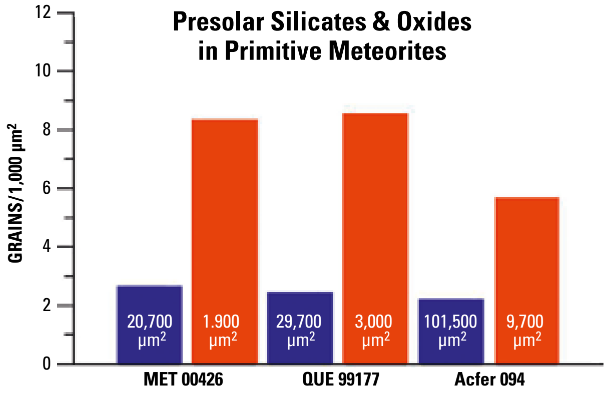

*Figure 2: Grain density of presolar silicates and oxides in three primitive meteorites. Conventional NanoSIMS ion imaging results are shown in blue, high-resolution results in red. The numbers inside the bars indicate the sizes of analyzed areas.*

*(ii) Terrestrial Nitrogen:* Nitrogen, the most abundant element in the terrestrial atmosphere, plays a key role in the evolution of Earth's biosphere. Recently, we started a thorough investigation of the various organic and inorganic nitrogen carriers in chondritic meteorites (Figure 3) to gain a detailed understanding of the origin of Earth's nitrogen, whose $^{15}N/^{14}N$ ratio is significantly lower (~40 %) than that of our Sun. Our first isotopic and mineralogical results suggest that ammonia-bearing ices were important sources of nitrogen on the early Earth (Harries et al., 2015). Beyond these studies of extraterrestrial materials, we developed methods to measure the N-isotopic ratio of nitrate and nitrite species with the NanoSIMS and to differentiate N-containing species commonly observed in atmospheric aerosol particles with micrometer or submicrometer resolution (Li et al., 2016).

*(iii) Microfossils:* In cooperation with the Climate Geochemistry Department, we recently began studies of elemental distributions of Ca, Na, Mg, Mn, Sr, and Ba in foraminifera shells at submicro-meter resolution using the NanoSIMS. These data will permit us to track important environmental parameters, such as ocean temperature and salinity, over the last thousands to millions of years.

## OUTLOOK

We will continue our nanoanalytical studies of different types of stardust from primitive meteorites. We will also continue and expand our studies of the early Earth (origin of Earth's nitrogen; Radioactive decay of $^{60}Fe$ as a potential heat source for melting of planetesimals) and of microfossils. Of particular importance for these studies will be the new oxygen primary ion source on our NanoSIMS that permits to conduct isotope and elemental abundance studies at smaller scales than was possible before.

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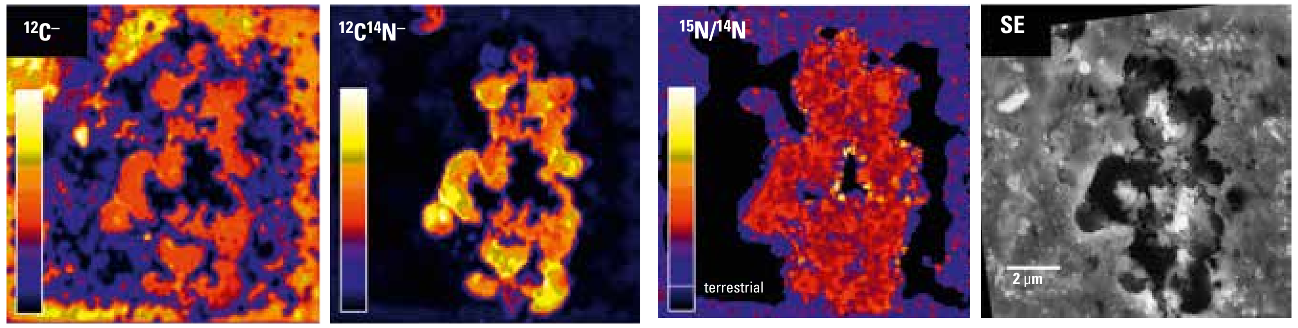
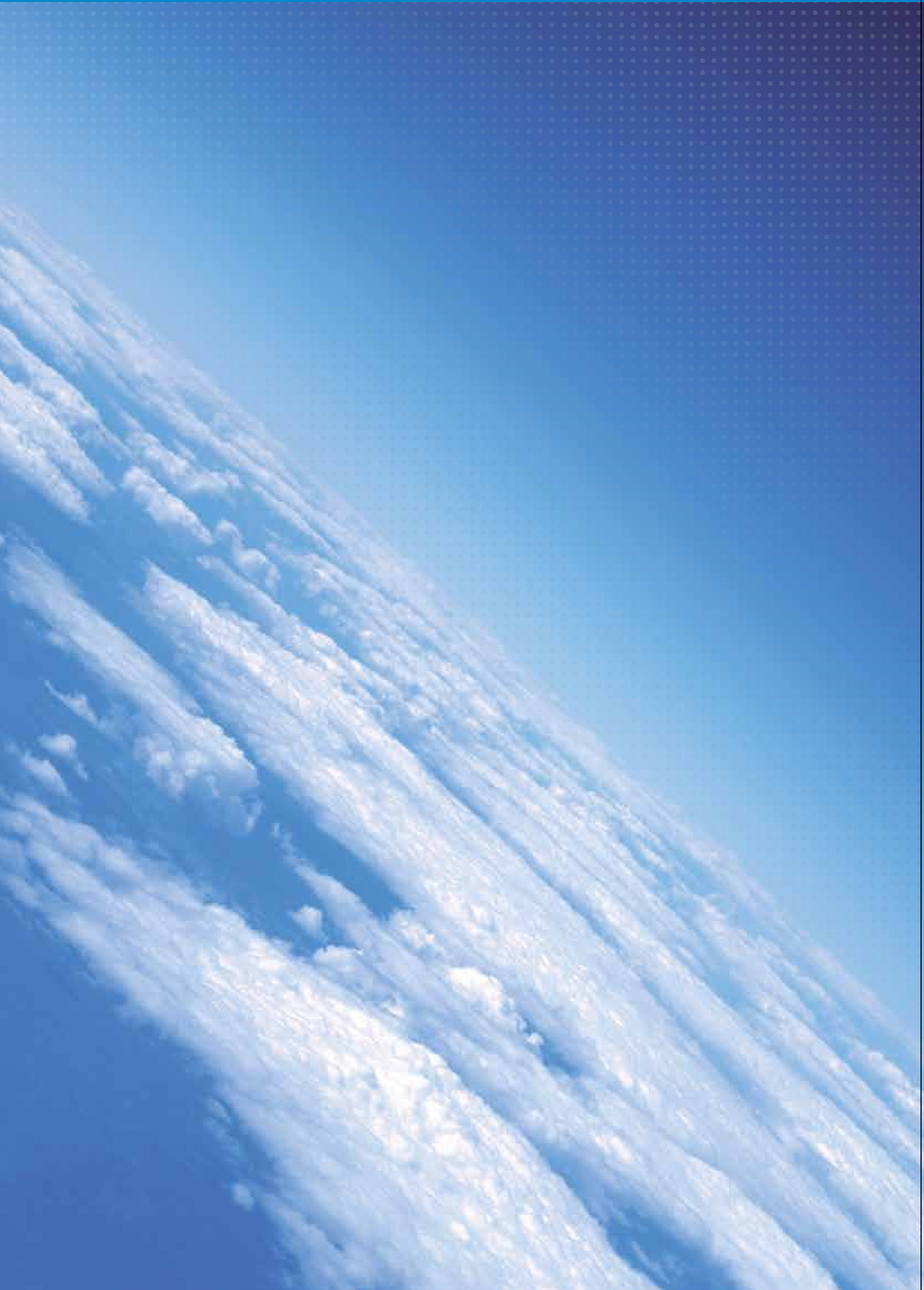


*Figure 3: A large aggregate of organic matter from the Renazzo meteorite. NanoSIMS ion images of $^{12}C$ and $^{12}C^{14}N$ are shown, together with a $^{15}N/^{14}N$ isotopic ratio image and a scanning electron (SE) image of the same sample region.*



# FURTHER RESEARCH GROUPS

## FURTHER RESEARCH GROUPS

Aerosols and regional air quality,
terrestrial palaeoclimates,
high pressure chemistry and physics,
and satellite remote sensing.

