MAX PLANCK INSTITUTE
FOR CHEMISTRY

SCIENTIFIC REPORT
2012–2014

MAX-PLANCK-GESELLSCHAFT

MAX PLANCK INSTITUTE
FOR CHEMISTRY

Atmospheric Chemistry · Biogeochemistry · Multiphase Chemistry · Particle Chemistry

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CONTENT

PREFACE

The Max Planck Institute for Chemistry celebrated its centennial anniversary in 2012. This anniversary provided an opportunity to contemplate not only the successful history but also the future perspectives of our Institute. A dedicated lecture series, exhibition, and publication illustrated the wide scope of chemical research covered and advanced by the scientific members, departments and groups of the Institute, ranging from classical organic and inorganic chemistry, via radiochemistry, nuclear physics, cosmochemistry and various other fields to the current main research direction of Earth System chemistry.

The benefits of free scientific evolution, following the Harnack principle and traditions of the Max Planck Society, are well reflected by the achievements of the Institute's members, which include groundbreaking discoveries and method developments, large publication and citation impact, and numerous awards and recognitions. The overarching aim of the Institute's research today is the integral understanding of chemical processes in the Earth System from climate to public health and from molecular to global scales.

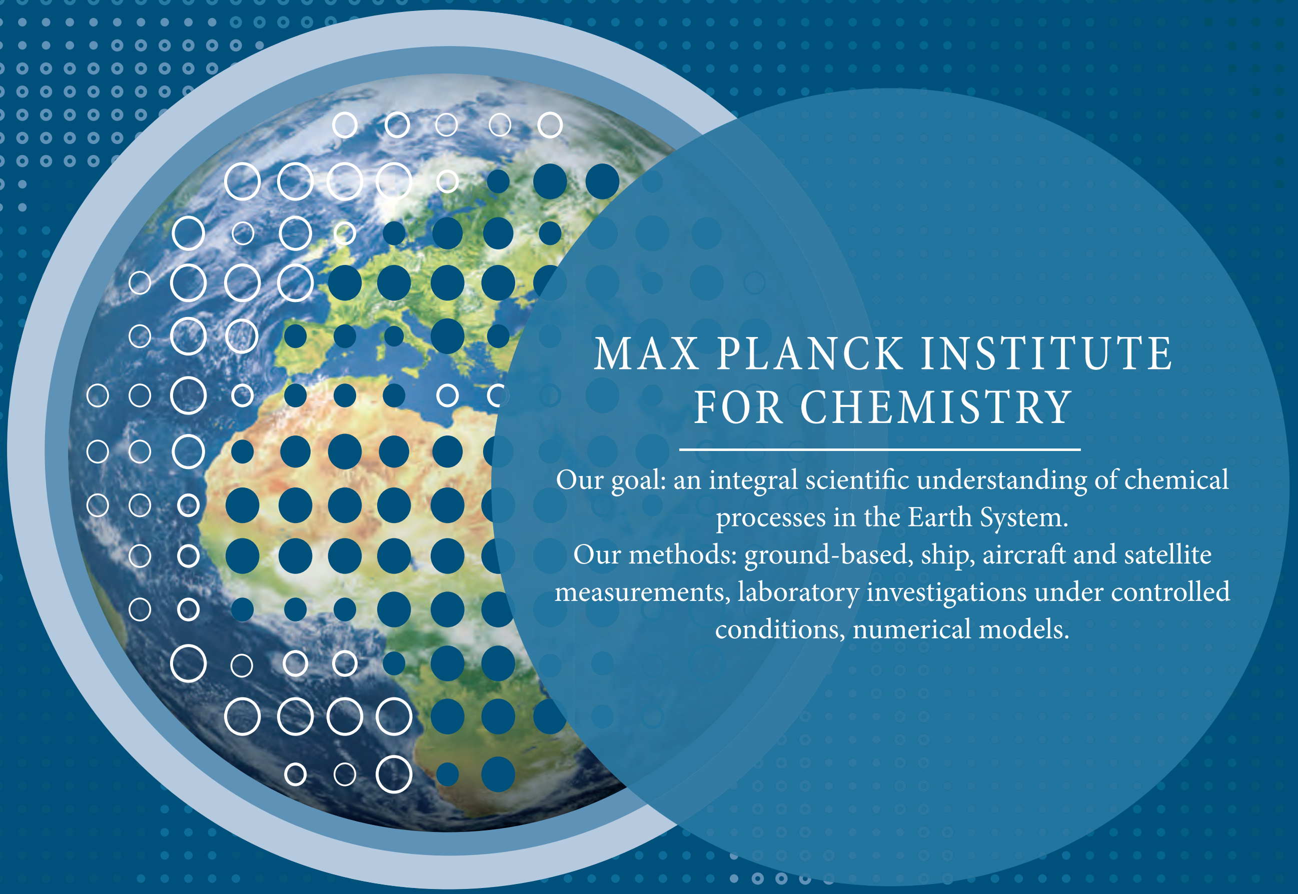
Complementary to the preexisting departments of Atmospheric Chemistry, Biogeochemistry, and Particle Chemistry, the Multiphase Chemistry Department newly established in 2012 is focusing on the chemical mechanism, kinetics, and role of interactions between gases, liquids and solid matter in the interplay of climate, life and health, such as the influence of air pollutants on clouds and precipitation as well as on inflammatory and allergic diseases.

For the present era of globally pervasive and steeply increasing human influence on planet Earth, the Institute's latest Nobel laureate Paul Crutzen has coined the term Anthropocene. This term and related concepts are intimately linked to recent and ongoing research at our Institute, and they bear great potential for the holistic perception and constructive handling of the challenges of global environmental change. Accordingly, one of the highlights of the year 2013 was the Anthropocene Symposium on the occasion of Paul's 80th birthday, where renowned international scientists, political representatives, and Institute members gathered and discussed related issues.

To foster fundamental understanding and to enable robust predictions of future developments of the Earth System, it is essential to gain further insight into the role of chemistry in climate change and Earth history. In this context the launch of a new department in the field of Climate Geochemistry will strengthen our Institute as well as the Earth System Research Partnership (ESRP) with the Max Planck Institutes for Biogeochemistry and Meteorology and further partners. We are excited that Gerald Haug will join us next year to establish the new department, and we look forward to welcoming him and his team to the Max Planck Institute for Chemistry.

Ulrich Pöschl, Managing Director
December 2014

GENERAL INFORMATION

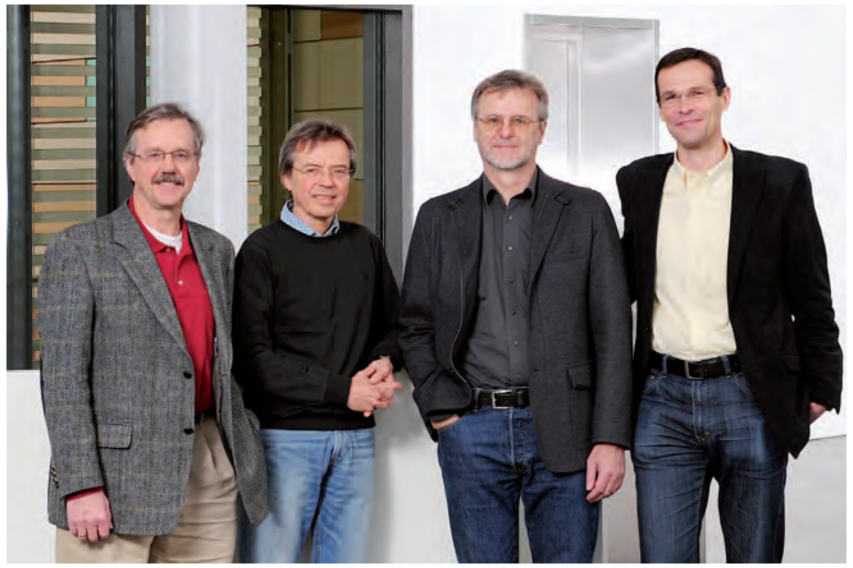


MAX PLANCK INSTITUTE FOR CHEMISTRY

Our goal: an integral scientific understanding of chemical processes in the Earth System.
Our methods: ground-based, ship, aircraft and satellite measurements, laboratory investigations under controlled conditions, numerical models.

OBJECTIVES AND ORGANIZATION

CURRENT RESEARCH AT THE MAX PLANCK INSTITUTE FOR CHEMISTRY AIMS AT AN INTEGRAL UNDERSTANDING OF CHEMICAL PROCESSES IN THE EARTH SYSTEM, PARTICULARLY IN THE ATMOSPHERE AND BIOSPHERE.



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

Investigations address a wide range of interactions between air, water, soil, life and climate in the course of Earth history up to today's human-driven epoch, the ***Anthropocene***. Scientists conduct laboratory experiments, collect samples and data during field campaigns utilizing airplanes, ships, and vehicles. The practical work is complemented by mathematical models that simulate chemical, physical, and biological processes from molecular to global scales. One of the major goals is to find out how air pollutants, including reactive trace gases and aerosols, affect the atmosphere, biosphere, climate, and public health.

At present, the Institute employs some 300 staff in four departments and four additional research groups. Each of the departments is led by a director, who, as a scientific member of the Max Planck Society, has sole responsibility for the field of research in his department. The directors decide jointly on the Institute's development and elect a managing director out of their circle every three years. In January 2014 Ulrich Pöschl succeeded Jos Lelieveld in this position.

DEPARTMENTS

The **Atmospheric Chemistry Department** directed by Jos Lelieveld focuses on ozone, radical reaction mechanisms, their role in atmospheric oxidation pathways and the global cycles of trace compounds. These processes 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.

The **Biogeochemistry Department** directed by Meinrat O. Andreae investigates interactions between the terrestrial and marine biosphere and the chemistry of the earth. It performs field experiments to study exchange processes of trace gases and aerosols between the soil-vegetation system and the atmosphere. This includes the environmental effects of vegetation fires. Laboratory studies are performed to analyze geological records to elucidate the past states of the Earth System.

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 Earth System, climate, life and public health. The applied methods include laboratory experiments, field measurements and model studies using physical, chemical and biological techniques.

The **Particle Chemistry Department** directed by Stephan Borrmann is operated jointly by the MPIC and the University of Mainz. Its research focuses on the composition and physical properties of micro- and nanoparticles in the earth's environment, and on interactions between atmospheric aerosols and clouds. Methodologies 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 deals with 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 under extremely high pressure. The research is being supported from 2011 until 2016 by an Advanced Grant from the European Research Council.

The **Theoretical Chemistry** group led by Luc Vereecken is part of the Max Planck Graduate Centre. It applies quantum chemical theories to relate the chemical structure of compounds to their reactivity, with a focus on atmospheric applications.

The **Satellite Remote Sensing** group led by Thomas Wagner analyses 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.

The **ORCAS** group led by Frank Keppler was funded through a European Young Investigator Award (EURYI) and investigated the production of climate-relevant volatile organic compounds and their life cycles.

The **Reactive Nitrogen** group led by Ivonne Trebs investigated the cycling of nitrogen compounds at the surface-atmosphere interface of forest ecosystems with a Minerva research award of the Max Planck Society.

External Scientific Members are Ulrich Platt, from the University of Heidelberg, Germany and Stuart A. Penkett from the University of East Anglia, United Kingdom.

SCIENTIFIC ADVISORY BOARD

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

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

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.

ORGANIZATION CHART

Managing Director: U. Pöschl | Directorship: M. O. Andreae, S. Borrmann, J. Lelieveld, U. Pöschl

ATMOSPHERIC CHEMISTRY *J. Lelieveld*	BIOGEOCHEMISTRY *M. O. Andreae*	MULTIPHASE CHEMISTRY *U. Pöschl*	PARTICLE CHEMISTRY *S. Borrmann*	FURTHER RESEARCH GROUPS	CENTRAL SERVICES
Global Atmospheric Observations *C. Brenninkmeijer*	Isotope Biogeochemistry *S. Galer*	Bioaerosols and Microbiology *J. Fröhlich*	Instrumental Aerosol Analytics *F. Drewnick*	Aerosols and Regional Air Quality *Y. Cheng*	Communications *S. Benner*
Kinetics and Photochemistry *J. Crowley*	Fire Ecology *J. Goldammer*	Semivolatile Organic Compounds *G. Lammel*	Aerosol and Cloud Chemistry *J. Schneider*	High Pressure Chemistry and Physics *M. Eremets*	Administration and Technical Services *J. Egler*
Optical Spectroscopy *H. Fischer*	Paleoclimate Research *K. Jochum*	Inflammatory Processes *K. Lucas*	NAMIP – Nano and Micro-Particle Research *P. Hoppe*	Theoretical Atmospheric Chemistry *L. Vereecken*	IT *T. Disper*
Radical Measurements *H. Harder*	Plant Physiology *J. Kesselmeier*	Organic Aerosol and Oxidants *M. Shiraiwa*	Atmospherical Hydrometeors *M. Szakáll, K. Diehl (University Mainz)*	Satellite Research *T. Wagner*	Administration *J. Egler*
Fire Emissions *J. Kaiser (since Aug. 2014)*	Microscopy and Spectroscopy on Biogenic Aerosols *C. Pöhlker*	Aerosol, Cloud and Biosphere Interactions *H. Su*	Aerosol and Cloud Physics *R. Weigel (University Mainz)*	ORCAS *F. Keppler (until Jan. 2014)*	Instrument Development and Electronics *F. Helleis*
Atmospheric Modeling *A. Pozzer*	GEOROC database *B. Sarbas*	Cryptogamic Covers *B. Weber*		Reactive Nitrogen *I. Trebs (until Sept. 2013)*	Facility Management *C. Pallien*
Organic Reactive Species *J. Williams*	Reactive Nitrogen Species *M. Sörgel*				Graduate Schools *K. Sulsky*
	Micrometeorology and Flux Measurement Methodology *F. X. Meixner (until July 2014)*				Workshops *R. Wittkowski*

October 2014

Group picture during the Institute meeting in June 2013.

LOCATION AND BUILDING

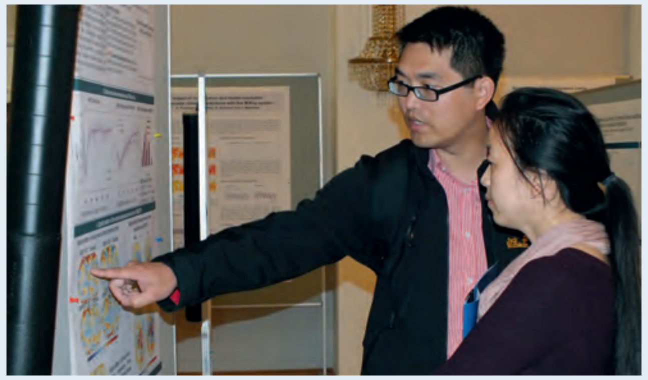
In January 2012, the Institute moved into its new building on the campus of the University of Mainz in the direct vicinity of the Max Planck Institute for Polymer Research.

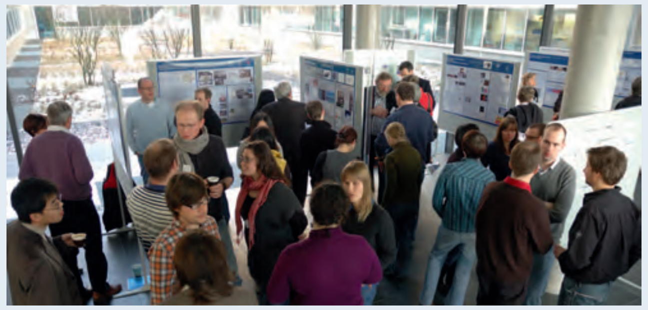
The new facility with approximately 8,700 square meters of floor space houses all departments and service groups. It was designed and developed by Fritsch und Tschaidse Architects in Munich.

The Institute building has three main parts: the central four story laboratory and office building for the scientific departments, the six story tower for central services such as the library, seminar rooms, and offices, and finally a workshop complex including space for vehicles used for field campaigns and an experimental greenhouse.

A spiral staircase in the four story entrance hall connects the laboratory areas with the central services. The open construction fosters communication and interaction among the staff. The building's exterior and the central garden court have different layers, reflecting the Institute's numerous research topics, which range from the inner earth up to the atmosphere.

Whereas for the past 60 years the Institute was spread over six separate buildings, the new single building housing the whole Institute will continue to promote interdepartmental scientific cooperation.





EDUCATION

The education of young scientists is of great importance to the Institute. To pursue this objective two doctoral programs have been established which attract students from all over the world.

INTERNATIONAL MAX PLANCK RESEARCH SCHOOL (IMPRS)

The International Max Planck Research School of Atmospheric Chemistry and Physics (IMPRS) offers a well monitored education program in close cooperation with the Johannes Gutenberg University Mainz and the Universities of Frankfurt and Heidelberg.

The curriculum of the IMPRS guarantees supervision by experts throughout the whole PhD period by a PhD advisory committee (PAC), consisting of at least three scientists. Regular meetings and reports provide constructive feedback and enable the PhD student to work independently within a network ensuring support when necessary. Time schedules can be adjusted in case of scientific or other problems. Lectures, workshops, seminars, conferences and summer or autumn schools are part of a credit-point based curriculum that enhances professional and social exchange. Soft skill seminars on, e.g., Rules of Good Scientific Practice and Intercultural competence as well as career guidance events, are fixed elements of the curriculum.