# *AEROSOLS & REGIONAL AIR QUALITY*

**YAFANG CHENG - MINERVA GROUP**

> **“We investigate the thermo-dynamics and molecular properties of nanoparticles, the role of multiphase chemical reactions in rapid haze formation, and the climate effects of atmospheric black carbon.”**

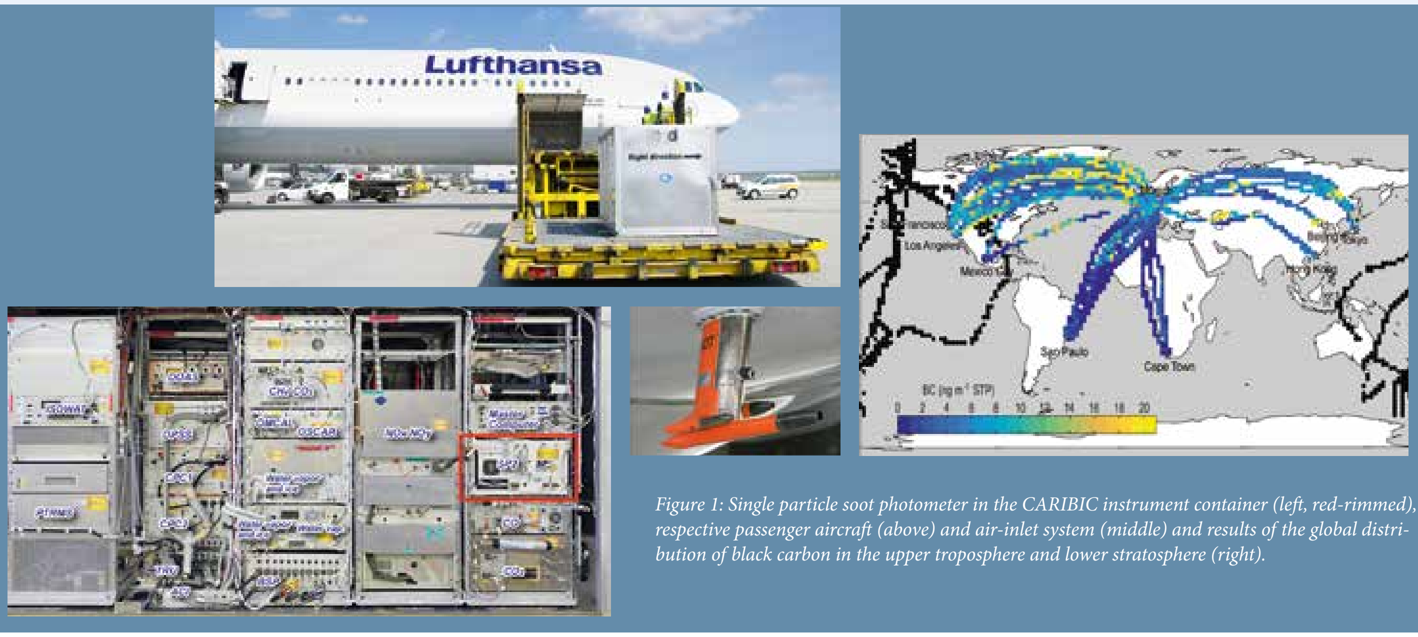


*Figure 1: Single particle soot photometer in the CARIBIC instrument container (left, red-rimmed), respective passenger aircraft (above) and air-inlet system (middle) and results of the global distribution of black carbon in the upper troposphere and lower stratosphere (right).*

## BLACK CARBON MEASUREMENTS ON A PASSENGER AIRCRAFT (CARIBIC-SP2)

Black carbon (BC) aerosols play an important role in regulating Earth´s climate due to their light-absorbing properties. The radiative forcing of BC particles is highly dependent on their vertical distribution; however, our current knowledge of this vertical distribution, especially in the upper troposphere and lower stratosphere, is very limited.

Since August 2014, we have been collecting large-scale and long-term measurements of black carbon in the free troposphere using a single particle soot photometer (SP2) carried by a passenger aircraft during the CARIBIC project. To date, more than 600 flight hours of data have been successfully collected through regular flights between Europe, North America, South America, and East Asia covering large areas of the Northern Hemisphere and part of the Southern Hemisphere. Our results provide new insights into the spatial distribution and mixing state of BC in the atmosphere and enable better estimations of its climate radiative forcing, which are currently under way.

## REACTIVE NITROGEN CHEMISTRY IN AEROSOL WATER AS A SOURCE OF SULFATE DURING HAZE EVENTS IN CHINA

Fine-particle pollution associated with winter haze threatens the health of more than 400 million people in the North China Plain. Sulfate is a major component of fine haze particles. Record sulfate concentrations of up to ~300 µg m$^{-3}$ were observed during the January 2013 winter haze event in Beijing. State-of-the-art air quality models that rely on sulfate production mechanisms requiring photochemical oxidants cannot predict these high levels because of the weak photochemistry activity during haze events. We find that the missing source of sulfate and particulate matter can be explained by reactive nitrogen chemistry in aerosol water. The aerosol water serves as a reactor, where the alkaline aerosol components trap $SO_2$, which is oxidized by $NO_2$ to form sulfate. High reaction rates are sustained by the high neutralizing capacity of the atmosphere in northern China. This mechanism is self-amplifying because higher aerosol mass concentration corresponds to higher aerosol water content, leading to faster sulfate production and more severe haze pollution.

## SIZE DEPENDENCE OF PHASE TRANSITIONS IN AEROSOL NANOPARTICLES

Phase transitions are of fundamental importance in aerosol science, but current understanding is insufficient to explain observations at the nano-scale. In particular, discrepancies exist between observations and model predictions of deliquescence and efflorescence transitions and the hygroscopic growth of salt nanoparticles. These discrepancies can be resolved by considering particle size effects with consistent thermodynamic data. We developed a new method for determining water and solute activities and interfacial energies in highly supersaturated aqueous solution droplets (Differential Köhler Analysis).

Our analysis reveals that particle size can significantly alter the characteristic concentration of phase separation in mixed systems, similar to the influence of temperature. Owing to similar effects, atmospheric secondary organic aerosol particles at room temperature are always expected to be liquid at diameters below ~20 nm. We thus propose and demonstrate that particle size should be included as an additional dimension in the equilibrium phase diagram of aerosol nanoparticles.

Further studies performed in close collaboration with Hang Su’s group in the Multiphase Chemistry Department provided new insights into aerosol-cloud interactions, the atmospheric budget of nitrous acid, and the properties of fluorescent aerosol particles.

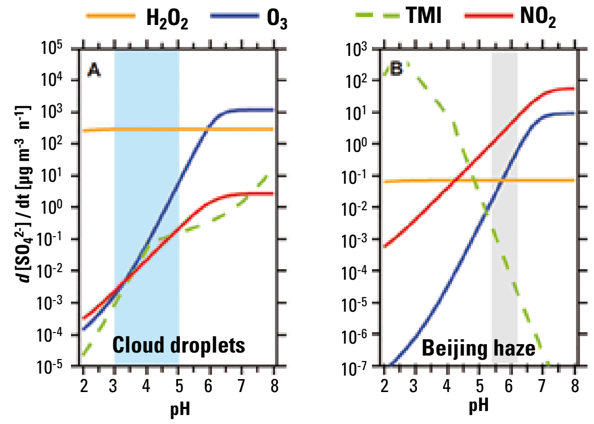


*Figure 2: Aqueous-phase production of sulfate by different pathways of sulfur dioxide oxidation under conditions characteristic for cloud droplets and Beijing haze droplets (Cheng et al., 2016).*

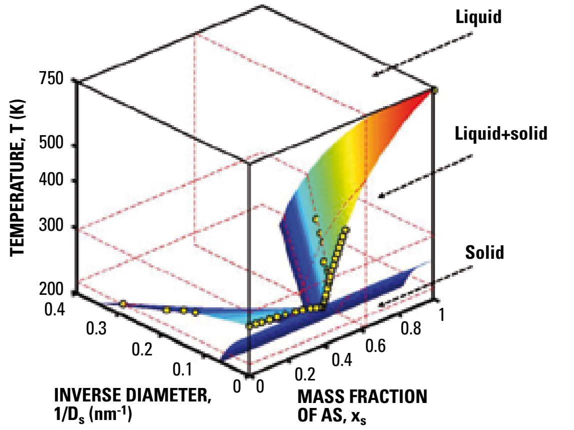


*Figure 3: Three-dimensional liquid–solid equilibrium phase diagram for the ammonium sulfate (AS) - water system as a function of inverse particle diameter, 1/Ds, temperature, T, and ammonium sulfate mass fraction, xs (Cheng et al., 2015).*

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# *HIGH PRESSURE CHEMISTRY AND PHYSICS*

**MIKHAIL EREMETS**

> **“Our aim is to achieve pressures greater than five million bar, at which point metallic hydrogen should become a high-temperature superconductor.”**

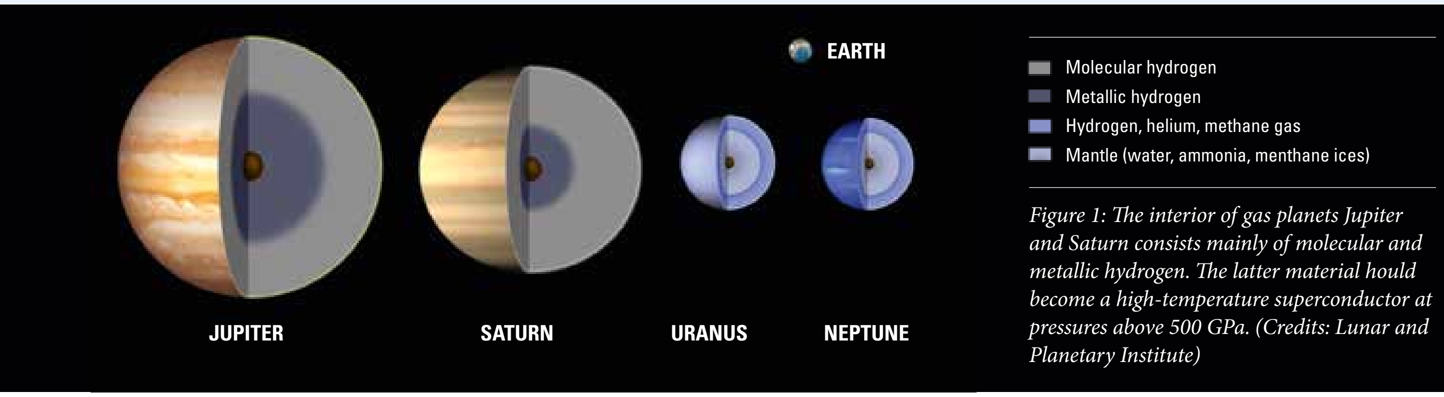

*Figure 1: The interior of gas planets Jupiter and Saturn consists mainly of molecular and metallic hydrogen. The latter material hould become a high-temperature superconductor at pressures above 500 GPa. (Credits: Lunar and Planetary Institute)*