Currently approximately 80 PhD students participate in the IMPRS. Most of them are based in Mainz, some in Frankfurt and Heidelberg. About 42% come from abroad, especially from China, India, South America and European countries.

MAX PLANCK GRADUATE CENTER (MPGC)

The Max Planck Graduate Center is a virtual department of the Max Planck Institute for Chemistry, the Max Planck Institute for Polymer Research and four faculties of the Johannes Gutenberg University in Mainz. These University faculties are 1) Medicine, 2) Physics, Mathematics and Computer Science, 3) Chemistry, Pharmaceutical Science and Geoscience and 4) Biology. It was established in 2009 and created for interdisciplinary projects. It offers an advanced PhD program to candidates whose research topics can be assigned to two or more classical disciplines. These interdisciplinary research fields span a wide range of topics from material science and spectroscopy across geosciences to medical applications.

The MPGC has its own application procedure to attract excellent students and its own doctoral degree regulations. The curriculum is closely aligned to that of the IMPRS.

In addition to the education of university students, the Institute also offers internships for school students.

Max Planck Graduate Center
mit der Johannes Gutenberg-Universität Mainz

International Max Planck Research School for
Atmospheric Chemistry and Physics

MAJOR COLLABORATIONS

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

CROSS-DEPARTMENTAL LARGE-SCALE PROJECTS

Earth System Research Partnership (ESRP)

In October 2003, the MPI for Chemistry in Mainz, the MPI for Meteorology in Hamburg and the MPI for Biogeochemistry in Jena established an "Earth System Research" partnership. The objective of this partnership is to understand how the earth functions as a complex system and to improve the predictability of the effects of human actions. The partnership was funded by the Strategic Innovation Fund until 2011. Among other things, an annual conference with the associated partners takes place. The associated partners include the Max Planck Institute for Terrestrial Microbiology in Marburg, for Microbiology in Bremen, for Solar System Research in Katlenburg-Lindau and for Dynamics and Self Organization in Göttingen as well as the Institute for Advanced Sustainability Studies in Potsdam.

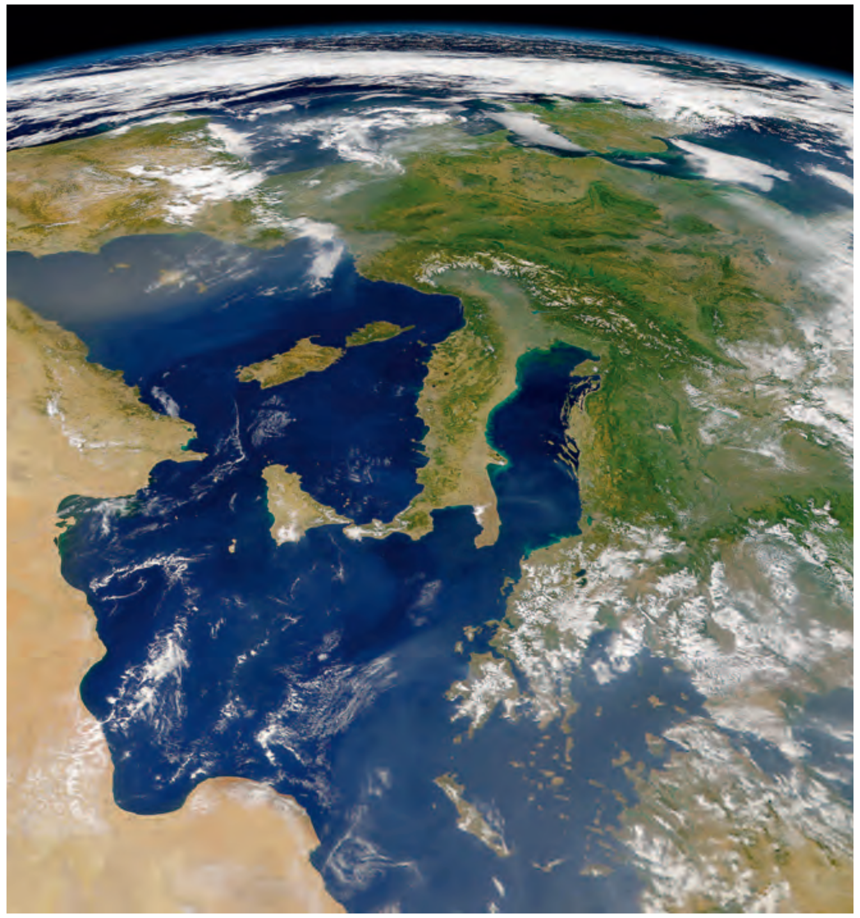
HALO Aircraft

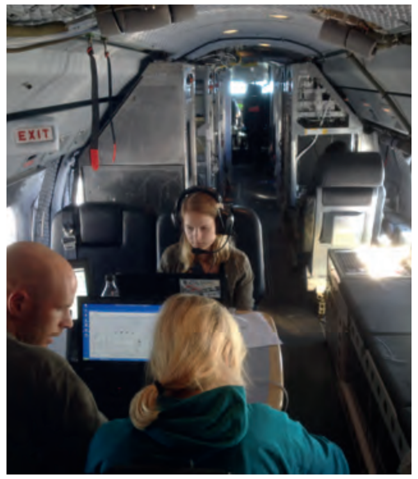
For the optimization of atmospheric research and earth observations, the Institute uses HALO, a research aircraft stationed at the Deutsches Zentrum für Luft- und Raumfahrt, DLR. HALO stands for "High Altitude and Long Range Research Aircraft". The aircraft has a range of 12,000 km, and is able to operate 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 the MPI for Chemistry 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 the elucidation of aerosol-cloud-precipitation interactions. In particular, the differences between unpolluted air and polluted air as well as the impact of anthropogenic aerosol were studied and quantified.

ESRP Meeting in Waldthausen near Mainz in 2013.





2015: Oxidation Mechanism Observation (OMO): The aim of this mission is to determine which natural and anthropogenic compounds are converted by oxidation processes in the upper troposphere.

SPOCES Partnership

A German-California cooperation "SPOCES" was entered in 2012 into with the Scripps Institute for Oceanography (SIO) and the Department of Physics of the University of San Diego (UCSD). SPOCES stand for SIO/UCSD-Max Planck Program for Observing the Changing Earth System.

Large-Scale European Research Projects

Currently, the Institute is involved in three FP7 and one HORIZON 2020 large-scale projects of the European Union: PEGASOS (Pan-European Gas-AeroSOls climate interaction Studies), BACCHUS (Impact of Biogenic versus Anthropogenic emissions on Clouds and Climate: towards a Holistic UnderStanding), StratoClim (Stratospheric and upper tropospheric processes for better climate predictions) and MACC III (Monitoring atmospheric composition & climate). The aim of PEGASOS and BACCHUS is to better understand the interaction of air quality, aerosols and clouds in the climate system. StratoClim deals with chemical and physical processes in the stratosphere and upper troposphere, in order to improve climate forecasts. MACC III is aimed at improving the data analysis and modeling systems for a number of atmospheric trace gases, including O_3, NO_2, CO, SO_2 and formaldehyde.

PUBLICATION IMPACT

The Institute's scientific publications are largely covered by the citation indexes accessible under the Web of Science (WoS). Between 2003 and 2013 about 2,250 peer-reviewed journal articles and reviews have been published with at least one author assigned to the address of the Institute, yielding an average rate of 172 papers per year. Many studies have shown that citation counts and research performance assessed by peers correlate highly, provided that the ensembles of papers are sufficiently large. Therefore, citation counts may be taken as proxy data for measuring research performance and for revealing the strengths and weaknesses of a research institute. Between 2003 and 2012 the Institute's papers received altogether about 51,000 citations with an average of 29.5 citations per paper.

Between 2003 and 2012, the Institute has published papers which belong on average to the top 25% most cited papers within their subject categories. It has achieved a subject based observed-to-expected citation ratio well above (>1.5) the international standard of the corresponding field in 15 different subject categories, eight of them having ratios better than 2.00 which indicates an outstanding performance.

Approximately a quarter (24.4%) of the papers published between 2003 and 2012 belong to the 10% most cited papers within their subject categories. With regard to this and other citation impact parameters, the Institute is among the top scientific institutions worldwide. Moreover, several Institute members have been ranked as "Highly Cited Researchers".

Over 30% of the Institute's peer-reviewed scientific articles are published in open access journals. Institute members also co-founded four internationally leading scientific open access journals which are:

- Atmospheric Chemistry and Physics (ACP), U. Pöschl et al.
- Atmospheric Measurement Techniques (AMT), T. Wagner et al.
- Biogeosciences (BG), J. Kesselmeier, et al.
- Geoscientific Model Development (GMD), R. Sander et al.

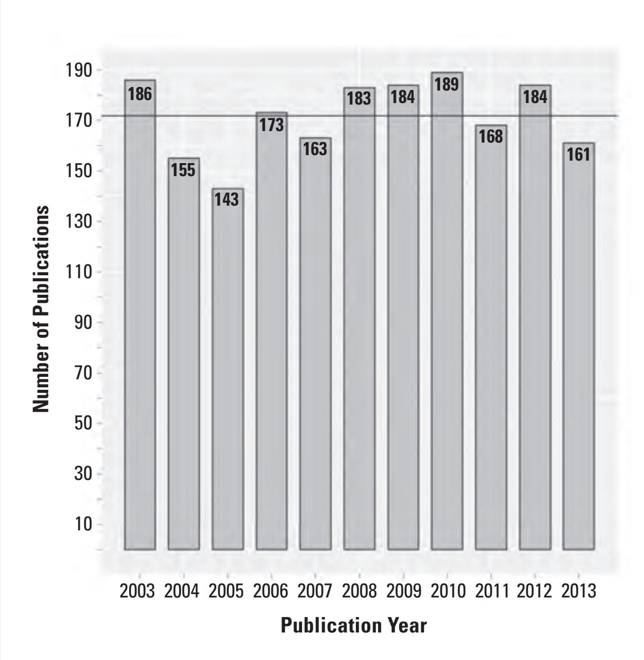
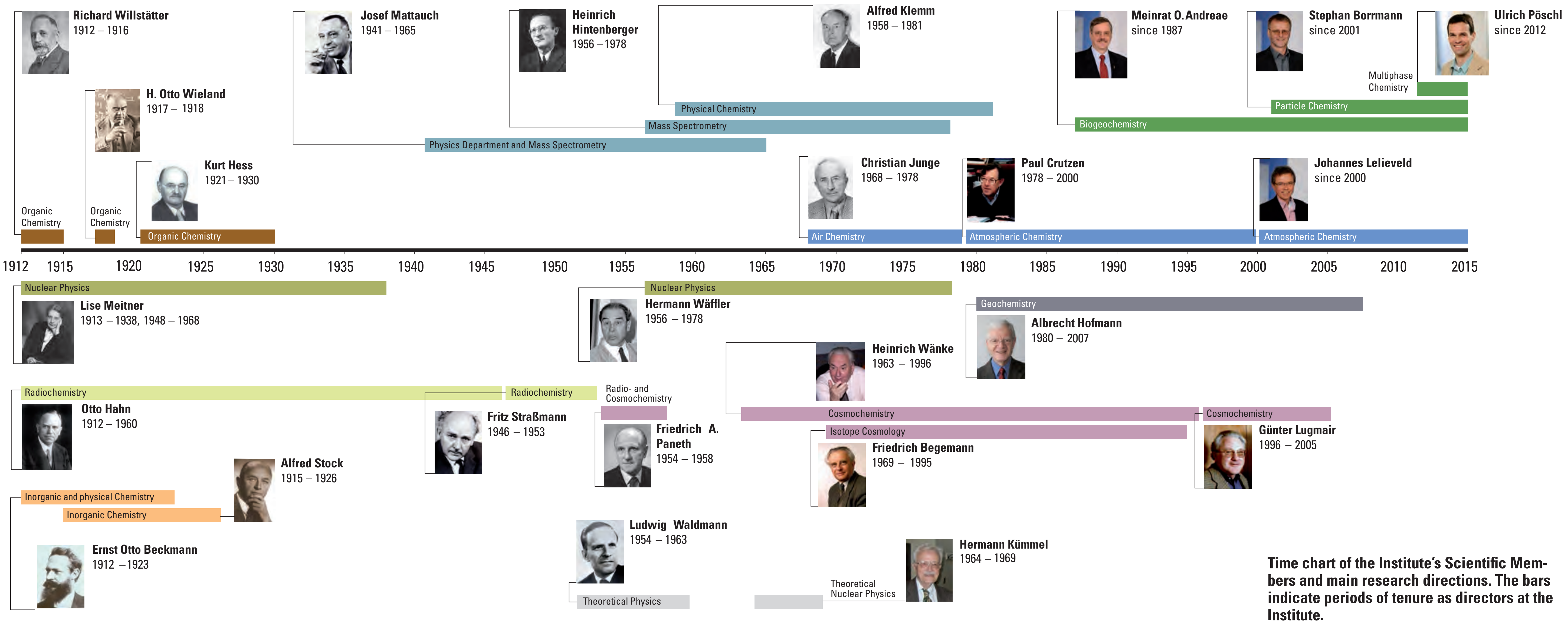


Figure 1: Peer-reviewed journal publication output of the Institute per year (articles and reviews) in the years 2003 to 2013 (the black line marks the average across all years).

Figure 2: Interactive open access journals initiated and co founded by Institute members.

Impressions of the centennial celebration and the Anthropocene Symposium in honor of Paul Crutzen.

HISTORY



Time chart of the Institute's Scientific Members and main research directions. The bars indicate periods of tenure as directors at the Institute.

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.

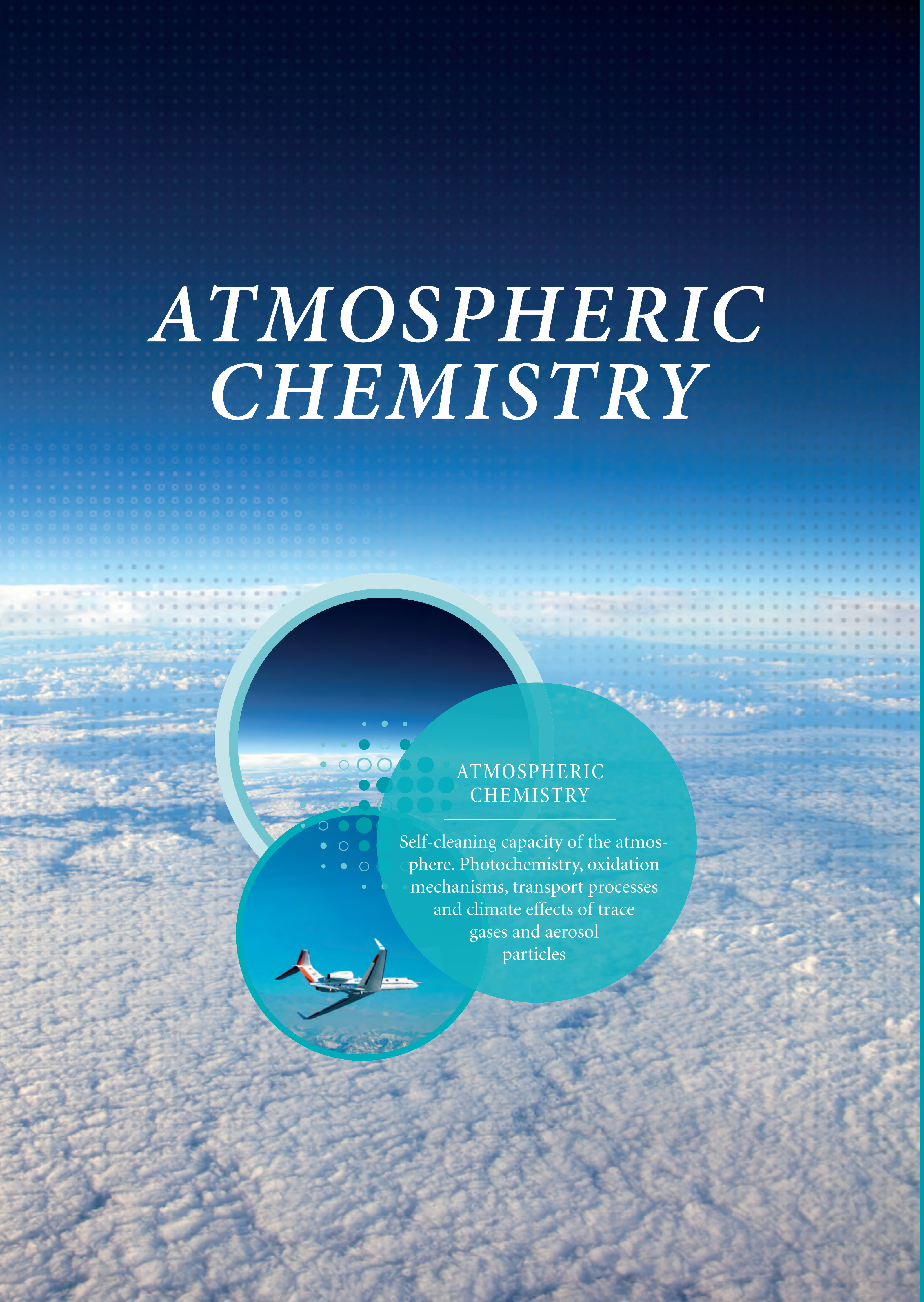
The research departments and focal points of the Institute have gone through a history of change and scientific evolution as illustrated in the time chart above. What began in 1912 with classical organic, inorganic and physical chemistry at the Kaiser Wilhelm Institute for Chemistry in Berlin evolved 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, and in 2012 the new Multiphase Chemistry 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

Born on 25 July 1955 in The Hague. Study of natural sciences Leiden University (1984), research associate at Geosens B.V. (1984–1987), research scientist at the Max Planck Institute for Chemistry (1987–1993), PhD in Physics and Astronomy Utrecht University (1990), Professor of Atmospheric Physics and Chemistry University of Wageningen and Utrecht (1993–2000), Director and Scientific Member at the Max Planck Institute for Chemistry (since 2000), Professor in Atmospheric Physics, University of Mainz, and Professor at the Cyprus Institute, Nicosia.