Our group studies substances at extremely high record pressures. Such high pressure is a powerful tool that can dramatically change the properties of substances. Hydrogen is the most prominent example. In 1935, Wigner and Hungtinton predicted that insulating molecular hydrogen dissociates into an atomic metallic state at high pressures. Since then, compressed hydrogen has been of great scientific interest because of its remarkable properties, such as room temperature superconductivity. Study of metallic hydrogen is critically important to many areas of physics, including astrophysics, planetary science (Figure 1), and material science. As it turns out, achievement and theoretical description of metallic hydrogen is an extremely difficult problem. However, this big goal greatly stimulated development of high-pressure techniques, and recently we achieved required pressures of about 500 GPa. There is now dramatic progress in the theoretical understanding of compressed hydrogen. It was found that besides dissociation, another way of metallization is possible – in the molecular state, through gradual overlapping electronic bands. Current calculations are not precise enough to predict which way of metallization is preferable.

Our experiments indicate that hydrogen transforms to metal in the molecular state of pressure of 360 GPa when reflection of the sample significantly increases. At that pressure, hydrogen has poor electrical conductivity while showing metallic temperature dependence. With increasing pressure, electrical conductivity strongly increases approaching the values of metals (Figure 2). At the same time, hydrogen exhibits the molecular state as the Raman spectra of the molecular phase persist. Our conclusion that the molecular hydrogen is semimetal at pressures above 360 GPa is consistent with the recent theoretical works showing that the metallization happens through closing of an indirect band gap in molecular hydrogen at pressure of 350 GPa. At pressures above 440 GPa we measured only Raman spectra up to the record 480 GPa, and observed that the Raman signal gradually disappears, indicating transformation into a good molecular metal or its dissociation to an atomic state. We are close to reach the superconducting state of hydrogen, but more effort is needed to reach pressures above 500 GPa and provide electrical and optical measurements at these pressures.

While studying hydrogen, it is reasonable to search for superconductivity in hydrogen-dominant materials such as $SiH_4$ (Aschcroft 2004). It is likely that this material and many others can achieve the high critical temperatures of superconductivity ($T_c$) for the same reasons as pure hydrogen: high-frequency phonons and strong electron-phonon coupling but the pressure of metallization is much lower. Indeed, we have found that hydrogen sulfide is a superconductor, with the record $T_c$ =203 K at 150 GPa (Figure 3). Superconductivity in hydrogen sulfide is well established from studies of the electrical conductivity, Meissner effect, infrared and Raman spectroscopy, and structure. This superconductivity is well described in terms of the Bardeen–Cooper–Schrieffer (BCS) theory, which in turn, opens great opportunity in searching for new candidates with very high $T_c$. Moreover, the BCS-Eliashberg theory does not restrict the upper limit for $T_c$ and allows the existence of the room temperature superconductivity. Following this theory, compounds that have high frequencies of phonons in addition to strong bonding of hydrogen atoms, are the best candidates. In this respect, not only hydrides but carbon-based materials are also very promising for high $T_c$. Thus, the high-temperature superconductivity discovered and studied in our group has established new ways to design new high-temperature superconductors and ultimately find a room temperature superconductor.

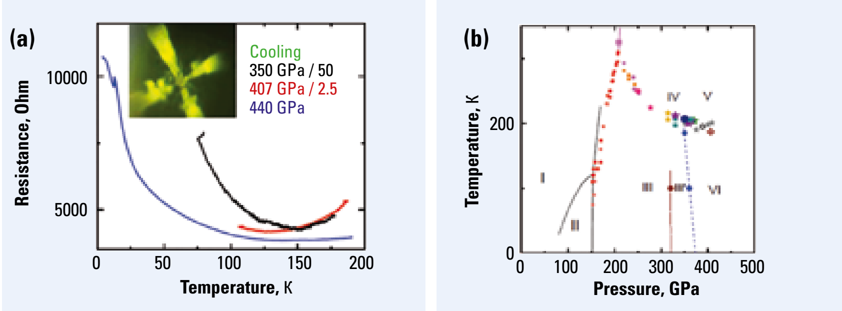

*Figure 2: (a) Temperature dependence of resistance of hydrogen at different pressures. Photo: Hydrogen sample in the center with four attached electrical leads. (b) The phase diagram of hydrogen. I-VI domains of different phases of hydrogen. VI indicates domain of metallic hydrogen.*

Additionally, we are working on related topics. Carbon as an element is central to human societies as fuel, to Earth's climate in terms of greenhouse gases, and to life itself as part of all biologically relevant molecules. Yet, it is estimated that up to 90% of Earth's carbon is located in its interior, well out of reach for field studies and direct measurements. As a result, the chemical and physical behavior of carbon-containing compounds inside Earth is still largely unknown, uncharted territory that can be explored by high-pressure studies in our group. In cooperation with the group of Jonathan Williams, we found that, contrary to conditions of ambient pressure and common belief, carbonic acid ($H_2CO_3$) is a significant component in aqueous $CO_2$ solutions above 2.4 GPa and 110 °C – conditions at subduction zones at 85 km depth in Earth. This is highly significant for speciation of deep C–O–H fluids. Knowledge of speciation in and interactions of deep carbon-containing fluids is essential for the understanding of the global carbon cycle and its evolution from the times of the early, pre-life Earth to its present form.

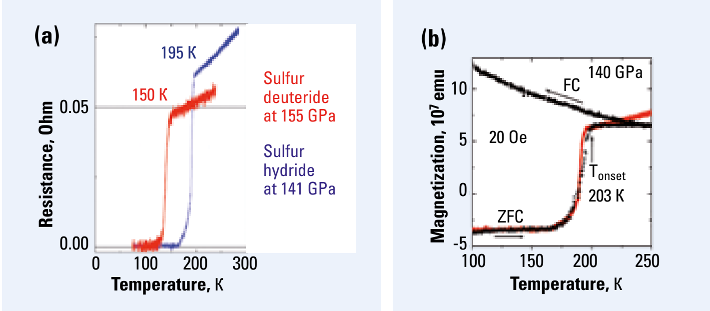

*Figure 3: High temperature superconductivity in sulphur hydride. (a) Typical superconductive steps for sulphur hydride (blue trace) and sulphur deuteride (red trace). (b) Temperature dependence of the magnetization of sulphur hydride at a pressure of 155 GPa in zero-field cooled (ZFC) and 20 Oe field cooled (FC) modes (black circles). The onset temperature is $T_{onset}$ =203 K. For comparison, the superconducting step obtained for sulphur hydride from electrical measurements at 145 GPa is shown by red circles. Resistivity data ($T_{onset}$ =195 K) were scaled and moved vertically to compare with the magnetization data.*

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# TERRESTRIAL PALAEOCLIMATES

**KATHRYN FITZSIMMONS**

> **“We aim to generate quantitative data for past climatic change in continental Central Asia, far from marine and ice core records.”**

*Figure 1: Impressions of fieldwork in Kazakhstan (L-R): continuous sampling by abseil at Remizovka; Group members probe 80 m of climate archives at Charyn Canyon; luminescence dating samples are collected in light-proof steel tubes at Remizovka (Credits: Charlotte Prud’homme).*

Central Asia lies at the core of the largest and most populous continent on Earth – Eurasia. However, we know little about its role in global climate dynamics. This lack of knowledge is largely because we have yet to recognize the full potential of Eurasia’s most widespread, and valuable, archive for past environmental change: wind-blown dust, or loess. Long sequences of primary loess and loess soils blanket Eurasia and record responses to past climatic changes over at least the last million years. Central Asian loess deposits are particularly sensitive to the interplay between three major Northern Hemisphere climate subsystems: the North Atlantic temperate latitude westerlies, polar fronts, and Asian monsoons. Ongoing uplift of the Asian high mountains has also affected the climate of the Central Asian basins, driving aridification. In spite of its key position at the transition between major climate subsystems, the climatic history – and trajectory – of arid Central Asia remains largely unknown.

In regions such as the Chinese loess plateau and Danube basin of Europe, the link between loess deposition and climate is relatively straightforward: loess accumulation intensifies during cold phases of mountain glacier advance, and decreases and is overprinted by soil formation under relatively milder climates. Our initial work on Central Asian loess suggests that the climatic link here is more complex. The glaciers of the Asian high mountains respond more to changes in precipitation than temperature, whereas loess accumulation rates increase both during glacial advance under warmer, wetter climates, as well as during cold periods. Our group aims to disentangle this link by quantitatively reconstructing past temperature, precipitation, and seasonality, and placing these data within robust chronological frameworks for correlation with global palaeoclimate events. These reconstructions will, in turn, enable us to elucidate the variability and intensity of the dominant climate subsystems over the region through time.