JOS LELIEVELD

ATMOSPHERIC OXIDATION PROCESSES CONVERT REDUCED AND PARTLY OXIDIZED GASES, RELEASED BY NATURAL AND ANTHROPOGENIC SOURCES, INTO COMPOUNDS THAT CAN BE EFFICIENTLY REMOVED BY DEPOSITION TO THE SURFACE.

The atmospheric oxidation capacity is a critical factor in the self-cleaning mechanism that removes millions of tons air pollutants and greenhouse gases each year. A key question is to what extent this mechanism is "stressed" by the enormous and growing emissions of contaminants in the Anthropocene, the geological epoch shaped by humanity. While recently air pollution emissions have moderated in the western world, the total volume continues to increase due to urban and industrial development in emerging economies, particularly in Asia. How much pollution can the atmosphere cope with until the oxidation capacity starts dwindling?

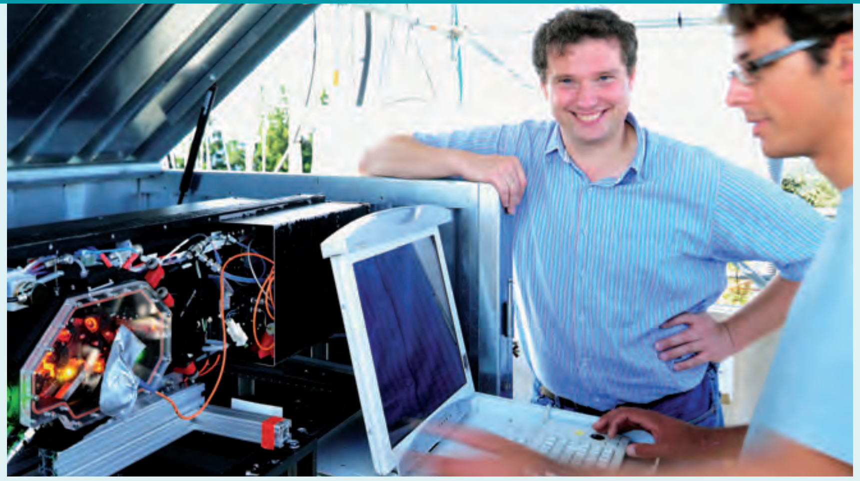
There are several options for pursuing this question, based on experimental and theoretical investigations. In the past years we studied "natural pollution" by performing measurement campaigns in forests, as the vegetation releases vast amounts of volatile organic compounds (VOCs). It is intriguing how the pristine atmosphere manages this abundance. We explored tropical, temperate and boreal environments where the characteristics of VOCs can be very different. Tropical forest emissions are dominated by isoprene, and we have discovered that the oxidation chemistry is buffered. This means, for example, that the hydroxyl radical (OH), the primary oxidizing agent of the atmosphere, is recycled after it has been consumed by its reaction with isoprene. Boreal forest emissions of terpenes, on the other hand, appear to be less efficient in OH recycling while maintaining oxidation capacity through reactions with ozone, also during the night. In general, we find ever more evidence that oxidation processes continue after sunset.

Our department investigates the large-scale atmospheric environment using mobile platforms, especially aircraft, to gain insight into interdependencies between emissions, chemical conversions and atmospheric transport. We have groups that investigate radicals, including OH, by a laser-induced fluorescence technique (1); measure atmospheric reaction intermediates such as aldehydes and peroxides, using optical detection methods (2); employ laser-cavity methods and chemical ionization mass spectrometry to investigate atmospheric nitrogen oxide chemistry (3); measure VOCs and their reaction products by proton-transfer mass spectrometers and GC-MS (gas chromatography – mass spectrometry) (4); and integrate a suite of instruments in a flying laboratory that travels on a Lufthansa passenger aircraft (5). Recently we invested much effort in developing instrumentation for the new German High-Altitude Long-range (HALO) aircraft. In the next years we will use HALO to explore "new territory," previously inaccessible with conventional platforms.

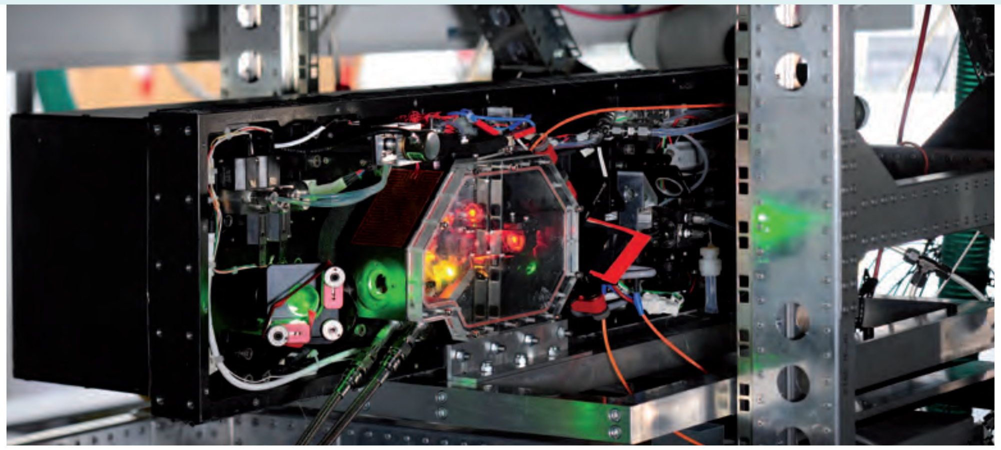
Field measurements are accompanied by model calculations to mimic the controlling processes, integrate their effects and help identify key feedback mechanisms. In one modeling group a hierarchy of local process to regional and global models is employed to use the measurement data in studies of atmospheric composition change on a range of scales (6). Another group interprets these studies in terms of impacts on global air quality and climate (7). The results suggest that dramatic air quality deterioration, especially in the developing world, should be halted by intensive control measures. Such findings motivate our research of the governing atmospheric processes that must provide the foundation of effective mitigation strategies.

RADICAL FORMATION AND RECYCLING OVER A BOREAL FOREST

HARTWIG HARDER



"New oxidation pathways by Criegee intermediates."



The oxidation capacity of the atmosphere is controlled by closely linked radical-radical cycles, notably those of HO_x ($OH+HO_2$) and NO_x ($NO+NO_2$). The OH radicals initiate the oxidation of many natural and anthropogenic trace gases while they can also be recycled, preventing radical recombination reactions (e.g. forming peroxides) and thus maintaining the oxidation capacity. The HO_2 radicals are closely linked to the NO_x cycle as they react with NO to form NO_2 and subsequently O_3, contributing to the primary source of OH.

Our investigations of the HO_x cycle in the Finnish Boreal forest revealed that under predominant moderate OH reactivity conditions ($k'OH \leq 15\ s^{-1}$) OH is recycled by known reaction schemes via RO_2/HO_2, NO and O_3 (OH reactivity, k'OH, is the reciprocal of the OH lifetime). In the absence of direct NO_x emissions the photo-stationary state assumption between NO and NO_2 is valid, which can give insight into the number of radicals that oxidize NO into NO_2. Previous studies reported tremendous discrepancies between the modeled radical concentrations and concentrations derived from the measured photo-stationary state. For the boreal forest conditions at moderate OH reactivity, however, making use of measured radical concentrations and constraining a model with the observed OH reactivity, we obtained good agreement. This indicates that radical cycling is relatively well understood under these conditions.

However, during periods of high OH reactivity ($k'OH > 15\ s^{-1}$), observed in the Boreal forest during high summer temperatures – when biogenic VOC emissions are enhanced – important discrepancies emerged. Also during periods when extensive biomass burning plumes from Russia impacted the region, the HO_2 concentration was much larger than simulated by the model, based on OH initiated VOC oxidation only. Simultaneous under-prediction of HO_2 and OH reactivity in periods in which OH concentrations were simulated realistically suggests that the unaccounted for OH reactivity is a source of HO_2. Hence this implies additional HO_2 sources that do not involve OH. Apparently, the oxidation capacity is not solely driven by OH formation and recycling processes, and an important contribution appears to be "missing" by other yet to be identified compounds.

In the measurement campaign in Finland we made the remarkable discovery that our laser-induced fluorescence instrument measures an additional signal of an unknown species that decomposes into OH inside the detection cell. We distinguished between OH and this unknown species by using a pre-injector that consecutively removes OH from the ambient air. The significance of this species as a potential oxidant became evident by its contribution to SO_2 oxidation into H_2SO_4. Only about 50% of the H_2SO_4 formation was due to OH, the other 50% was highly correlated with the product of SO_2 oxidation and the unknown species (Figure 1). Laboratory studies were performed showing that stabilized Criegee intermediates produced by ozonolysis of different unsaturated VOCs, notably alkenes, decompose into OH. Criegee intermediates, i.e. carbonyl oxides with mostly zwitterionic and weak biradical character, were previously known to contribute to organic acid formation, while this pathway provokes rethinking of oxidation chemistry.

Using our instrument for HO_x detection, we could also estimate the unimolecular decomposition rate of stabilized Criegee intermediates at 20±10 s^{-1}, depending on the kind of Criegee. Theoretical studies accompanied our laboratory and field investigations to determine the reaction rates of Criegee intermediates with trace gases and their relevance for the atmosphere (see report by Luc Vereecken, Theoretical Atmospheric Chemistry Group). In the field campaign we also occasionally added SO_2 leading to the removal of the unknown species, consistent with the chemistry of Criegees. These results provide evidence that stabilized Criegee intermediates act as the "missing" oxidant measured in the field campaign. This suggests unique chemistry in the mixture of biogenic VOCs emitted from the boreal forest, an ecosystem that covers nearly 17 million km^2 of the globe. Since these conditions occurred in periods of elevated temperature, they are expected to become more frequent due to climate warming.

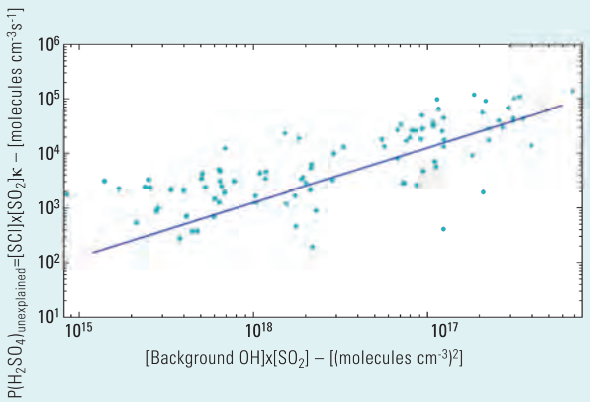


Figure 1: Correlation between the OH generated from unimolecular decomposition of an unknown species (OH excluded) in our instrument and the production rate of H_2SO_4 over the Boreal forest.

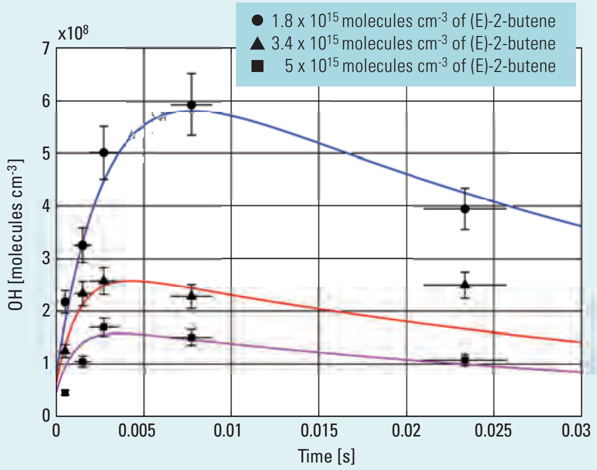


Figure 2: Temporal profiles of the OH signal (solid symbols) inside the detection cell of the LIF-FAGE instrument for the ozonolysis reaction of (E)-2-butene and model simulations (lines) for 3 different concentrations of (E)-2-butene. OH is produced by unimolecular decomposition of the resulting Criegees while the losses are dominated by known reactions with butene and deposition on the reactor walls.

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ROLE OF FORMALDEHYDE AND HYDROGEN PEROXIDE IN THE TROPOSPHERIC OXIDATION CAPACITY

HORST FISCHER

"Aldehydes and peroxides are twofold protagonists as sources and sinks of HO_x radicals."

Figure 1: Measurement on board the HALO aircraft in September 2012, flying along the African continent.

The group develops and applies instruments based on infrared laser absorption, chemiluminescence and fluorescence spectroscopy for atmospheric trace gas detection. Target molecules are O_3, NO, NO_2, N_2O, CO, CO_2, CH_4, HCHO, H_2O_2 and organic peroxides (ROOH). Recently, we dedicated several studies to HCHO and H_2O_2. Instrumentation based on fluorescence techniques has been used for ground-based measurements, while a combination of a quantum-cascade laser spectrometer for HCHO, CO and CH_4 and a dual enzyme fluorescence monitor for H_2O_2 and ROOH has been deployed on the HALO aircraft. Since the dual-enzyme technique can only provide an integral measurement of total ROOH, a specific measurement technique for individual ROOHs has been developed based on high-pressure liquid chromatography.

Both HCHO and H_2O_2 strongly influence the oxidation capacity of the troposphere due to their twofold role, acting as radical reservoir species (releasing OH and HO_2 through photodissociation), and being ultimate sinks through wet and dry deposition to the surface. These molecules are essential in the interplay between chemistry, transport and physical removal. Since they are controlled by a variety of processes it is interesting to contrast the measured concentrations with results from our computer model EMAC that comprehensively simulates global atmospheric chemistry, physics and dynamics. We carried out the measurements during a number of airborne, ship and ground based field campaigns.

In the free troposphere above the boundary layer the concentrations of HCHO and H_2O_2 are principally controlled by chemistry, transport and cloud processes. A comparison of airborne HCHO measurements with EMAC over Europe shows generally good agreement. Due to the short lifetime of HCHO of a few hours or less and its moderate solubility, HCHO is relatively strongly affected by chemistry. The good agreement with EMAC thus indicates that our understanding of the relevant chemical processes is satisfactory. H_2O_2 is slightly longer lived (up to days) and much more soluble. Here the comparison shows that EMAC significantly underestimates H_2O_2 mixing ratios in the free troposphere. Sensitivity studies indicate that wet deposition (rainout) in the model is too strong and is responsible for the discrepancy. We are investigating the hypothesis that H_2O_2 is released from freezing cloud particles in deep convection, a process not yet included in models, which reduces the efficiency by which H_2O_2 is removed by rain.

Ship-based measurements of H_2O_2 in the marine boundary layer over the South Atlantic Ocean indicate good agreement of observations with model results at conditions with low and moderate wind speed, but strong deviations at high wind speeds. Here deposition of H_2O_2 to the ocean surface is the most critical process that determines its concentration. It seems that the description of dry deposition in EMAC, which depends on the transfer velocity to the surface and the solubility of the trace gas, is overestimated at high wind speeds.

The processes become more intricate in the continental boundary layer, for example over the Boreal forest in Finland. Due to the emission of biogenic volatile organic compounds (VOCs) additional HCHO sources must be considered. Also the deposition is more complex due to exchange with the vegetation, affecting H_2O_2 and HCHO. Another complication is the strong diel cycle of the boundary layer height. A shallow boundary layer during the night promotes dry deposition loss, in particular of H_2O_2. After sunrise, air from aloft is mixed downward, bringing higher concentrations of H_2O_2 (mixing ratio increases with altitude) and lower concentrations of HCHO (mixing ratio decreases with altitude) to the surface. This multifaceted environment, where transport, mixing, complex VOC chemistry and exchanges with the vegetation play significant roles, poses real challenges to atmospheric models. Comparisons with our measurements thus far suggest that EMAC generally overestimates both species over the Boreal forest, while it is not possible to unambiguously identify the causes of the discrepancies. A new model generation, accounting for forest ecosystem dynamics, could help resolve the problem.

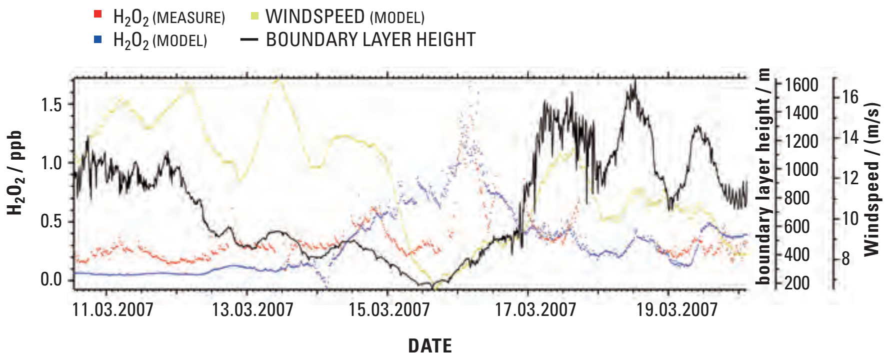

Figure 2: H_2O_2 observations and EMAC simulations in the marine boundary layer over the southern Atlantic Ocean. The model tends to underestimate H_2O_2 at high wind speeds during the first half of the campaign, but agrees well at wind speeds below 10 m/s.

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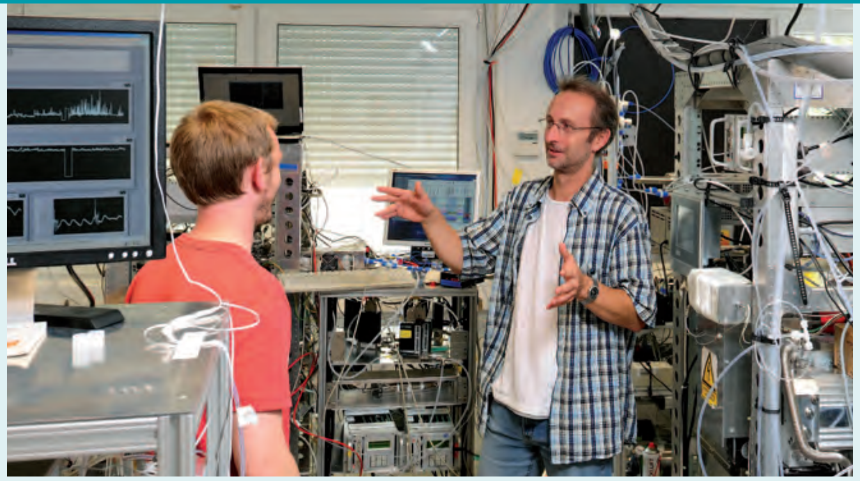
LABORATORY AND FIELD STUDIES OF DAY- AND NIGHT-TIME RADICAL PROCESSES

JOHN CROWLEY



> **“Combined laboratory and field measurements provides unique insight into gasphase and particle chemistry.”**

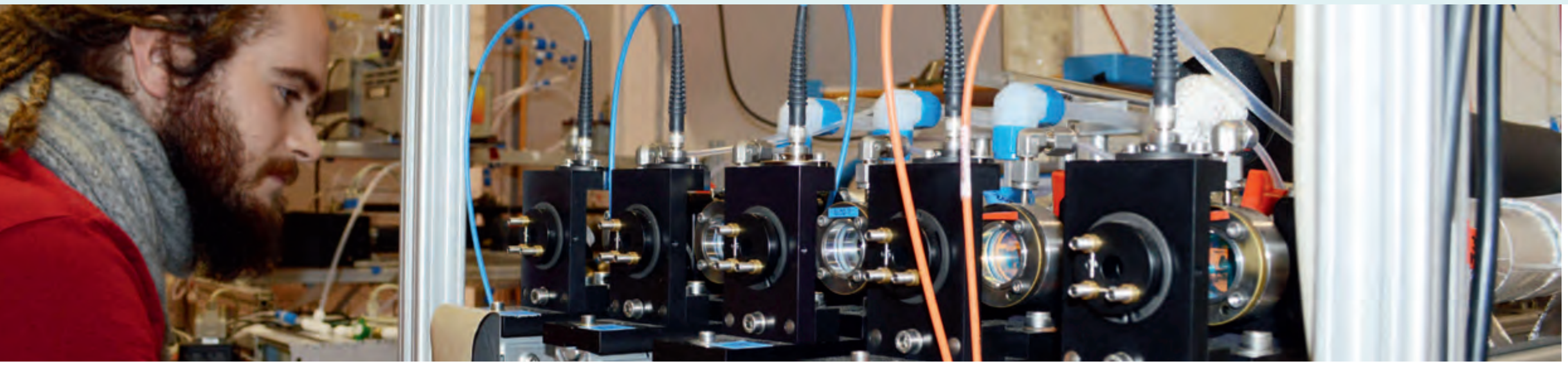


Figure 1: Cavity-ring-down spectrometer.

Atmospheric oxidation is not limited to the daytime when photochemical radical formation dominates, but continues through the night when “dark” radicals such as NO_3 are important. Figure 2 summarizes some centrally important reactions, both in the gas and aerosol particulate phase, playing a role over the entire diel cycle. We apply a combination of laboratory and field studies to unravel the complex reactions occurring both day and night and deepen our understanding of the relative role of oxidation by the OH radical (dawn to dusk), NO_3 (dusk to dawn) and Cl atoms (dawn to midday).

The gas and particle phase species in green, red, and blue in Figure 2 are those which we measured in two recent field campaigns on a semi-rural mountain site in central Germany. NO_2, NO_3, N_2O_5, and Σ $RONO_2$ were simultaneously monitored using blue and red laser-cavity-ring-down spectrometers. $ClNO_2$ (and also PAN) was monitored using iodide chemical ionization mass spectrometry and particle nitrate was measured using an aerosol mass spectrometer.

A major unknown in the tropospheric NO_x budget is the efficiency of transfer of gaseous reactive nitrogen to the particle phase, which is partially determined by the efficiency of uptake of N_2O_5 (γ). By measuring the concentrations of N_2O_5 and $ClNO_2$ in the gas-phase and the surface area and nitrate content of the particles we were able to derive relative humidity dependent uptake coefficients of between 0.1 and 0.01. Efficient uptake of N_2O_5 results in activation of particle chloride to the gasphase in the form of $ClNO_2$. $ClNO_2$ is photolysed and per molecule forms one NO_2 (returning NO_x to the gasphase) and a chlorine atom. We showed that in the first few hours after dawn Cl atoms are more important for degradation of certain hydrocarbons than OH. Measurements of the particle phase chloride and sodium content using ion chromatography revealed that the particulate chloride was of marine origin, its largest concentrations (and those of $ClNO_2$) associated with westerly winds transporting sea-salt aerosol over polluted, continental Europe. The chlorine may repeatedly cycle between the gas and particle phase before it is removed by rainout.

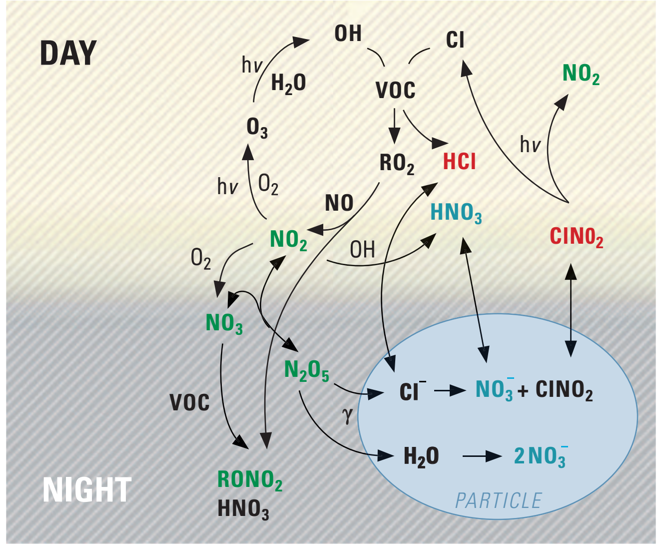


Figure 2: By influencing daytime NO_x and also via the formation of Cl atoms, heterogeneous chemistry during the night can have a profound impact on daytime photochemical processes.

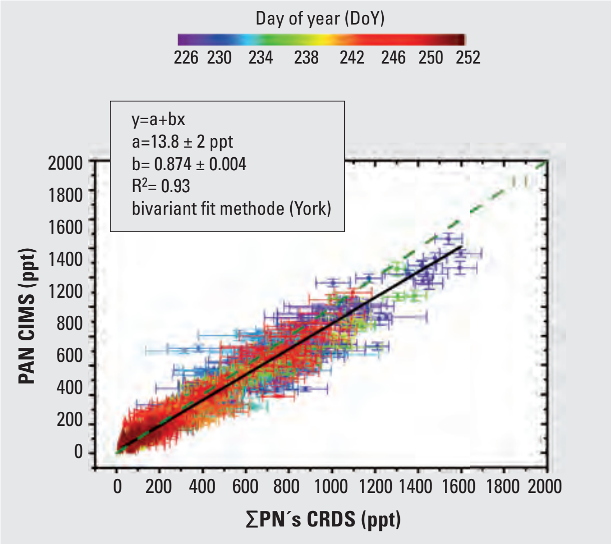


Figure 3: PAN (measured by chemical ionization mass spectrometry) is about 80–90% of total peroxy nitrates (Σ[PNs]).

Photochemical ozone production is controlled by NO_2 concentrations, which are dependent on the formation rates and lifetimes of NO_y species (reactive nitrogen). Whilst some peroxy nitrates (PNs) represent a mode of transport of NO_x (NO and NO_2) from polluted to remote regions, the formation of organic nitrates ($RONO_2$) via reaction of NO with RO_2 is an important chain termination step in photochemical ozone production. In order to investigate these processes, we constructed a thermal dissociation cavity-ring-down spectrometer to measure total PNs (Σ PNs) and total alkyl-nitrates (Σ ANs). On the semi-rural mountain site in Germany a significant fraction (~20%) of NO_z ($NO_z = NO_y\text{-}NO_x$) was in the form of organic nitrates. Their formation was accelerated in the early morning, likely reflecting the contribution of Cl atoms (from $ClNO_2$) photolysis to hydrocarbon degradation and thus to RO_2 formation. At the same site $CH_3C(O)O_2NO_2$ (peroxyacetyl nitrate, PAN) was found to contribute about 80–90% of total PNs (peroxy nitrates)], see Figure 3.

In the laboratory we have examined the photochemical formation and loss processes of substituted organic radicals and their role in radical recycling. Using a novel, bromine based, radical scavenging method, we derived quantum yields of photolysis (to form CH_3CO and CH_3) of acetone at atmospherically relevant wavelengths, temperatures and pressures and also clearly demonstrated the central role of the exited triplet state of acetone in the photo-excitation process. We also quantified the yield of OH from the reaction of CH_3CO and O_2 at various pressures and detected unexpected radical reformation in low temperature methanol oxidation, via the reaction of CH_2OH with HO_2:

$$CH_3C(O)CH_3 + h\nu\ (p,t,\lambda) \rightarrow CH_3CO + CH_3$$

$$CH_3CO + O_2 \rightarrow OH + HCHO + CO$$

$$HOCH_2 + HO_2\ (+O_2) \rightarrow OH + HO_2 + HC(O)OH$$

None of these radical reformation processes were known a few years ago, highlighting the continued importance of conducting detailed kinetic studies in understanding atmospheric photochemistry, especially with the new capability to directly detect radicals among the reaction products.

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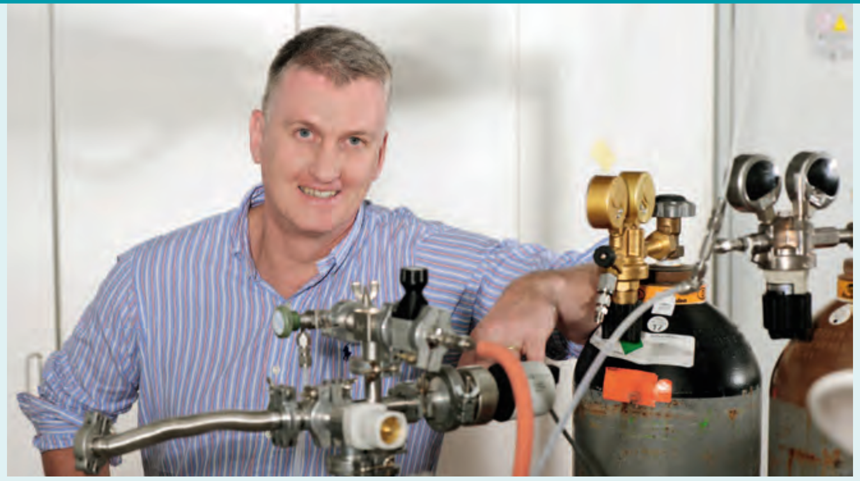
SOURCES, SINKS, AND CHEMISTRY OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE

JONATHAN WILLIAMS



"Diel cycle of OH reactivity in a megacity is opposite to that in a forest."

Our group investigates volatile organic compounds (VOCs) primarily through field measurements. Of particular interest is how these species interact with ozone and OH radicals. We develop and deploy instrumentation in airborne, ship-borne and ground-based field measurement campaigns. The analysis of such data leads to a better understanding of the sources, sinks and chemistry of VOCs, and ultimately to global budget estimations. We specialize in measurements with PTR-MS (Proton Transfer Mass Spectrometers) and of GC-MS (Gas chromatography – Mass Spectrometry).

In addition to field measurement intensives coordinated by the department, the group is involved in interdepartmental collaborations with Biogeochemistry and Particle Chemistry Departments and in externally funded projects, for example on air-sea exchange of trace gases (BMBF) and organohalogens in soils (DFG).

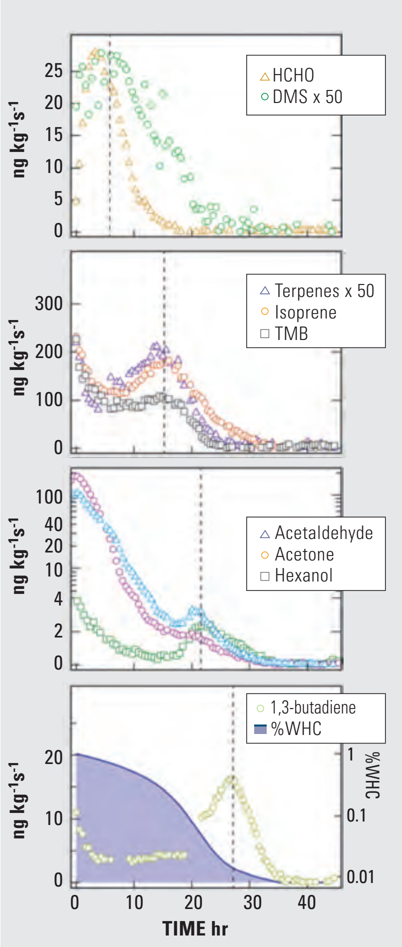
In recent years, we have obtained and reported on new datasets for biogenic VOC emissions from boreal, temperate, and tropical forests as well as from plants under controlled laboratory conditions. The natural marine environment has also been investigated for organohalogens and dimethylsulfide, focusing on the influence of increasing CO_2 levels. Furthermore the physical process of air-sea transfer of organic species has been characterized. We have also applied our measurement techniques to natural soil emissions and have discovered microbial and abiotic sources of carbon, nitrogen, and sulfur containing compounds (Figure 1). Considering the growing influence of humanity on the global atmosphere we have also investigated anthropogenic emissions.

In one study we exploited our proximity to a football stadium to gain insights into how people en masse influence their atmospheric environment. The VOCs from 30,000 football fans could be classified into several distinct source categories including human respiration/breath, ozonolysis of skin oils, and cigarette smoke/combustion. Even though human emissions of VOCs have a small contribution to the global atmospheric budget, high fluxes of ethanol and acetone were observed, suggesting the potential for significant impact on local air chemistry and even at regional scales. In addition, we have also been involved in studies of fire emissions, and highly oxidized anthropogenic pollution transported over the eastern Mediterranean Sea in Cyprus under conditions of intense sunlight and absence of removal mechanisms through clouds and rain.

Building on the successful development of a new method for determining total atmospheric OH reactivity (reciprocal of the OH lifetime), we have made technical improvements and have applied this methodology to globally relevant environments. We have deployed our OH reactivity system for one year in the Amazon rainforest, so that seasonal, vertical (0-80 m) and diel variations could be determined for the first time. The patterns observed were in stark contrast to those measured in Beijing city center the following year: while the Amazon OH reactivity peaked by day, was dominated by the VOC isoprene, and anti-correlated to CO_2, in Beijng the OH reactivity is higher by night, dominated by NO_2 and aromatic compounds, and correlated with CO_2 (Figure 2).

In addition to these contrasting environments, the OH reactivity system was deployed in a photochemical chamber to investigate the oxidation mechanism of isoprene and to test a newly developed chemistry scheme (by the modeling group). The total OH reactivity was compared to the individual measurements of isoprene and its oxidation products to assess the significant contributors to the overall OH loss rate. Measured total OH reactivity showed excellent agreement to the calculation based on individual compounds detected by a PTR-TOF-MS (TOF is time-of-flight). On average 97% of the measured total OH reactivity could be explained by isoprene and its major oxidation products. Comparison of the results with a model of the comprehensive isoprene degradation mechanism revealed some discrepancies, providing vital clues for improvement of the scheme.

The first international OH reactivity meeting was held at the Max Planck Institut for Chemistry in October 2014.