In order to improve our understanding of climate dynamics in the terrestrial zone, we need high-resolution, quantitative palaeoenvironmental records that can be placed within reliable chronological frameworks for comparison with other records. Existing data for past environmental conditions in loess are strongly geographically biased toward the North Atlantic and Asian monsoonal regions with little information for Central Asia. Furthermore, quantitative proxies for past continental temperature, precipitation, and seasonality are in developmental stages. Recently developed climate proxies based on bacterial and plant lipid biomarkers within marine sediments have the potential to be developed for terrestrial sediments such as loess, as do proxies based on the stable isotope compositions of biogenic and soil carbonates. One major focus of our group will be to develop and apply these powerful new, quantitative climate proxies to the Central Asian loess, in collaboration with the Climate Geochemistry Department.

Our other focus is to generate chronologies for our geochemical results using the combined techniques of palaeomagnetism, cosmogenic burial dating and luminescence dating. The latter method measures the time elapsed since sediments were last exposed to sunlight, and we will investigate the application of luminescence to proxy materials such as plant silicates, so developing new chronologic tools which furthermore directly date the proxy itself.

Our group was established in early 2017, and is therefore still in its infancy. During our first field campaign to southeast Kazakhstan, we continuously sampled two sedimentary sequences, 25 m and 80 m thick, that provide high-resolution, long palaeoclimatic archives. Plans for a second campaign to southern Tajikistan in 2018 are underway; we visited Tajikistan in July with view to selecting appropriate sampling sites and have signed a cooperation agreement with key partners.

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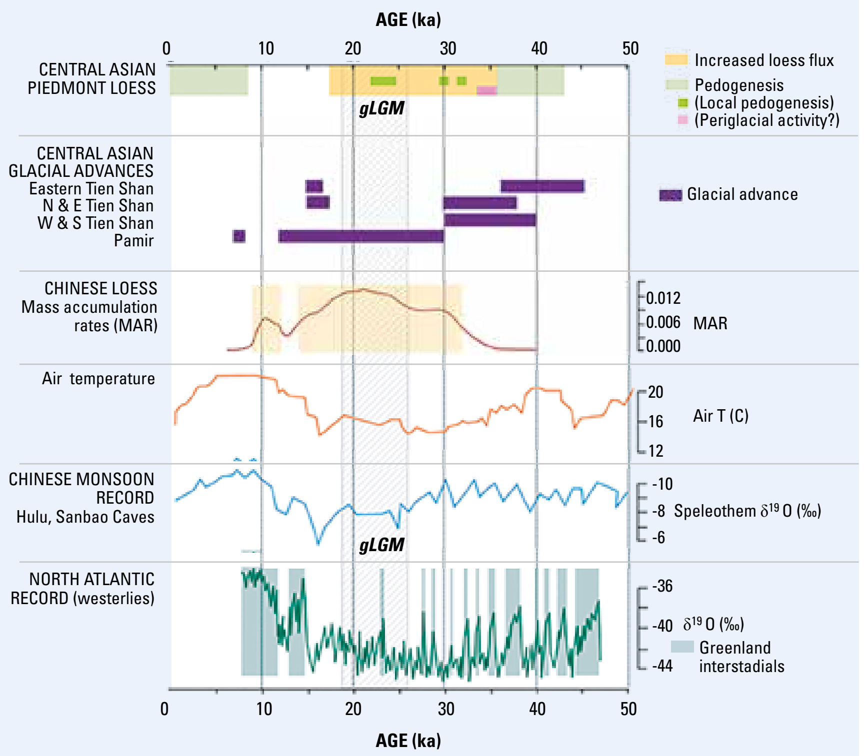
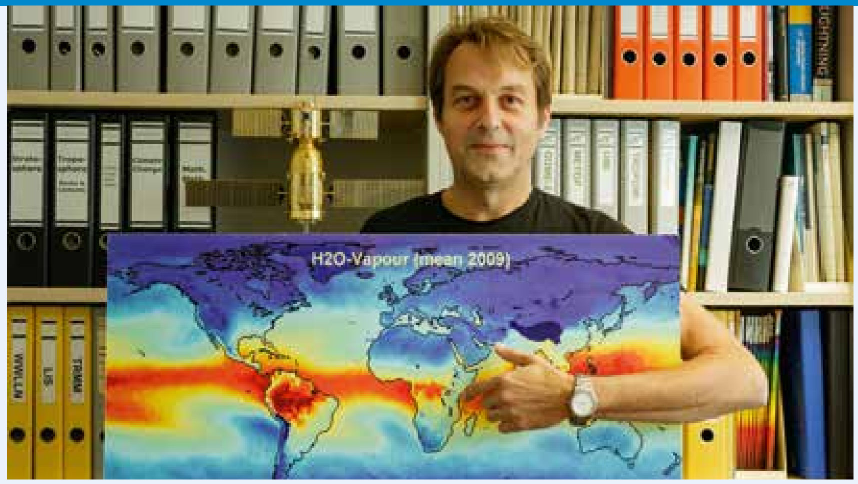


*Figure 2: Central Asian loess dances to a complex tune: increased loess accumulation (top) only sometimes links with glacial expansion (purple); we will generate records to better identify links with the Asian monsoon (blue) and North Atlantic westerly systems (dark green).*

# SATELLITE REMOTE SENSING

**THOMAS WAGNER**



> **“Satellite instruments provide the view from outside.”**

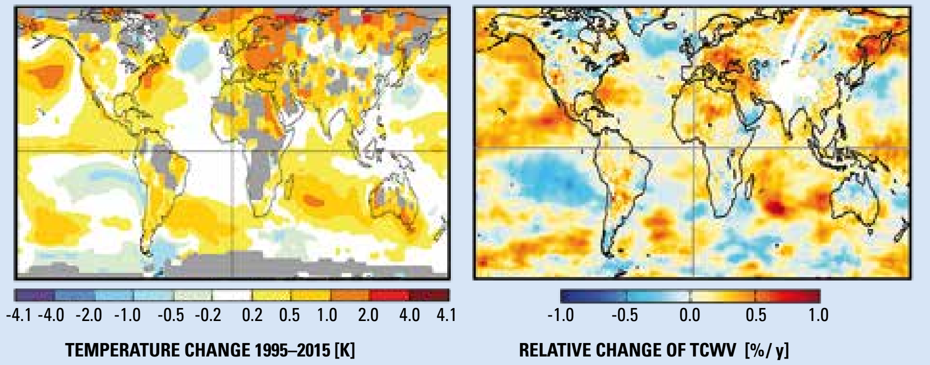


*Figure 1: Left: Trends of the surface temperature (in K per two decades) from the GISS Surface Temperature Analysis (NASA Goddard Institute for Space Studies). Right: Trends of the TCWV (in % per year) derived from our satellite analysis. The missing data over Asia result from gaps of GOME-1 Earth observations due to instrument calibration measurements.*

## INTRODUCTION

The research activities of the Satellite Remote Sensing Group focus on the exploitation of the spectral information gathered from ultraviolet/visible satellite instruments such as the Global Ozone Monitoring Experiment (GOME) on ERS-2 and its successors. In additon to information about trace gases, data on clouds, aerosols, and surface properties are retrieved from the satellite data and studied in our group. Satellite observations are usually very stable, making the obtained data sets very well suited for global trend studies. However, the merging of time series collected by different satellite instruments is a great challenge (see case study below).

## GLOBAL TRENDS OF THE ATMOSPHERIC WATER VAPOR COLUMN

We developed an algorithm to determine total column water vapor (TCWV) from satellite observations in the red spectral range. Compared to other spectral ranges, measurements in the red spectral range have two main advantages: they cover the whole globe and they are sensitive to the whole atmospheric column down to Earth’s surface. We retrieve TCWV from three satellite instruments: GOME-1 (1995–2003), SCIAMACHY (2002–2012), and GOME-2 (2006–present). Although we used exactly the same settings for the analysis of the satellite spectra in our study, there remain systematic differences in the retrieved TCWV from different satellite sensors, mainly due to different ground pixel sizes, swath widths, and overpass times. To correct for these differences, our group developed sophisticated algorithms, taking into account the specific properties of the individual instruments (for details see Beirle et al., 2017). As a result, we obtained a consistent global TCWV data set that currently covers more than 20 years and will be continuously extended by the measurements of the GOME-2 instrument and its successors (until about 2025). Our satellite product has a somewhat coarse temporal (monthly means) and spatial (1° × 1°) gridding, but it is very well suited for trend studies. By comparing observations from radiosondes and GNSS networks to our data set, it has been shown that our data set is stable within ±1% per decade.