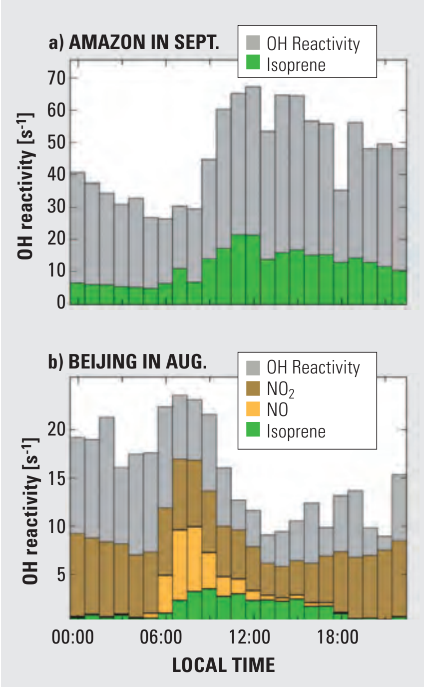


Figure 1 (left): Emission of VOC from soil as a function of soil water content. Dotted lines mark emission optima during the drying process.

Figure 2 (right): Comparison of OH reactivity (and selected contributors) in the Amazon rainforest and Beijing.

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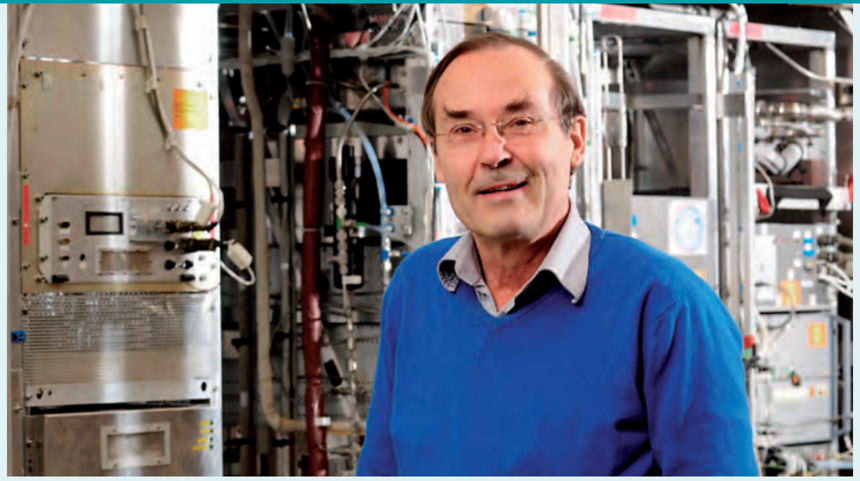
GLOBAL ATMOSPHERIC OBSERVATIONS

CARL A. M. BRENNINKMEIJER



"Flying observatory monitors global air quality."

Figure 1: The 1.5 ton measurement container is loaded into the cargo bay of an Airbus 340-600 for 4 consecutive regular passenger flights. The inlet system visible in front of the belly fairing is a permanent part of this aircraft.

The group manages the CARIBIC airborne observatory (Figure 1), which entails the monthly deployment of an automated set of experiments aboard a Lufthansa aircraft (www.caribic@mospheric.com). The 1.5 ton airfreight container that accommodates this compact laboratory is installed in a near monthly rhythm in the cargo bay of an Airbus A340-600 passenger aircraft for 4 consecutive long distance flights; for instance, Munich-San Francisco-Munich-Sao Paolo-Munich and many other destinations worldwide. The container is situated in the aircraft cargo bay and is connected to a special air inlet system.

Characteristic for the CARIBIC observatory is: (1) the global scale of the observations, (2) direct access to the upper troposphere (UT) and lower stratosphere as well as the free troposphere in the tropics at a cruising altitude of 10-12 km, (3) the monthly repetition of deployment, (4) the long time span of the project since 2005, and (5) the large number of atmospheric constituents measured – trace gases and aerosols. Air and aerosol samples are also collected for detailed post-flight chemical analysis. The unique inlet system houses remote sensing telescopes that measure trace gases along different viewing angles. An important opportunity of the CARIBIC observatory is the possibility to extend the scientific payload over time based on new analytical developments and requirements.

With our partners in CARIBIC, the Institute for Meteorology and Climate Research of the Karlsruhe Institute for Technology, the Leibniz Institute for Tropospheric Research, the Institute for Atmospheric Physics of DLR and the Institute for Environmental Physics of the University of Heidelberg (a full list is on our website), a wide range of research topics is addressed. Our group, besides being responsible for coordination and operation, deploys an air sampling system and measures CO, volatile organic compounds (VOCs), and also monitors greenhouse gases. Various international research groups request data from the growing database, for example, to validate and complement satellite observations of CO_2 and other gases. Measurements during different seasons and for many years allow the identification of representative and recurrent events, as shown by our study of the atmospheric composition over Eurasia.

Our observations were used to investigate the distribution and seasonal cycles of a number of trace gases in the European and Asian UT, and this information was then used to identify processes that control composition. Interestingly, we found that elevated levels of C_2-C_4 VOCs are particularly ubiquitous over South Asia during summer. This was attributed to the convective lifting of urban and biomass burning emissions (concomitant with elevated combustion products) and mid-range transport of fossil fuel related emissions from the Middle East and Eastern Europe. This study also found a strong and persistent influence of long-range transport of North American pollutants to the UT over Europe and western Asia, and of emissions from local biomass burning on the UT in Southeast Asia.

A remarkable event is illustrated in figure 2. The CARIBIC observatory flew over an extensive (~ 480 km) thunderstorm cloud system in the Caribbean area (near Guadalupe) in the afternoon of 11 August, 2011, enabling a rare glimpse into remarkable chemistry. Cruising at 11 km altitude, the aircraft penetrated towers of the cumulonimbus system (spotted by a camera in the inlet system). Cloud water was monitored and elevated levels of NO, NO_2, HONO and formaldehyde (HCHO) were detected. NO peaks up to 5 ppb together with elevated NO_2 and HONO could be related to lightning activity. Elevated formaldehyde was due to the rapid updraft of polluted air masses from the Atlantic sector, analyzed by model calculations. Lightning emissions and updraft rates were implemented in our atmospheric chemistry model EMAC, yielding emission estimates of the amount of NO per lightning flash and the formaldehyde updraft strength related to convection. This work corroborates the importance of thunderstorm convection that short-circuits the chemistry of the boundary layer with the UT.

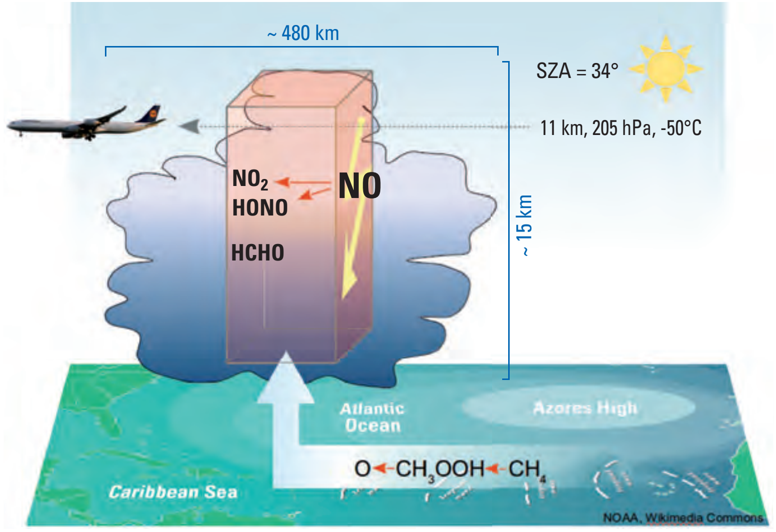


Figure 2: Schematic of the main features of the event near the island of Guadalupe. The multiple reflection of photons inside the cloud enhanced the detection limit for HCHO and HONO by DOAS remote sensing. Both trace gases were more abundant. HONO due to the production of NO_x by lightning. HCHO due to convection giving an input of surface air with higher HCHO and precursor levels.

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NUMERICAL MODELING OF ATMOSPHERIC CHEMISTRY

ANDREA POZZER

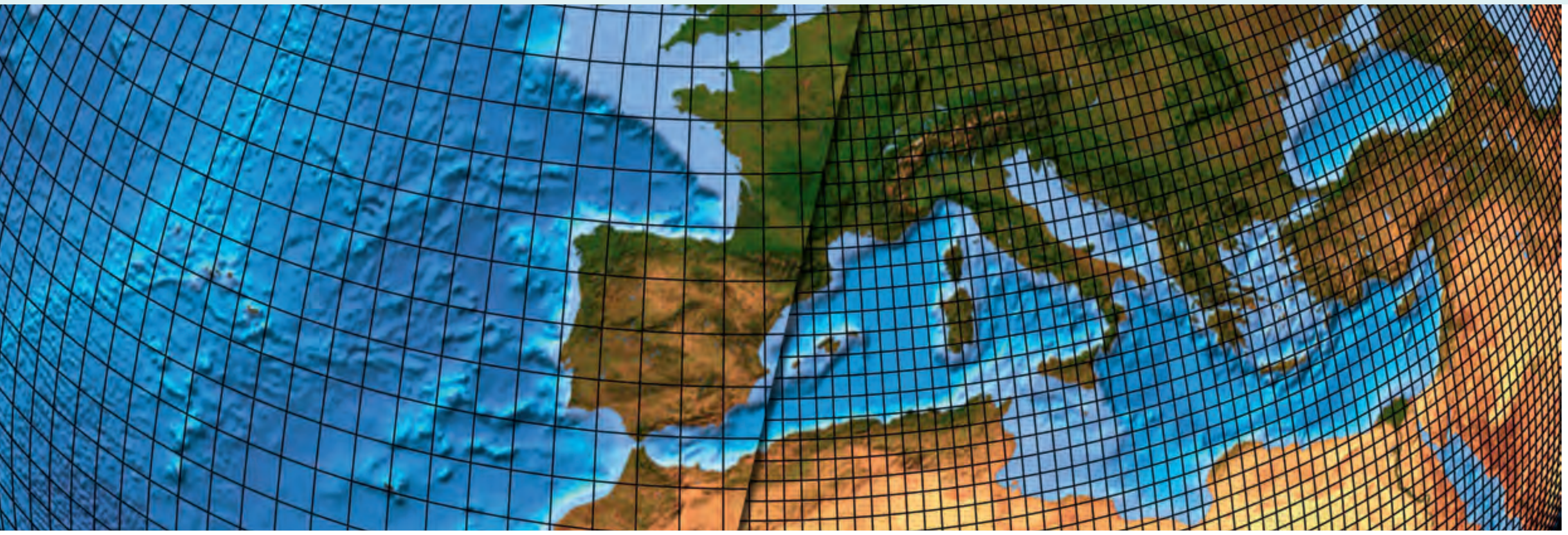

Figure 1: Resolution grid for a typical global numerical model.

Concentrations of the highly reactive OH radical are controlled by many factors such as the intensity of sunlight, water vapor, ozone and air pollution. The mutual dependencies of OH and O_3 on precursor species (such as NO_x, CO, CH_4 and other VOCs), transport, mixing, cloud and deposition processes are intricate and cover many space and timescales. Hence, a hierarchy of numerical models with varying levels of complexity is needed to study the governing processes, support the analysis of data gathered in measurement campaigns, and predict the spatial and temporal distributions of these species (Figure 2).

The group develops and maintains a comprehensive chemical box model (CAABA – Chemistry as a box model application), a mixed layer model (MXL), a regional model (WRF Chem – Weather Research, Forecast and Chemistry) and a global model (EMAC, ECHAMS/MESSy atmospheric chemistry). These models can mostly be coupled and/or nested and allow studies on different topics of varying complexity and extent, from pure numerical research to field campaign analyses and biogeochemical budget estimates. The global EMAC model is our main tool and is maintained by a multi-institutional consortium, initiated by MPIC. The link to measurements is made by using EMAC at high resolution (e.g. 50-100 km grid size) and driving it with the same meteorological data as the models that address smaller scales.

In recent years we have increasingly focused on the chemistry of biogenic VOCs, for example isoprene, which is emitted in large quantities by vegetation. Measurements over Tropical forests suggest that hydroxyl radicals are recycled following reaction with isoprene, but the underpinning chemistry is uncertain. We developed a detailed chemical mechanism for the oxidation of isoprene by OH. The photo-oxidation of unsaturated hydroperoxy-aldehydes – a product of isoprene oxidation – is a central part of the mechanism. Their photolysis initiates an OH production cascade that is limited by the reaction of hydroperoxy-aldehydes with OH itself. We incorporated this mechanism into the EMAC model and found that OH measurements over the Amazon forest are captured well. On the basis of this agreement, we suggest that isoprene oxidation can buffer OH concentrations, by serving both as a sink and a source of these radicals.

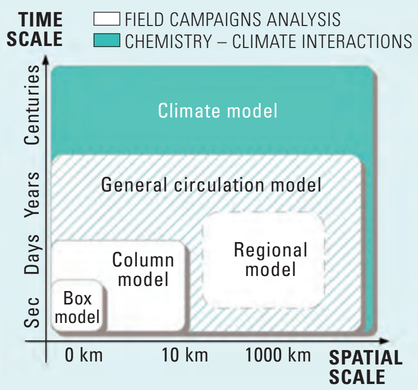

Figure 2: A hierarchy of connected models can be used to study atmospheric processes from local to global scales.

> **"Testing numerical models against observations is essential to gain new insights into atmospheric science."**

In more polluted air the photolysis of HONO is important for the HO_x ($OH+HO_2$) budget and ozone formation. Owing to the incomplete knowledge of HONO sources, realistic HONO mechanisms have not yet been implemented in regional and global models. From measurement data sets from 15 field measurement campaigns conducted in different countries worldwide, we derived a parameterization for the EMAC model, yielding realistic HONO mixing ratios, being about one order of magnitude higher than the reference calculations with only the known gas phase reaction $OH+NO \rightarrow HONO$. This significantly changes HO_x levels and photo-oxidation products (e.g. O_3, PAN), mainly in polluted regions during winter, thus enhancing the oxidation capacity when other photolytic OH sources are of minor importance (Figure 3). Nevertheless, a mechanistic description of the HONO formation is still missing. We are developing a detailed representation of aromatics and nitrophenols and their degradation pathways, which lead to the production of HONO and organic aerosols.

Because oxidation processes by OH also influence the formation of particles, an extensive model evaluation was performed for gaseous and aerosol compounds, the latter simulated with the GMXe submodel (Global Modal-aerosol Extension). GMXe performs comprehensive aerosol microphysics, chemistry and thermodynamics calculations. It was shown that the enhanced oxidation capacity in polluted air during winter, through HONO, resolves a discrepancy between model results and measurements of SO_2 and sulfate, notably over Europe where the conversion of SO_2 into sulfate was previously underestimated. Another recent extension of GMXe is the more complete description of gas-aerosol partitioning and chemical aging of organic particulates. EMAC simulations corroborate the widespread abundance of secondary organic aerosols, formed from semi-volatile, compounds of intermediate-volatility and VOCs, both in polluted and background air.

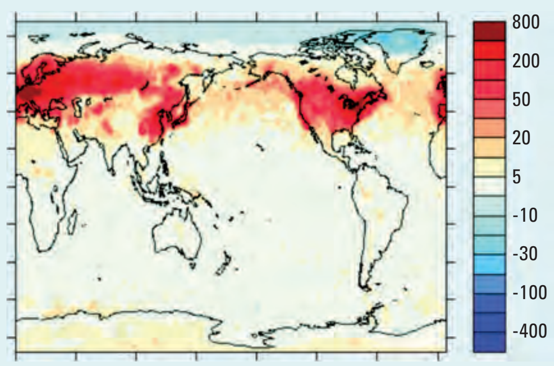

Figure 3: EMAC model calculated relative change in OH (in %) near the surface in December, indicating the relative difference between the standard and the parameterized HONO representation for the month January.

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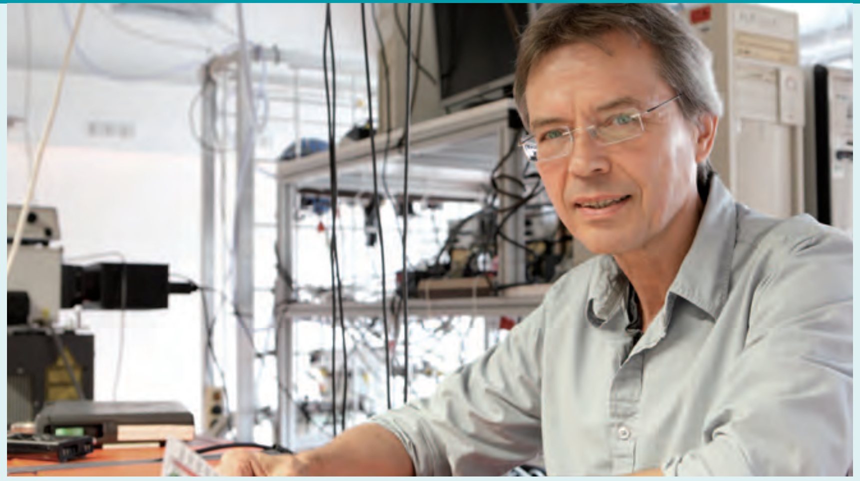
IMPACTS OF CHANGING ATMOSPHERIC CHEMISTRY ON AIR QUALITY AND CLIMATE

JOS LELIEVELD



"In the past decade medium strength volcano eruptions have reduced the rate of climate warming."