To determine trends, we applied the following fit to the time series of TCWV in each 1° x 1° grid box:

$$TCWV(t) = c + b\cdot t + a_{12}\cdot \sin(2\pi\frac{i_{month}}{12} + p_1)$$
$$+ a_6\cdot \sin(2\pi\frac{i_{month}}{6} + p_2) + \sum_i f_i\cdot index_i(t)$$

Here, c and b represent an offset and linear trend, respectively. The sin functions describe the seasonal and half-seasonal cycles (with $i_{month}$ the number of the month and the $p_1$ and $p_2$ the respective phases). The sum contains the time series of different teleconnection indices and correpsonding fit coefficients $f_i$: El Niño-Southern Oscillation (ENSO), North Atlantic Oscillation (NAO), Pacific Decadal Oscillation (PDO), Pacific North American Pattern (PNA), and the Quasi-Biennial Oscillation (QBO). The scaling factors of all terms are determined simultaneously during the fit process.

Figure 1 compares the global patterns of the derived relative trends for TCWV between 1995 and 2015 to the trends of surface temperature obtained from GISS (https://data.giss.nasa.gov/gistemp/maps/). The GISS data set is based on station data over land and satellite data over ocean. Over most of the globe, similar positive or negative trend patterns are found in both data sets, with the largest positive trends over eastern Europe and northeasterm Asia, and the largest negative trends over the southeastern Pacific and the North Atlantic. Overall, the observed trends of surface temperature and TCWV are consistent with the Clausius-Clapeyron relationship that predicts an increase of the TCWV of about 6 % to 12 % per 1°C temperature increase.

Figure 2 presents the time series of the different teleconnection indices and the corresponding spatial patterns obtained from the fit to the TCWV data. Systematic patterns for all teleconnections are evident. The ENSO phenomenon represents the strongest pattern: systematic positive and negative patterns can be seen over the whole globe.

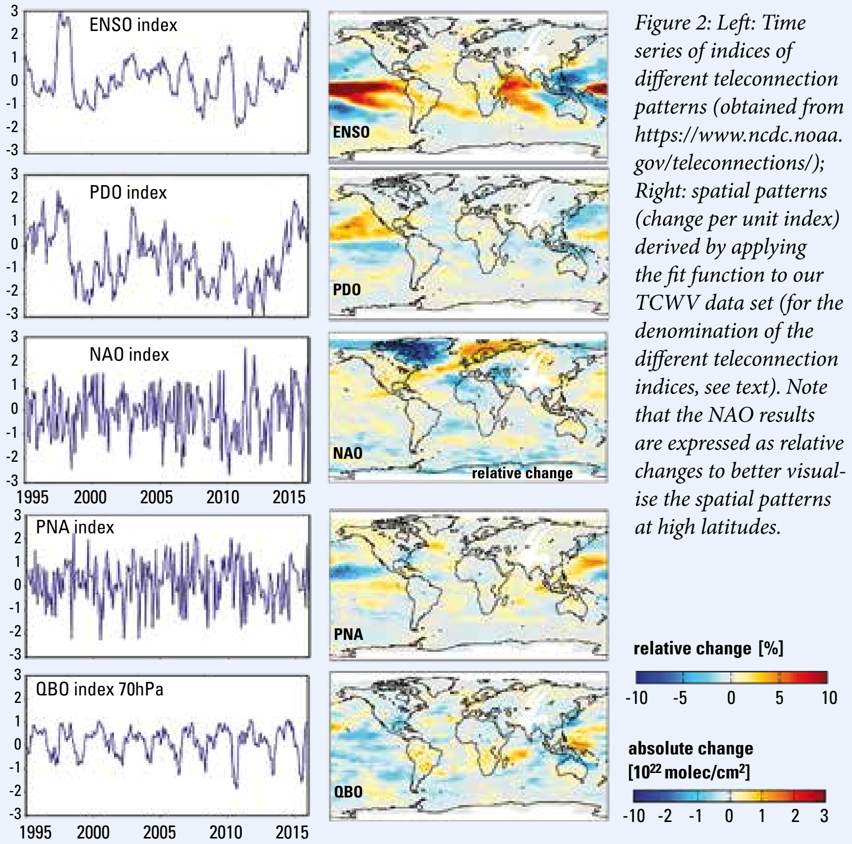


*Figure 2: Left: Time series of indices of different teleconnection patterns (obtained from https://www.ncdc.noaa.gov/teleconnections/); Right: spatial patterns (change per unit index) derived by applying the fit function to our TCWV data set (for the denomination of the different teleconnection indices, see text). Note that the NAO results are expressed as relative changes to better visualise the spatial patterns at high latitudes.*

## OUTLOOK

Our future work will focus on the relationship between the trends of TCWV and surface temperature in more detail, including the investigation of changes of circulation patterns. In addition, we will apply our trend model (see equation above) to results from atmospheric models. The comparison with the results for the satellite measurements will provide insights into how well these models represent real climate phenomena.

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# *JOINT SERVICES*

JOINT SERVICES

Administration, information technology, instrument development and electronics, workshops, facility management and communications.

The **Joint Services** assist the scientific research departments and groups in practical matters and maintain the Institute's infrastructure: administration, information technologies (IT), instrument development and electronics, mechanical workshops, facility management, and communications.

## ADMINISTRATION

We provide economic, legal, and organizational support for the research at the Max Planck Institute for Chemistry. This involves the personnel administration of approximately 330 employees, implementation and monitoring of procurement policies, administrative execution of projects and third-party funding, bookkeeping and accounting of the Institute's budget, and accounting of travel expenses. Consequently, the administration is divided into the areas Human Resources, Purchasing and Finances. Associated with the Institute's administration are all provision and support facilities, including the facility management.

As the Institute is part of the Mainz Research Alliance, a network of universities, scientific institutions, and companies located in and around Mainz, the administration maintains contact with management at those institutions and collaborates through this network to keep current with science policy and general developments in science management.

In 2017, MPIC contracted with International SOS, a worldwide operating firm for medical and travel security service, to provide the best possible care on excursions, especially with regard to the AQABA campaign in summer 2017.

## INFORMATION TECHNOLOGIES (IT)

We ensure the smooth operation of the IT infrastructure at the Institute in Mainz as well as for outside operations. Five staff members support the daily computer work of approximately 300 users, with over 600 clients and network devices and a wide range of operating systems. Our team manages all physical and virtual servers necessary for working at the MPIC, as well as services and network installations. Major changes over the last three years include the migration of the file service to a parallel file system with a tape library for hierarchical storage management (HSM) and backup. The new file service offers a high throughput and currently up to one petabyte of online storage.

Since 2013, the IT group has been supporting research outside the Institute building, for example, the Amazon Tall Tower Observatory (ATTO) in the Brazilian rainforest. Due to ATTO's remote location, a reliable Internet connection is absolutely necessary. It is not only used for the automated transfer of data or the remote monitoring of instruments, but also for communication, which can be life-saving in the event of accidents. The steadily growing number of instruments and thus of data requires a steady adjustment of IT infrastructure. Due to extremely IT-hostile conditions in the rainforest, on-site maintenance is now part of the day-to-day business of the IT group.

We also support non-stationary missions such as the HALO campaign OMO in 2015 or research cruise AQABA in 2017. An individual concept is developed for each campaign, based on the scientific requirements. A new network infrastructure (LAN and WLAN) with Internet access via satellite has been istalled for the AQABA campaign, as well as a firewall and a local file service. In addition, the IT team writes programs for the automatic storage and efficient transfer of measured data.

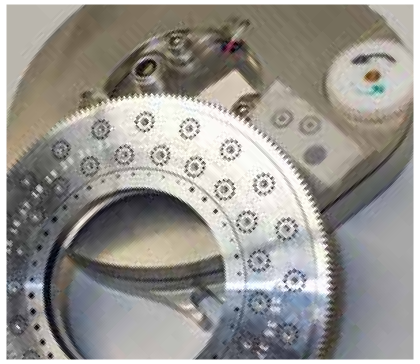
## INSTRUMENT DEVELOPMENT AND ELECTRONICS

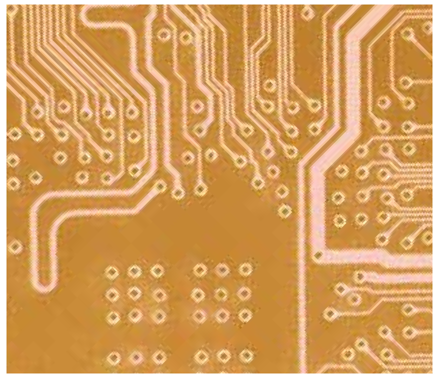
Scientific projects and missions such as HALO, ATTO or AQABA require precise measurement devices that are not always commercially available or must be modified. These instruments have to comply with stringent requirements, for usage on board of satellites, aircraft, or ships. Together, the instrument development and electronics group, Institute’s scientists, engineers, and workshop staff discuss specific instrumentation needs such as air or water inlet systems for analytical instruments, which are then developed and produced in house.

Professional CAD software, the latest software development environments, and unique infrastructure such as a fully automated surface mount dispense-, pick-and-place-system and the newly built EMI measurement chamber enables us to design, produce, and verify electronic and electromechanical components at a level well above professional solutions.

Within the last couple of years, the focus of our work has shifted from development and manufacturing of electronic components, process controllers, and system-to-application level software toward the full design, simulation, realization, and verification of instrumentation subsystems as well as complete instruments not available commercially. Worldwide field campaign support is included for our researchers.

A wide range of key projects realized in the last three years demonstrates the versatility of the Instrument Development Group. For example, we developed and implemented a fully automated miniature aerosol mass spectrometer (MiniAMS) for the CARIBIC measurement project on a commercial airliner; improved inlet pressure regulation and delayed extraction mechanisms for the ERICA instrument operated on the Russian Geophysica research aircraft; designed and supervised the building of the complete power system for the research sailing vessel Eugen Seibold, which is currently under construction; developed a stabilized optical system for differential optical absorption spectroscopy (DOAS) operation on board research ships (AQABA); implemented a fully temperature, pressure, and humidity conditioned STXM Environmental Micro-Reactor for in situ X-ray absorption analysis of single aerosol particles; and designed and constructed an infrared camera detection system for a new developed Twin Ice Nucleation Assay (TINA).



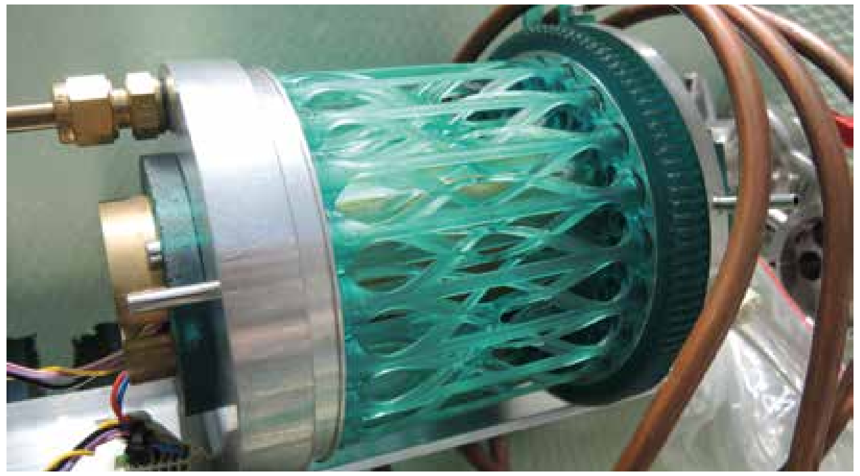


## MECHANICAL WORKSHOPS

We contribute to the development of scientific instruments as well as to the maintenance of the Institute’ infrastructure, closely collaborating with researchers, the instrument development and electronics group, and the facilities management.

Our highly qualified workshop staff performs a wide range of operations, such as welding of high-quality materials, bracing of special metals, and electroplating. We also apply new technologies; for example, two 3D printers are being used for additive production of light and high-complexity workpieces that cannot be realized with conventional CNC machines.

The Institute has been training apprentices in the mechanical workshop since 1949. The apprentices not only craft practice pieces, they also carry out practical machining tasks for the scientific departments. In addition, they are trained in CNC techniques, pneumatics/hydraulic systems, and welding technology, partly through attending interinstitutional courses. The technicians, who train for their qualification in the instrument development and electronics group, are also provided with a basic education in metal techniques.



## FACILITY MANAGEMENT

We maintain the Institute´s infrastructure and take care of all building equipment including the high tech ventilation and temperature control systems for laboratories and clean rooms. As a team we are also devoted to supply a proper work environment by taking over responsibility for areas ranging from general care taker services to the inspection of all electrical equipment. In addition, our unit is also responsible for the reception desk and the arrival of goods.

## COMMUNICATIONS

According to a recent survey, 58% of the Germans are interested in science and technology and the majority believes they personally profit from research (Wissenschaftsbarometer.de, 2017). Interestingly, climate and energy (40%) as well as health and nutrition (39%) are considered the most important fields for future research activities.

Because the Max Planck Institute for Chemistry is publicly funded, our outreach program actively responds to general community interest in science. Our outreach activities target the media and the public equally, through dissemination of press releases and information on social media platforms, interacting with the public and showcasing our research at exhibits at local events, and opening the Institute to public visits.

In terms of media outreach, from 2015 to present, the Institute has published more than 50 press releases, often in close cooperation with the MPG central press department and other institutions such as the Johannes Gutenberg University Mainz. The press releases have resulted in numerous articles and reports in national and international newspapers, magazines, and radio and television shows. One release from May 2016 in particular attracted media and political attention. Entitled “Climate-exodus expected in the Middle East and North Africa“, it was based on the 2016 paper by Lelieveld et al. in the journal Climate Change titled “Strongly increasing heat extremes in the Middle East and North Africa (MENA) in the 21st century“.

In terms of public outreach, the Institute regularly presents its research activities to a broad audience, including the inhabitants of Mainz and the surrounding area. Many Institute members participate in local activities such as the annual science fair (Mainzer Wissenschaftsmarkt) in the heart of the city. The joint exhibition of the MPIC and the Mainz University Medical Center on chemical aspects of allergies and food intolerances in 2016, was extremely well attended. In 2017, an exhibit about research at the ATTO site in the Amazon rainforest and a “cloud aquarium”, presented in cooperation with the Institute for Atmospheric Physics of the JGU, was used to help communicate the importance of clouds in the Earth system. This exhibit was also shown at the huge fair on the occasion of the “Tag der Deutschen Einheit” (Day of German Unity) in Mainz and attracted several hundreds of guests.

At regular intervals, the Institute opens its doors and invites the public to observe authentic research and interact with scientists. In 2016, more than 1,000 people visited our laboratories and learned about Earth studies from our researchers.

Additionally, the Institute hosts several groups of visitors every year, including school children, such as the nationwide Girls' Day that aims to encourage girls to enter scientific and technical professions.

Our team facilitates communication and exchange across the Institute. It is responsible for public relations, internal communication, support for visiting scientists and guests, the supervision of school internships, the graphics office, and the library.

# *STAFF & BUDGET*

In December 2016, a total of about 330 persons worked at the Institute, among them 101 scientists, 75 PhD students and 10 apprentices. 36% of the staff were female, 64% male.

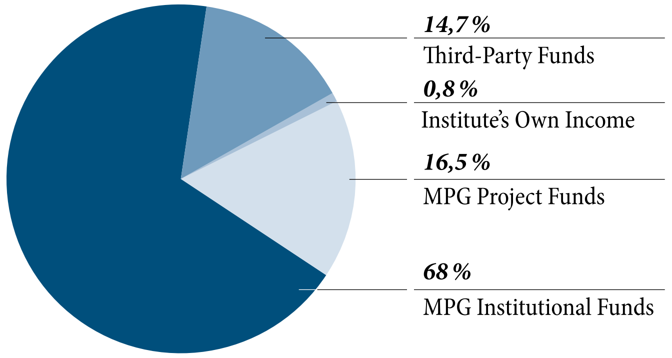
218 staff members were paid from institutional funds, 35 scientists were paid from third-party project funding and 60 from scholarships and graduate schools.

The annual budget of the Institute is approximately € 25 million. A major fraction derives from MPG institutional funds provided by federal and state governments. An overview of revenues and expenditures is given below.

The Institute has been certified according to the berufundfamilie audit. This audit supports companies and organizations in implementing family-friendly staff politics. As a strategic management tool, it serves to reconcile work and family. In accordance with the principles of the Max Planck Society, the Max Planck Institute for Chemistry supports its employees in their diverse life models. We offer family-friendly working conditions for women and men.

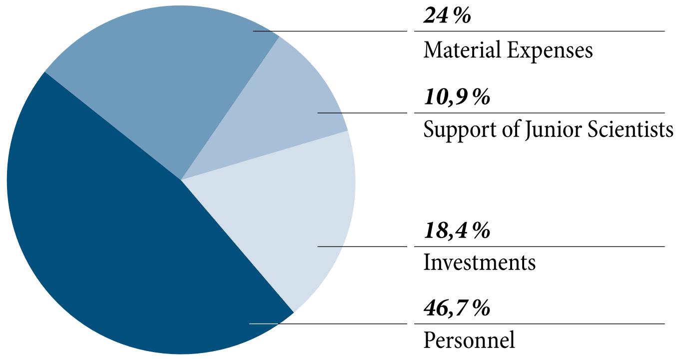
### REVENUES 2016

Percentage distribution excluding construction activities.



### EXPENDITURES 2016

Percentage distribution excluding construction activities.