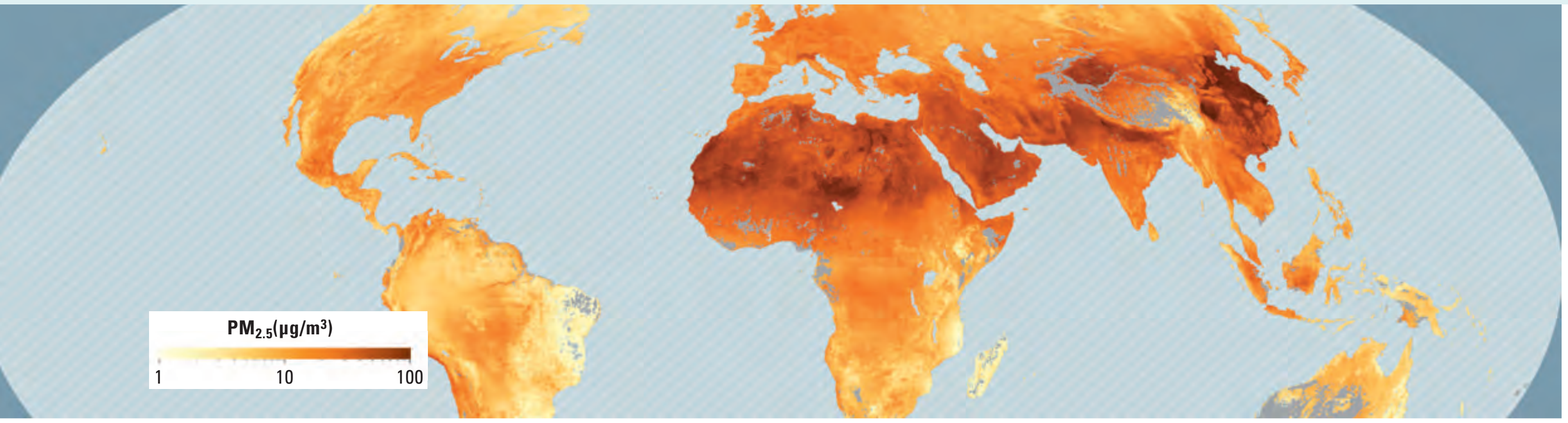


Figure 1: Global view of fine aerosol particles ($PM_{2.5}$). The map was compiled from satellite measurements (acquired between 2001 and 2006) and from model data.

Human induced emissions are drastically changing the chemical composition of the atmosphere with consequences for air quality and climate. We used the global EMAC model to assess such consequences. To achieve this, we have improved the model representation of organics in the gas and aerosol phase, gas-aerosol interactions, and linked the chemical composition of particles to their hygroscopic growth and cloud formation.

Fine aerosol particles efficiently scatter solar radiation, in effect increasing the planetary reflectivity. An increase of scattering particles exerts a negative climate forcing (cooling). Depending on the amount of light-absorbing material in the particles, e.g. black carbon, the solar energy can be trapped in the aerosol layer, thus heating the atmosphere. Therefore, increasing black carbon exerts a positive climate forcing (warming). The relative importance of scattering and absorption not only depends on the concentrations of these two classes of compounds, but also on the aerosol mixing state. Whilst climate models often treat aerosol compounds separately (externally mixed) we have shown that a fully (internally) mixed aerosol – being closer to reality – exerts a climate forcing that is nearly a factor of two larger. We have also developed model options to simulate inhomogeneous aerosols mixtures.

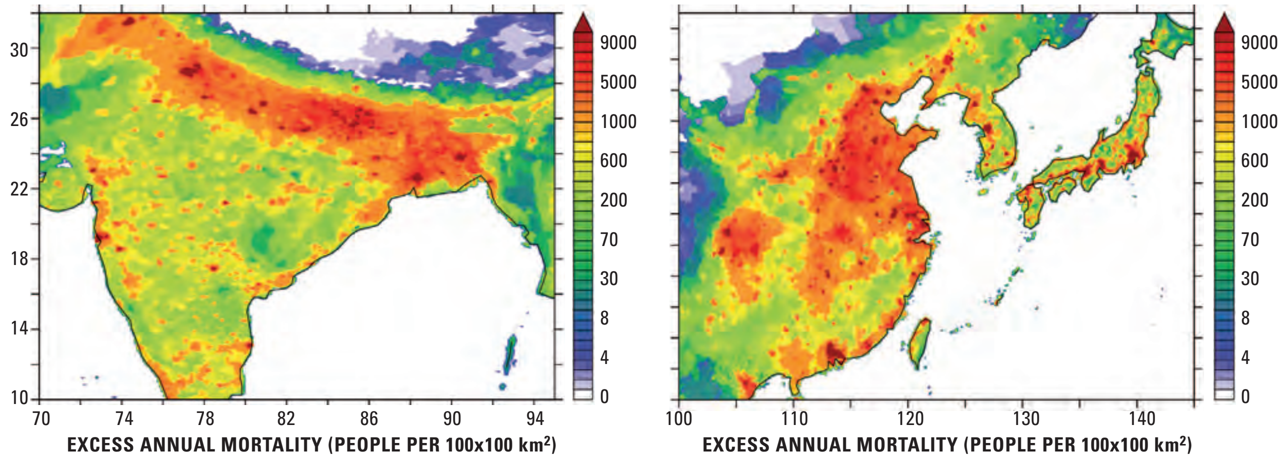


Figure 2: Sum of cardiovascular, lung cancer and respiratory mortality related to anthropogenic air pollution in South and East Asia. The color scale indicates the number of deaths attributable to air pollution per area of 100 km × 100 km.

Based on a multiyear study with the EMAC model we demonstrated that the sulfur gases COS and SO_2, the latter from medium strength volcanic eruptions, predominantly control the formation of stratospheric aerosols. Marine dimethyl sulfide and other SO_2 sources, including strong anthropogenic emissions in Asia, were found to play a minor role. Our results suggest that enhanced photolysis of H_2SO_4, formed from the oxidation of SO_2, and a meteoric dust sink for H_2SO_4 need to be accounted for to reproduce observations of SO_2 in the upper stratosphere and mesosphere. The stratospheric sulfate aerosol from medium strength volcano eruptions since the early 2000s has caused a significant negative climate forcing, which contributed to the reduced rate of global warming in this period.

We used EMAC to simulate cloud effects by aerosols that act as cloud condensation nuclei. EMAC consistently accounts for aerosol number, size and composition effects on particle hygroscopic growth and droplet nucleation. Globally, relatively small size Aitken mode particles are a primary source for cloud droplet nucleation. Although in polluted regions the abundance of larger (accumulation and coarse mode) aerosols can suppress the activation of the small Aitken particles, in most of the atmosphere the latter are still more relevant. Since for small particles the chemical composition, i.e. the solute (Raoult) effect, is more critical than for larger, more dilute aerosols, we find a relatively strong sensitivity of cloud droplet formation to the aerosol chemical composition. The aerosol-cloud coupling in EMAC generally increases the cloud droplet number concentration, decreases the formation of precipitation in stratiform clouds and increases the cloud water loading. This sequence of effects leads to larger cloud cover and longer cloud lifetime, higher cloud optical thickness, which cools the Earth's surface, increases atmospheric stability and reduces convective activity. While the global integral of these effects limits climate warming, on a regional scale it can vary strongly.

In collaboration with public health specialists, the EMAC model calculations have been "translated" into mortality attributable to air pollution. The global model output has been combined with epidemiological concentration-response functions to estimate mortality by lung cancer, respiratory and cardiovascular diseases. Airborne desert dust is estimated to lead to about 400,000 premature deaths per year, being mostly natural (about 75%), largely in North Africa, the Middle East and parts of Asia. Anthropogenic air pollution effects are found to be strongest in South and East Asia (Figure 2). Megacities can be clearly distinguished in Figure 2, where air pollution related mortality is particularly high. Scenario calculations for the coming decades suggest that especially in countries with many megacities strong air quality control measures will be needed to prevent dramatically increasing mortality. We estimate mortality attributable to air pollution in the year 2010 at 3.5 million (including desert dust), which could increase to 5.1 million in 2025 and 7.2 million in 2050, unless effective air pollution control measures will be implemented.

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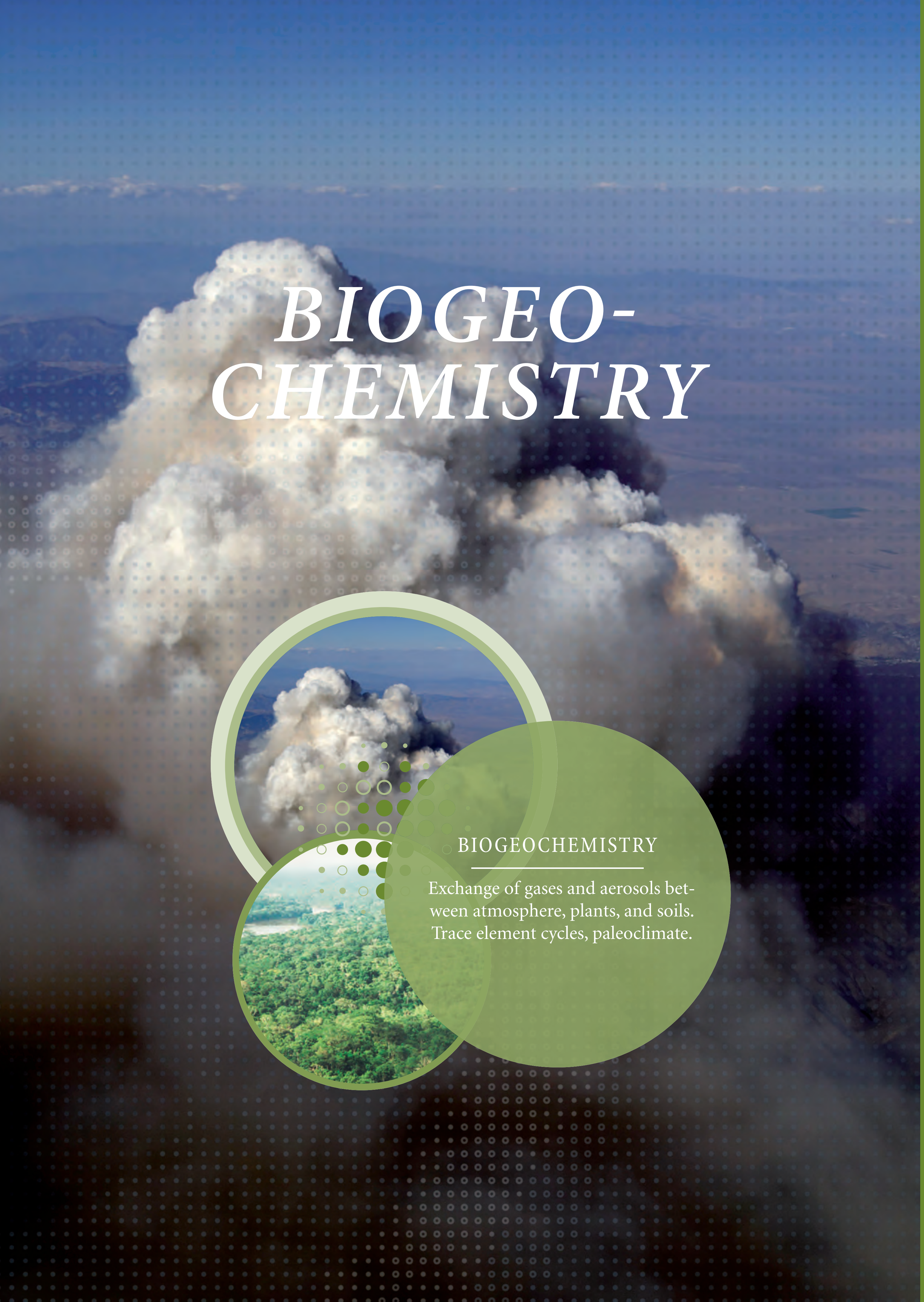
BIOGEO-CHEMISTRY



BIOGEOCHEMISTRY

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

Born on 19 May 1949 in Augsburg. Study of mineralogy/geochemistry Karlsruhe and Göttingen University, doctorate in oceanography at Scripps Inst. of Oceanography (1977), Assistant Professor of Oceanography (1978–1982), Associate Professor (1982–1986), Professor of Oceanography Florida State University (1986–1987), Director and Scientific Member at the Max Planck Institute for Chemistry (since 1987).

MEINRAT O. ANDREAE

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

We are investigating the exchange of volatile species by plants and soils in tropical and temperate ecosystems. Major objectives of this research are to understand the role of volatile organic compound (VOC) exchange in the carbon budget and in the atmospheric self-cleansing mechanism. Oxidation of VOC leads to the formation of low volatility substances, which condense to form organic aerosol particles. Our research on VOC exchange is complemented by investigations on the fluxes of trace gases such as NO, NO_2 and HONO from temperate and semiarid sites, in combination with laboratory studies and remote sensing. The sulfur species COS has been proosed as a tracer for biological carbon uptake. The investigation of the production mechanisms of biogenic organic aerosols is a central research topic in the Biogeochemistry Department. We have found that a large fraction of the aerosol over remote areas is made up of biogenic particles. In the larger size fraction, they consist mostly of fungal spores and similar material, while the smaller particles are formed by condensation of organic vapors from the oxidation of VOCs. Our research shows that the numbers of aerosols and cloud condensation nuclei (CCN) over pristine continents are low, similar to values found over the oceans. As a result, cloud microphysical processes and rain formation mechanisms over the remote Amazon Basin resemble those over clean marine regions. Large-scale vegetation fires lead to a strong increase of aerosol and CCN concentrations, which have dramatic effects on cloud properties and rainfall production, leading to redistribution of the transport of energy and chemical species in the atmosphere.

We are studying the role of fire in ecology, climate and atmospheric chemistry in the Amazon and other regions. The department maintains the Global Fire Monitoring Center (GFMC), which 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. Here, we are constructing a 325-m tall tower 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.

In the Paleobiogeochemistry group, we are investigating changing biogeochemical cycles and their interaction with the climate system using isotopic techniques. We are exploring 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. In collaboration with Mainz University, we are investigating the use of novel paleoarchives, e.g., bivalve shells, ostracods, and speleothems, to reveal changes in climates and biogeochemical processes in the past. The database group maintains data bases on geochemical data and reference materials.

AEROSOLS AND CLOUDS IN THE REMOTE 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: From the cockpit of the research aircraft HALO (right picture) one can see a special probe for air flow measurements aiming at the clouds.

The prominent icon of Global Change is the record of increasing CO_2 in the atmosphere since the 1950s, the “Keeling curve,” and its extensions into the past, based on ice core measurements. Imagine how difficult it would be to convince the world of the reality of Global Change, if we had this record only for the last few years, and then only with poor accuracy and spotty coverage. But this is exactly the situation that we find ourselves in with regard to aerosols, the second most important climate forcing agent. The climate effects of aerosols remain the largest uncertainty in assessing present and future climate change, and model studies show that among the uncertainties related to aerosol climate forcing, the largest one pertains to the state of the atmosphere before the onset of human pollution.

The challenge thus becomes to find evidence that lets us estimate what the atmosphere might have been like before we polluted it with anthropogenic aerosols. Because of the pervasiveness of air pollution, this is not an easy task. Aerosol particles can survive in the atmosphere long enough to travel once or twice around the planet, so that no place is immune from pollution. This applies in particular to continental atmospheres, where most pollution sources are located. To address this problem, we are making measurements in some of the remotest continental areas of the globe, to look for remnants of the pristine biosphere and its interactions with the atmosphere. Our research focuses on two contrasting ecosystems, which together represent a large fraction of the world’s terrestrial productivity and biomass: the tropical moist forest and the boreal forest.

For our studies, we have chosen mid-continental locations with natural vegetation, one in the middle of the Amazon Basin, the other in Central Siberia. Here we investigate biosphere–atmosphere interactions, and particularly the exchange of trace gases and aerosols between the forest biota and the atmosphere. Our research shows that in both places, anthropogenic emissions dominate atmospheric composition for much, if not most of the time. But in both systems there are times, when airmasses have not made recent contact with large sources of human emissions, such as during some events of inflow of Arctic air in the boreal region in summer, or during the wet season in the Amazon. At these times, most of the anthropogenic aerosols have disappeared as a result of washout by rain, and the shorter-lived trace gases have been photochemically removed. These periods thus give us glimpses into what sort of trace substance concentrations and what kinds of atmospheric/biospheric processes may have prevailed in pre-human times.

We are continuing our measurements at the Siberian Tall Tower site, ZOTTO, and over the last few years we have intensified our work in the Central Amazon Basin at the Amazon Tall Tower Observatory (ATTO) by establishing a sophisticated set of instrumentation at an 82-m tower site. Our work shows that the Amazon forest’s emissions dominate the abundance and composition of the trace gases in the region during much of the wet season. The plants emit trace gases, such as isoprene and terpenes, whose oxidation products we find in the aerosol particles that go on to serve as cloud condensation nuclei. But the actual mechanisms that are responsible for the production of the different size classes of particles in the natural Amazonian atmosphere still remain enigmatic. The largest particles, those larger than a micron, are mostly fungal spores or similar material. But how and why are they released? The size class around 100-500 nm almost always contains potassium seeds, requiring a still puzzling mechanism of release by plants and fungi, followed by uptake of material from terpenoid oxidation. The next smaller size class, centered around 70 nm, is always present, but there is little evidence for its production in the lower troposphere. We are just now obtaining evidence for a potential production mechanism in convective clouds. A similar mechanism may produce the occasional bursts of 30 nm particles that we observe in the evening or during night.

Two major milestones in our Amazon research have been achieved at the time of this writing. Construction of the 325-m ATTO Tall Tower, some 150 km upwind of Manaus, began in August 2014 and is expected to conclude in December of this year. The first flight campaign into the Amazon Basin on the German research aircraft HALO took place in September 2014. This aircraft campaign has produced a huge data set with exciting first results that document the powerful influence of aerosols on the cloud and precipitation properties in this region.

Figure 2: ATTO is steadily growing – here it reached about 100 meters.

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ISOTOPE TRACERS IN THE EARTH SYSTEM

STEVE GALER

> **“We need to understand better how bioavailability of nutrient trace metals in the surface ocean modulates the local primary production and thus the ocean sink for carbon dioxide.”**

Figure 1: Hydrocasting with the NIOZ ultraclean Titan frame (left), a seasonal phytoplankton bloom in the SW Atlantic (middle), and diatoms under the microscope (right).

How do nutrients limit phytoplankton growth in the surface ocean, can we track Saharan dust blowing across the Atlantic Ocean and who-ate-whom in modern savannah ecosystems and in the fossil record? All of these questions have in common that they can be addressed using isotope tracer systems.

In the Isotope Biogeochemistry Group we measure changes in the isotopic compositions of elements and use these as tracers in the Earth System. The two main causes of variation are: firstly, natural long-lived radiogenic decay systems, which can be used, for example, to fingerprint geological terranes, dusts and anthropogenic pollutants, or more prosaically to “date rocks”; and secondly, mass-dependent stable isotope fractionation, which is the slight preference for lighter or heavier isotopes such as may occur during chemical exchange reactions, mineral deposition or biological uptake. Some simple applications would be tracing mineral dust in the atmosphere from source to sink, or finding tell-tale isotopic signatures of geological or biological processes and reconstructing these from a suitable archive. Below, a few of these applications are highlighted.

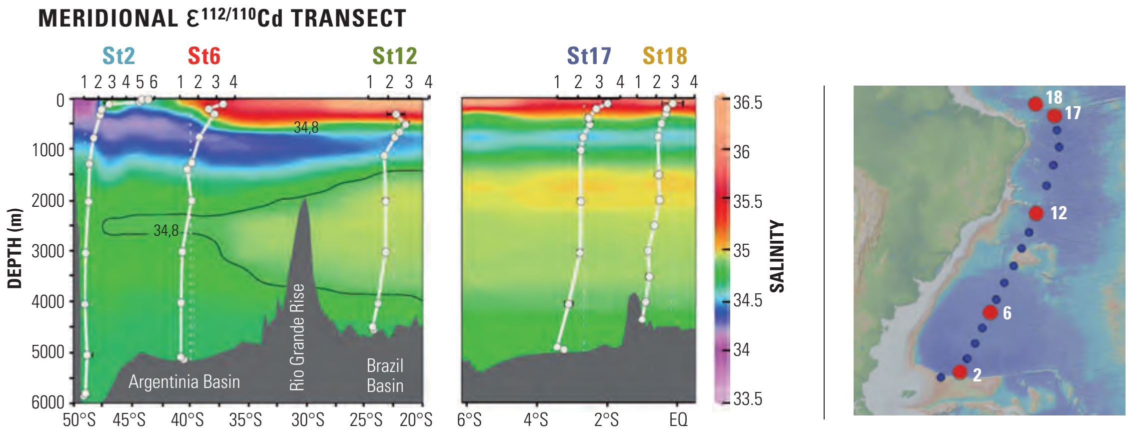

Figure 2: Cd isotope profiles (right) in the SW Atlantic from Geotraces cruise JC057 and stations (left).

MICRONUTRIENTS IN THE MODERN OCEAN

It is well known that the principal pathway for removal of carbon dioxide from the atmosphere is fixation by phytoplankton in the surface ocean, followed by export to the deeper ocean. Less well known is that in many parts of the world’s ocean, phytoplankton growth is limited by availability of micronutrients. Transition metal micronutrients, such as Fe, Zn and Cd, are cofactors embedded in vital metabolic enzymes such as carbonic anhydrase, which is involved in photosynthetic fixation of carbon dioxide, and when in short supply this impacts on the efficiency of the “biological carbon pump.” Classical examples of micronutrient limitation are the high nutrient, low chlorophyll (HNLC) regions, such as the Southern Ocean and Bering Sea, where primary productivity is low even though macronutrients (C, N, P, Si) are in abundance. Important micronutrient sources in these regions are from wind-blown dusts and upwelling of nutrient-rich deep waters.

We have been trying to understand better the biogeochemical cycling of key nutrient trace metals in the world’s oceans, how micronutrient supply impacts on ocean ecosystems and what implications this has for carbon dioxide drawdown in future climate scenarios. We have been concentrating on cadmium and cadmium stable isotopes. This is because cadmium exhibits nutrient-like behavior in the oceans, similar to that of nitrate and phosphorus, namely that it is extremely depleted in surface waters due to biological uptake into the phytoplankton crop and is released back into the deeper parts of the water column due to remineralization of sinking organic matter. This cycle of consumption and regeneration can be described mathematically in terms of the biological productivity in the surface mixed layer and the rates of upwelling and diapycnal mixing in the water column.

We have measured the concentration and the isotope fractionation of cadmium in a suite of seawaters from surface transects and depth profiles from the Atlantic Ocean collected under the auspices of the international GEOTRACES program (see: www.geotraces.org). The coverage includes the Southern Ocean, the Northwest Atlantic and Southwest Atlantic basins. An important result is that we can clearly document that phytoplankton preferentially incorporate “light” Cd during uptake, which results in the cadmium remaining in surface waters becoming progressively “heavier” (Figure 2). Further, the vertical consumption-regeneration cycle in the top ~2000 m of the water column appears to follow simple first-order Rayleigh kinetics. This means that Cd isotopes have potential for reconstructing the surface biological productivity in the past from suitable sedimentary archives, which is imperative for testing the hypothesised positive climate feedback in glacial times between low atmospheric CO_2, dustiness and increased primary production in HNLC regions.

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VEGETATION FIRES IN THE EARTH SYSTEM: A CROSS-DISCIPLINARY ANALYSIS FOR INTERNATIONAL POLICY SUPPORT

JOHANN GEORG GOLDAMMER

> **"Comprehensive assessments of the role of fire in the Earth System are needed to support the development of informed international policies addressing fire."**

Figure 1: Agricultural fires (burning of crop residues and pasture land) in temperate-northern Eurasia constitute a major source of black carbon transport and deposition to the Artic environment. A research and development program of the GFMC is addressing the use, impact and management of agricultural fires in Eastern Europe and the South Caucasus. Source: GFMC fire experiment in Georgia, South Caucasus, July 2014.

Several international legally binding conventions, which explicitly or implicitly address the role or consequences of vegetation fires, have been agreed upon in order to reduce the negative impacts of human interventions in the Earth System on the global environment and humanity. Examples are the United Nations Framework Convention on Climate Change (UNFCCC), the UN Convention on Biological Diversity (CBD) or regional conventions such as the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP), or voluntary frameworks such as the UN International Strategy for Disaster Reduction (UNISDR) or the "Hyogo Framework for Action (2005-2015): Building the Resilience of Nations and Communities to Disasters".

When addressing vegetation fires as causative agent or driver of changes, the dual role of fire must be considered. On the one side fire is an important ecological force, which has contributed in shaping the global environment during evolutionary and historic time periods, resulting in dependence, adaptation or tolerance of some ecosystems, or has constituted an important pre-human agent in biogeochemical cycles and the functioning of the atmosphere. On the other side, the importance of fire into fire-sensitive ecosystems by humans has resulted in degradation or destruction of some ecosystem and landscape functions, and in disturbance of biogeochemical cycles. This disturbance includes the increase of net transfer of terrestrial carbon to the atmosphere, which exceeds the balanced carbon exchange in a "natural", anthropogenically undisturbed vegetation-climate equilibrium. In addition, with increasing occupation of the natural landscapes by humans and the change of cultural landscapes during the late Anthropocene the vulnerability of society to natural and anthropogenic fires is increasing.

In order to provide state-of-the-art knowledge on the role of vegetation fires in the Earth System to policy and decision makers, the Fire Ecology Research Group/Global Fire Monitoring Center (GFMC) produced two major synthesis reports. The first volume entitled "Prescribed Burning in Russia and Neighbouring Temperate-Boreal Eurasia" (Goldammer 2013a), provides insight in the role of prescribed fire in the dynamics and management of natural and cultural landscapes of Eurasia, with new insights from Russia, including the initiation of the 200-year "Bor Forest Island Experiment" (1993-2192). This synthesis provides the rationale for a better understanding of natural and cultural fire regimes in the region.

The global analysis entitled "Vegetation Fires and Global Change. Challenges for Concerted International Action" is aimed at addressing a target group, as expressed by its subtitle "A White Paper directed to the United Nations and International Organizations" (Goldammer 2013b). Introduced with forewords by the Special Representative of the United Nations Secretary-General for Disaster Risk Reduction and the United Nations University, to which the GFMC and the Biogeochemistry Department are serving as an Associate Institute since 2005, the White Paper is a global state-of-the-art analysis of the role of vegetation fires in the Earth System, a collective achievement of 57 of the world's most renowned scientists and research groups working in fire science, ecology, atmospheric chemistry, remote sensing and climate change modeling, including contributions of four staff scientists from the Max Planck Institut for Chemistry. The aim of the White Paper is to support the endeavour of the United Nations and its affiliated processes and networks to address global vegetation fires and to provide rationale for coordinated, international action in crossboundary fire management at the global scale.

Essentials of the white paper have been partially pre-published in separate analyses, including a pre-publication of the review commissioned as part of the UK Government's Foresight Project "Migration and Global Environmental Change" (Goldammer and Stocks, 2011; Bowman et al., 2013).

Vegetation Fires and
Global Change

Challenges for Concerted International Action
A White Paper directed to the United Nations
and International Organizations

A Publication of the Global Fire Monitoring Center (GFMC)
Edited by Johann Georg Goldammer

Figure 2: The White paper "Vegetation Fires and Global Change".

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WHOLE-OCEAN CHANGES OF Ge/Si INDICATING HIGH GLOBAL SILICON FLUX FROM RIVERS DURING GLACIAL TIMES

KLAUS PETER JOCHUM

"Giant spicules of the deep-sea sponge *Monorhaphis chuni* are a suitable archive recording climate and biogeochemical cycles back to 14 ka B.P."

Figure 1: The mouth of the Morondava river (Madagascar) discharging into the Indian Ocean.

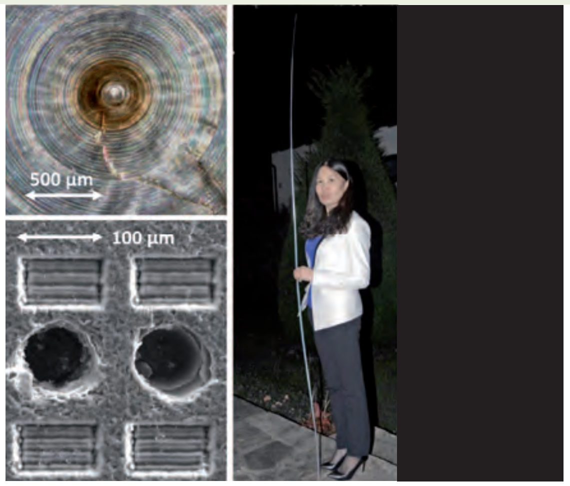

Figure 2: Giant spicule from the deep sea sponge Monorhaphis chuni *(right). Lamellar organization of the spicule and laser craters (rectangular scans and round spots for Si isotope and Ge concentration measurements, respectively) (left).*

The main scientific focus of the paleoclimate research group is the investigation of environmental samples, such as speleothems from caves, corals and shells from the ocean, and tiny ostracods from lake sediments. Such samples are useful archives of information on past environmental conditions, such as climate, vegetation, landscape, and influence of human activity.

A promising new application is the study of germanium (Ge) and silicon (Si) in glass sponges to constrain Ge and Si of the deep sea in the past. The biogeochemical behavior of both elements in seawater is similar, as demonstrated by the uniform present-day seawater Ge/Si ratio of 0.7 µmol mol^{-1}. However, changes of inputs to the oceans through rivers, eolian transport, hydrothermal activity, and low temperature sea floor weathering may have changed this ratio in earth history. Published analyses of diatoms reflect secular variations for the surface ocean. However, equivalent variations in the deep sea have not been comprehensively studied. We therefore analyzed giant spicules of the deep-sea glass sponge *Monorhaphis chuni*. These fascinating animals, which grow up to 3 m long, live on the seafloor at depths of about 1000 – 3000 m and represent the largest biogenic silica structures and possibly the oldest living animals on earth (Figure 1). Scanning electron microscopic inspection of the giant spicules reveals their lamellar organization and consequently their excellent stability. Because of their exceptional longevity (up to 14 ka), we recently demonstrated that giant spicules are suitable archives for the entire Holocene and the end of the last glacial period. We determined the silicon isotope ratios $^{29}Si/^{28}Si$ and $^{30}Si/^{28}Si$ in 2 – 6 mm wide cross sections by a new analytical technique, high-spatial-resolution in-situ, 200 nm - femtosecond - laser ablation – multi collector – ICP – mass spectrometry (200 nm-fs-LA-MC-ICP-MS). Si isotopes in spicules are excellent proxies for Si concentrations in the seawater. They are reported as δ values in per-mil, relative to the quartz reference material NBS 28:

$$\delta^{29,30}\mathrm{Si} = \left[\frac{(^{29,30}\mathrm{Si}/^{28}\mathrm{Si})_{\mathrm{sample}}}{(^{29,30}\mathrm{Si}/^{28}\mathrm{Si})_{\mathrm{NBS28}}} \ \text{-}1 \right] * 1000$$

The technique allowed an external reproducibility of 0.15 ‰ (2SD, n=32) and 0.23‰ (2SD, n=32) for $\delta^{29}Si$ and $\delta^{30}Si$, respectively, using a laser spot size of 20 µm and scanning over a surface of 65 x 100 µm^2. Germanium concentration measurements were performed adjacent to the crater lines produced by the Si isotope measurements (Figure 1) using 110 µm spots. The spicule data were converted into seawater concentrations using the inverse linear relationship of $Si(OH)_4$ in seawater and $\delta^{30}Si$ in spicules, as well as the linear relationship between Ge/Si in spicules and Ge in seawater.

Our results yield $\delta^{30}Si$ values ranging between -0.5 and -3.6‰ for the different specimens; they are much lower than the modern value of deep waters of around +0.8‰. This high fractionation is consistent with the high Si concentrations observed in the deep sea. We found also significant and systematic differences from the rim to the center of the cross sections, especially for the largest and oldest sample SCS4 (Figure 2). Measurements of the rim regions of the spicules, which were in contact with the present-day seawater at time of collection, yield a Ge/Si of the present-day seawater, which is uniform within 5%. The Si isotopes and the Ge concentrations in the giant spicules change with time, implying that the Ge/Si ratio of the deep sea has also changed over time. Our results demonstrate that the Ge/Si ratio slightly increased in the Holocene from 10.5 ka to the present. Remarkable is the high Ge/Si ratio at around 6 ka, which corresponds to the Holocene climatic optimum. Significantly low Ge/Si ratios (0.55 µmol mol^{-1}) are observed in the glacial period 11 – 14 ka B.P. These low ratios are similar to ratios published for diatomaceous opal in the glacial surface ocean and support the hypothesis of whole-ocean variations of Ge/Si.

River waters are, with about 80%, the major source of seawater Si. The only plausible explanation for the low glacial Ge/Si and high Si is that glacial periods are characterized by low continental chemical weathering intensity. This leads to incongruent dissolution, with elevated Ge/Si in secondary clay minerals and correspondingly lower Ge/Si and higher Si in glacial river waters than today. Budget considerations require then that the global Si flux from rivers to the ocean must have been about 60% higher during glacial times than at present.