# GLOSSARY

**ACLOUD**
Arctic Cloud Observation Using airborne measurements during Polar Day

**ACRIDICON-CHUVA**
Aerosol, Cloud, Precipitation, and Radiation Interactions and Dynamics of Convective Cloud Systems; Chuva is Portuguese word for rain

**AIRTOSS-ICE**
AIRcraft TOwed Sensor Shuttle Inhomogeneous Cirrus Experiment

**ALABAMA**
Airborne Laser Ablation Aerosol MAss Spectrometer

**AMA**
Asian Monsoon Anticyclone

**AMS**
Aerosol Mass Spectrometer

**AN**
Alkyl-Nitrates

**AOD**
Aerosol Optical Depth

**AQABA**
Air Quality and Climate Change in the Arabian Basin

**ATAL**
Asian Tropopause Aerosol Layer

**ATHAM**
Active Tracer High Resolution Atmospheric Model

**ATIs**
Amylase/Trypsin Inhibitors

**ATTO**
Amazonian Tall Tower Observatory

**AWI**
Alfred Wegener Institute

**BC**
Black Carbon

**BCO**
Barbados Cloud Observatory

**BCS theory**
Bardeen-Cooper-Schrieffer theory

**Beachon-RoMBAS**
Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, $H_2O$, Organics & Nitrogen – Rocky Mountain Biogenic Aerosol Study

**BEXIS**
Biodiversity Exploratories Information System

**BIOCOMBUST**
Biomass Combustion

**BMPO**
5-tert-Butoxycarbonyl-5-methyl-1-pyrroline-N-oxide

**BT**
Backward Trajectory

**BVOCs**
Biogenically Emitted Volatile Organic Compounds

**CAFE**
Chemistry of the Atmosphere: Field Experiment

**CALIPSO**
Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations

**CAMS**
Copernicus Atmosphere Monitoring Service

**CARIBIC**
Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container

**CCN**
Cloud Condensation Nuclei

**CDP**
Cloud Droplet Probe

**CI**
Criegee Intermediates

**CIP**
Cloud Imaging Probe

**CMIP**
Coupled Model Intercomparison Project

**CN**
Condensation Nuclei

**COPAS**
Condensation Particle Counter System

**CO**
Carbon Oxide

**$CO_2$**
Carbondioxide

**COS**
Carbonyl Sulfide

**CPC**
Condensation Particle Counter

**C-ToF-AMS**
Compact Time-of-Flight Aerosol Mass Spectrometer

**DACCIWA**
Dynamics-Aerosol-Chemistry-Cloud Interactions in West Africa

**DAMP**
Damage-Associated Molecular Patterns

**DDT**
Dichlorodiphenyltrichloroethane

**DIAPASON**
Deseart-dust Impact on Air Quality through model-Predictions and Advanced Sensors ObservatioNs

**DKRZ**
Deutsches Klima-Rechenzentrum (German Climate Computing Centre)

**DLR**
Deutsches Zentrum für Luft- und Raumfahrt (German Center for Aeronautics and Space)

**DOAS**
Differential Optical Absorption Spectroscopy

**ECHAM**
EC HAMburg based on ECMWF model

**EARS**
East African Rift System

**ECMWF**
European Centre for Medium-Range Weather Forecasts

**ELF**
Epithelial Lining Fluid

**ELISA**
Enzyme-Linked Immunosorbent Assay

**EMAC model**
The ECHAM/MESSy Atmospheric Chemistry model

**EMeRGe**
Effect of Megacities on the Transport on the Transport and Transformation of Pollutants on the Regional to Global Scales

**ENSO**
El Niño – Southern Oscillation

**EOSDIS**
Earth Observing System Data and Information System

**EPR**
Electron Paramagnetic Resonance

**ERICA**
ERC Instrument for Chemical Composition of Aerosols

**ERC**
European Research Council

**ERS-2**
European Remote Sensing Satellite 2

**ESRP**
Earth System Research Partnership

**EURYI**
European Young Investigator Award

**FAAM**
Facility for Airborne Atmospheric Measurements

**FACS**
Fluorescence-Activated Cell Sorting

**FAPs**
Fluorescent Aerosol Particles

**FP**
Framework Program

**FRP**
Fire Radiative Power

**GC-MS**
Gas Chromatography – Mass Spectrometry

**GEOROC**
GEOchemistry of Rocks of the Oceans and Continents

**GFAS**
Global Fire Assimilation System

**GFMC**
Global Fire Monitoring Centre

**G/IG cycles**
Glacial/Interglacial Cycles

**GISS**
Goddard Institute for Space Studies

**GISTEMP**
GISS Surface Temperature Analysis

**GOME**
Global Ozone Monitoring Experiment

**GPP**
Gross Primary Productivity

**GWDG**
Gesellschaft fur Wissenschaftliche Datenverarbeitung Göttingen (Organization for Scientific Data Processing)

**HALO Aircraft**
High Altitude Long Range Research Aircraft

**HALOHOLO**
High Altitude Long Range Research Aircraft

**HAMOCC5**
HAMburg Ocean Carbon Cycle Model 5

**HAPACO**
High Altitude Particle COllector

**HCHO**
Formaldehyde

**HeLa Cells**
Cell line derived from cancer cells taken from HEnrietta LAcks in 1951

**HONO**
Nitrous Acid

**HOx**
Hydrogen Oxide Radicals (OH, $HO_2$) **HPLC**
High-Pressure Liquid Chromatography

**HSPDP**
Hominin Sites and Paleolakes Drilling Project

**HyPHOP**
Hydrogen Peroxide and Higher Organic Peroxide monitor

**IAGOS**
In-service Aircraft for a Global Observing System

**IBAIRN**
Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen Budget

**IBBI**
Interdisciplinary Biomass Burning Initiative

**ICDP**
International Continental Scientific Drilling Program

**IFM**
Integrated Fire Management

**IGAC**
International Global Atmospheric Chemistry

**iLEAPS**
Integrated Land Ecosystem – Atmosphere Process Study

**IN**
Ice Nuclei

**INM**
Ice Nucleating Macromolecules

**INPA**
Brazilian National Institute for Amazonian Research

**IPA**
Institute for Physics of the Atmosphere

**IPCC**
Intergovernmental Panel on Climate Change

**ISPE**
Interstellar Preliminary Examination

**JGU**
Johannes Gutenberg-Universität (Johannes Gutenberg University Mainz)

**KWG**
Kaiser-Wilhelm-Gesellschaft (Kaiser Wilhelm Society)

**LA-ICP-MS**
Laser Ablation Inductively Coupled Plasma Mass Spectrometry

**LANCE**
Land, Atmosphere Near-real-time Capability for EOS

**LPS**
Lipopolysaccharides

**LS**
Lower Stratosphere

**MAVERT**
Mainz Vertical Wind Tunnel

**MESSy**
Modular Earth Submodel System

**MINA**
Mono-Plate Ice Nucleation Assay

**ML-CIRRUS**
Mid-Latitude-Cirrus

**MODIS**
Moderate Resolution Imaging Spectroradiometer

**MoLa**
Mobile Laboratory for Atmospheric Research

**MOM**
Methoxymethyl acetal

**MPG**
Max-Planck-Gesellschaft (Max Planck Society)

**MPGC**
Max Planck Graduate Center

**MPIC**
Max Planck Institute for Chemistry

**MXL**
Mixed Layer Model

**NAMIP**
Nano and Microparticle Research Group

**NanoSIMS**
Nano-scale Secondary-Ion Mass Spectrometry

**NAO**
North Atlantic Oscillation

**NETCARE**
NETwork on Climate and Aerosols: Adressing Key Uncertainities in Remote Canadian Environments

**NOAA**
US National Oceanic and Atmospheric Administration

**NOTOMO**
NOcturnal Chemistry of the Taunus Observatory

**NOx**
Nitrogen Oxides (NO, $NO_2$)

**NPF**
New Particle Formation

**OH**
Hydroxyl Radical

**OMO**
Oxidation Mechanism Observations

**ORACLE**
Organic Aerosol Composition and Evolution in the Atmosphere

**PAH**
Polycyclic Aromatic Hydrocarbons

**PAMP**
Pathogen-Associated Molecular Patterns

**PBL**
Planetary Boundary Layer

**PCB**
Polychlorinated Biphenyl

**PCD**
Particle Chemistry Department

**PCGS**
Paul Crutzen Graduate School

**PD**
Privatdozent (Associate Professor)

**PDO**
Pacific Decadal Oscillation

**PEPCO**
Phosphoenolpyruvate carboxylase

**PIP**
Precipitation Imaging Probe

**PM**
Particulate Matter

**PMOC**
Pacific Meridional Overturning Circulation

**PN (PAN)**
Peroxy(acetyl) Nitrate

**PNA**
Pacific North American Pattern

**PNC**
Particle Number Concentrations

**POA**
Primary Organic Aerosols

**POLARCAT**
Polar Study Using Aircraft, Remote Sensing, Surface Measurements and Models of Climate, Chemistry, Aerosols and Transport

**PRR**
Pattern Recognition Receptors

**PSC**
Polar Stratospheric Clouds

**PTR-MS**
Proton Transfer Reaction Mass Spectrometry

**QBO**
Quasi-Biennial Oscillation

**qPCR**
Quantitative Polymerase Chain Reaction

**RACEPAC**
Radiation-Aerosol-Cloud Experiment in the Arctic Circle

**RECONCILE**
Reconciliation of essential process parameters for an enhanced predictability of arctic stratospheric ozone loss and its climate interactions

**RIMS**
Resonance Ionization Mass Spectrometry

**RNS**
Reactive Nitrogen Species

**ROI**
Reactive Oxygen Intermediates

**ROOH**
Organic Peroxides

**ROS**
Reactive Oxygen Species

**RubisCO**
Ribulose-1,5-bisphosphate carboxylase

**RV**
Research Vessel

**SCIAMACHY**
SCanning Imaging Absorption spectrometer for Atmospheric CHartographY

**SEM/EDX**
Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy

**SFG Spectroscopy**
Sum Frequency Generation Spectroscopy

**SOA**
Secondary Organic Aerosol

**SP**
Soot Photometer

**SPI**
Science-Policy Interface

**STRATOCLIM**
Stratospheric and Upper Tropospheric Processes for Better Climate Predictions

**STXM-NEXAFS**
Scanning Transmission X-Ray Microscopy with Near Edge X-Ray Absorption Fine Structure

**TCWV**
Total Column Water Vapor

**TDLAS**
Tunable Diode Laser Absorption Spectroscopy

**TEM**
Transmission Electron Microscopy

**THP-1**
Tohoku Hospital Pediatrics 1 (Cell Line)

**TINA**
Twin-Plate Ice Nucleation Assay

**TLR4**
Toll-Like Receptor 4

**TMA**
Trimethylamine

**TNM**
Tumor-Node Metastasis System

**TRIHOP**
TRISTAR and HyPHOP

**TRISTAR**
Tracer In-situ TDLAS for Atmospheric Research

**TSP**
Total Suspended Particulates

**UHSAS**
Ultra High Sensitivity Aerosol Spectrometer

**UNFCCC**
United Nations Framework Convention on Climate Change

**UNISDR**
UN International Strategy for Disaster Reduction

**UT**
Upper Troposphere

**VERDI**
Vertical Distribution of Ice in Arctic Clouds

**VERTICO**
VERtical COlumn

**VOCs**
Volatile Organic Compounds

**WCRP**
World Climate Research Programme

**WFPS**
Water-Filled Pore Space

**WIBS**
Wideband Integrated Bioaerosol Spectrometer

**WMO**
World Meteorological Organization

**WRF Chem**
Weather Research, Forecast and Chemistry

**XRF**
X-Ray Fluorescence

**ZOTTO**
Zotino Tall Tower Observatory

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Stefan Weber (p 110)
Ulrike Weis (p 67)
Stefan Wolff (p 46 left, 49, 50 left)

p: page; All others if not stated separately: author of the respective article.

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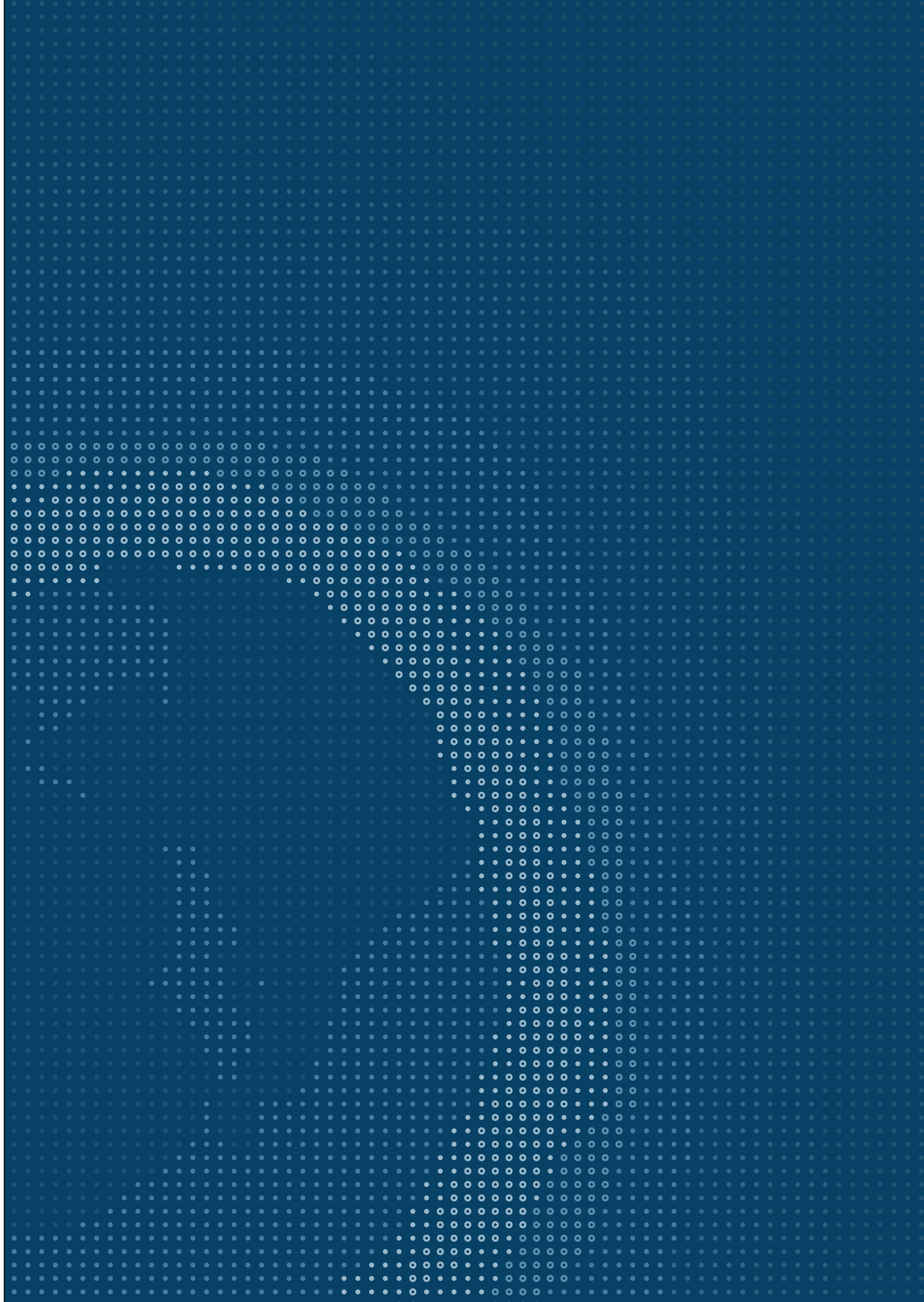

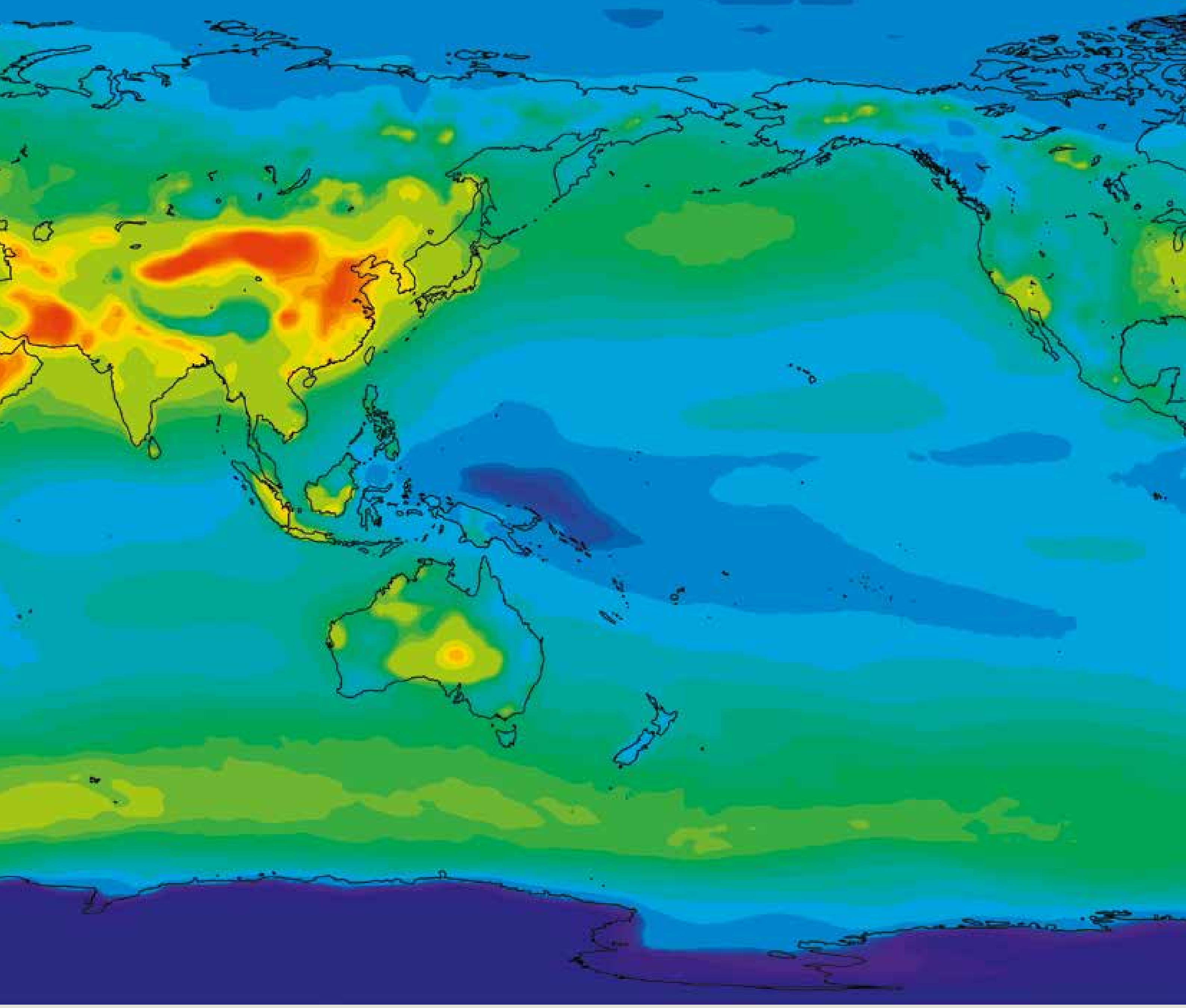

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