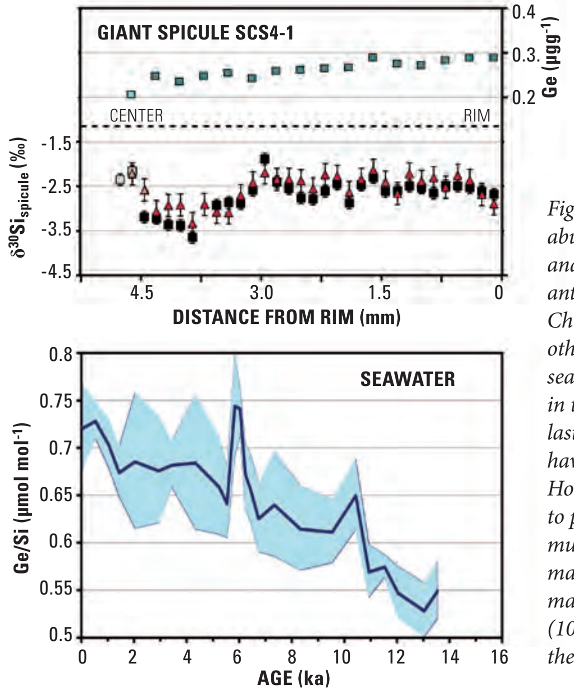

Figure 3: (Top) $\delta^{30}Si$ values and Ge abundances obtained from microanalyses of a cross section of the giant spicule SCS4-1 from the South China Sea. Data from this and other spicules are used to determine seawater Ge and Si concentrations in the deep-sea environment in the last 14 ka. (Bottom) Ge/Si ratios have slightly increased during the Holocene (from about 10.5 ka B.P. to present) with a possible maximum at about 5 – 6 ka B.P., which may be related to the Holocene climatic optimum. Low Ge/Si values (10.5 – 13.5 ka B.P.) correspond to the Younger Dryas cold period.

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PROCESS RELATED ENCLOSURE STUDIES WITH PLANTS AND SOILS OPEN THE VIEW FOR BIOSPHERE-ATMOSPHERE EXCHANGE

JÜRGEN KESSELMEIER

"Understanding of plant/soil metabolism and exchange regulation by enzymatic and enclosure studies is indispensable for interpreting or modeling larger scale processes."

Figure 1: Ecotypes and substructures with relevance for trace gas exchange investigated by enclosure or profile (tower) techniques: Tropical dry and flooded forest, soil vegetation with leaf colonized by biological crusts, dry soil with vegetation, decomposing leaf.

Two examples shall demonstrate that it is essential to understand the biological background for the exchange of trace gases in order to handle large scale measurements and modeling. One example is the uptake of carbonyl sulfide, which is reasonably well understood scaling down from the atmosphere to the biological metabolism based on three enzymes (ribulose-1,5-bisphosphate carboxylase-oxygenase, phosphoenolpyruvate carboxylase and carbonic anhydrase), all involved in the exchange of carbon dioxide (CO_2) and carbonyl sulfide (COS) as reported in our earlier work. Consequently, there is an ongoing discussion exploiting the uptake of COS as a proxy to estimate Gross Primary Productivity (GPP). However, there are influential unknowns such as the contribution of soils to the overall exchange of COS. Using an automated soil enclosure cabinet, we tested topsoil from an agricultural plow horizon of a wheat field in Mainz (Germany) in comparison to organic horizons from a boreal coniferous forest at Hyytiälä (Finland) as well as a mid-latitude spruce forest at Waldstein (Germany), the latter covered by either a young spruce understory or dense coverage of blueberries. All exchange studies were performed under two different atmospheric COS concentrations, 50 ppt and 1000 ppt. COS exchange with all soils exhibited a close relation to the soil water content (SWC), reflecting water dependent biological activity as well as limitations of gas diffusion with increasing water content. The uptake patterns showed an optimum for soils from Mainz and from Hyytiälä (Finland), matching our older reports reasonably well. The two other soil types showed an uptake pattern with deposition over a broad range of SWC (Figure 2). Contrasting to earlier results, we found a clear emission even under the high COS concentration scenario (2 x normal) when soils dry out.

Another highly interesting compound is peroxyacetyl nitrate (PAN) which plays an important role in the nitrogen cycle and is regarded as being toxic to plants. But a deeper understanding of its uptake by ecosystems is required. The main focus of our research was to determine the PAN deposition to plants in relation to ozone and to compare the partitioning of the deposition between plant stomata and plant surfaces. As observed in plant enclosure experiments under controlled environmental conditions (Figure 2, right panels), ozone and PAN are taken up by the plant in the light when stomata are open. In the dark, when stomata are mostly closed, the uptake is nearly completely reduced to zero. The small rest of ozone uptake could be reduced to zero by applying the hormone abscisic acid (ABA), causing total stomatal closure (data not shown). These data will help to evaluate the role of uptake and metabolic consumption of the trace gas by plants in relation to "simple" deposition to plant surfaces.

OUTLOOK

The partitioning of the deposition process of PAN between plant stomata and plant surfaces is a matter of discussion. Our approach will contribute to a better understanding of the uptake and consumption. The findings for the COS exchange are striking and demonstrate that the role of soils must not be regarded as constant. Depending on water availability as well as atmospheric mixing ratio, soils may change their behavior from an uptake optimum to a clear emission under conditions that exist under natural situations. Therefore, we may state that GPP estimates derived from gross COS uptake over ecotypes must be interpreted with care if there is no information available about the exchange with the underlying soils.

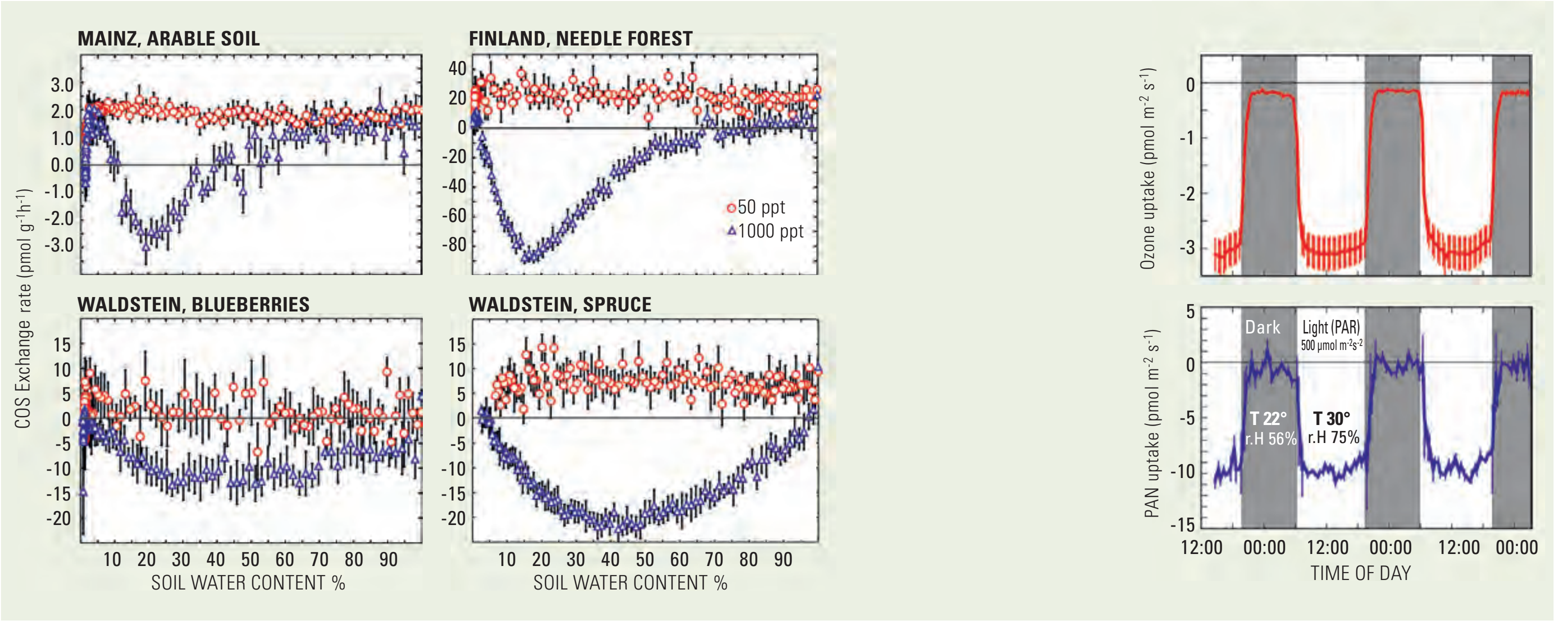

Figure 2: Dynamics of trace gas exchange between soils (COS), plants (PAN, O_3; Quercus ilex) and the atmosphere measured with soil or plant enclosures under controlled conditions. Error bars represent errors according to the Gaussian propagation method.

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AFTER 20 YEARS OF CONTINUOUS RESEARCH – THE IMPROVED BIOGEOCHEMISTRY SOIL LABORATORY CHAMBER SYSTEM

FRANZ X. MEIXNER

> **"Reliable quantification of trace gas emissions from soil and substantiated characterization of the underlying microbial processes require high precision measurements."**

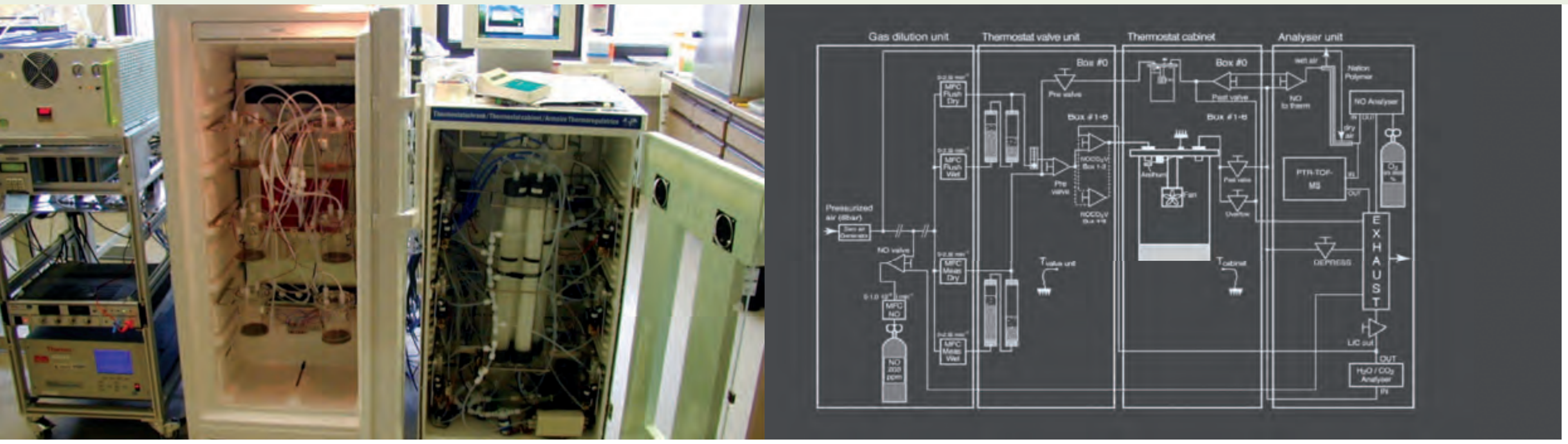

Figure 1: Fully automated incubation system for simultaneous fumigation of six soil samples under prescribed conditions of soil moisture, soil temperature and NO concentration: humidifiers, mass flow controls, and valve manifolds, dynamic soil chambers and soil sensors (left). Schematic setup of the improved laboratory incubation system (right).

Nitrogen oxides ($NO_X = NO + NO_2$) are key catalysts for the atmospheric oxidation of CO, CH_4, and VOCs by the hydroxyl and other radicals. While fossil-fuel combustion and biogenic emissions from plants are among the best documented global NO_X and VOC sources, knowledge of biogenic NO emissions from soil is still insufficient and there is almost no information on VOC emissions from soils. Laboratory incubation systems for the investigation of NO and VOC release from soil are usually dynamic chamber systems. Here, the net NO (VOC) release rate from an enclosed soil sample is determined from the NO (VOC) concentration difference between incoming and outgoing air. Within the last decade, the study of arid/hyper-arid as well as organic rich soils by laboratory dynamic chambers has manifested obvious and partly substantial difficulties. After continuous studies from 1994 to 2014, there was reasonable suspicion that these were due to insufficient precision of trace gas concentration and soil moisture measurements, as well as non-standardized pre-incubation protocols and sub-sample variability.

A comprehensive concept for the laboratory dynamic chamber method has been formulated to completely characterize soil NO production and soil NO consumption in terms of the three major influencing factors (soil moisture, soil temperature, and NO concentration) by measurements of the net NO release rate. However, compared with the postulated response of net NO release rates to these factors observations with results from earlier versions of the laboratory dynamic chamber system revealed obvious and large discrepancies. By a series of experiments on soil samples with very contrasting soil properties the present, extensively improved biogeochemistry soil laboratory system (see Figure 1) has been demonstrated to fully overcome these discrepancies. The improvements focused particularly on the precision of (a) the NO concentration measurement (< 1% for > 10 ppb; < 10% at 1 ppb) and (b) the measurement of the soil moisture content (< 0.5%). This resulted in the very sensitive and precise determination of the NO release rate (limit of detection: 80 pg nitrogen per kg of dry soil and second).

From the net release rate, all further quantities for the characterization of NO production and consumption are derived (NO production rate, NO consumption rate coefficient, NO compensation point concentration, Q_{10}-values of NO production and consumption). For calculation of all these quantities, a set of only four pairs of precisely measured NO concentrations is sufficient. Following a standardized method of initial wetting (up to water-holding capacity), the response of net NO release rates to the entire range of soil moisture content can be investigated by slow drying-out of the soil samples (by flushing soil chambers with air of very low dew point). The response of net NO release rates to soil temperature and NO concentration is studied by the step-wise changing of (i) the temperature of the entire chamber system, and (ii) using prescribed NO concentrations. Proper control and automation of the chamber system with respect to these step-wise changes has been designed such that all experiments for characterization of NO production and consumption could be performed on one soil sample and during one drying-out process only. This has completely eliminated the serious problem of sub-sample variability, which was due to the fact that former versions of the laboratory system needed experiments with four different sub-samples. Measurements of NO release rates from a hyper-arid Mongolian desert soil (low NO emissions, maximum at < 10% soil moisture, extremely low NO consumption rates) with both a former and the present day soil laboratory system demonstrate the result of the improvements (in Figure 2).

The soil laboratory system now also has a set of further, promising features available. In order to study the impact of heterotrophic microbial activity on the net release of NO and other trace gases, knowledge of a suitable proxy, the CO_2 release, is important. For its determination, the system can be temporarily switched into the static chamber mode. Using a PTR-TOF-MS in parallel to the NO, CO_2, and H_2O analyzers, net VOC release rates from an agriculturally managed, irrigated and heavily fertilized oasis soil (Xinjiang, P.R. China) have been investigated. These are dominated by substantial amounts of acetone (C_2H_4O) and acetaldehyde (C_3H_6O), which surprisingly share with NO identical shapes of optimum curves (with respect to soil moisture). These analogies between NO and C_2H_4O/C_3H_6O strongly support the concept that biological rather than abiotic processes are responsible for the soil release of C_2H_4O and C_3H_6O. Complete characterization of VOC production and VOC consumption with the improved laboratory dynamic chamber system now enables soil specific fingerprinting of corresponding microbial activities, which is of great importance for the newly emerging field of soil volatilomics.

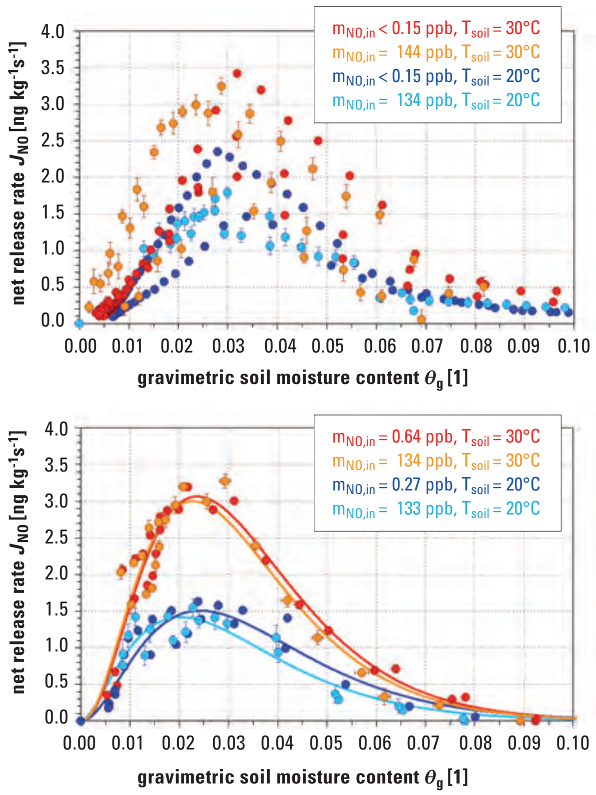

Figure 2: Results of individual NO net release rate (J_{NO}) measurements performed on 12 sub-samples of a desert soil from Mongolia. Measurements with the previous (before 2013) laboratory chamber system (top) and the present day system (bottom). Two (bottom) and three (top) replicates have been measured for each of the four measurement conditions indicated by the four different colors of shown data points.

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A HIGH RESOLUTION VIEW OF ATMOSPHERIC AEROSOLS

CHRISTOPHER PÖHLKER

> **"The microstructure of aerosols is a key determinant of their properties and role in the atmosphere. We use microscopy to link nano with global scales."**

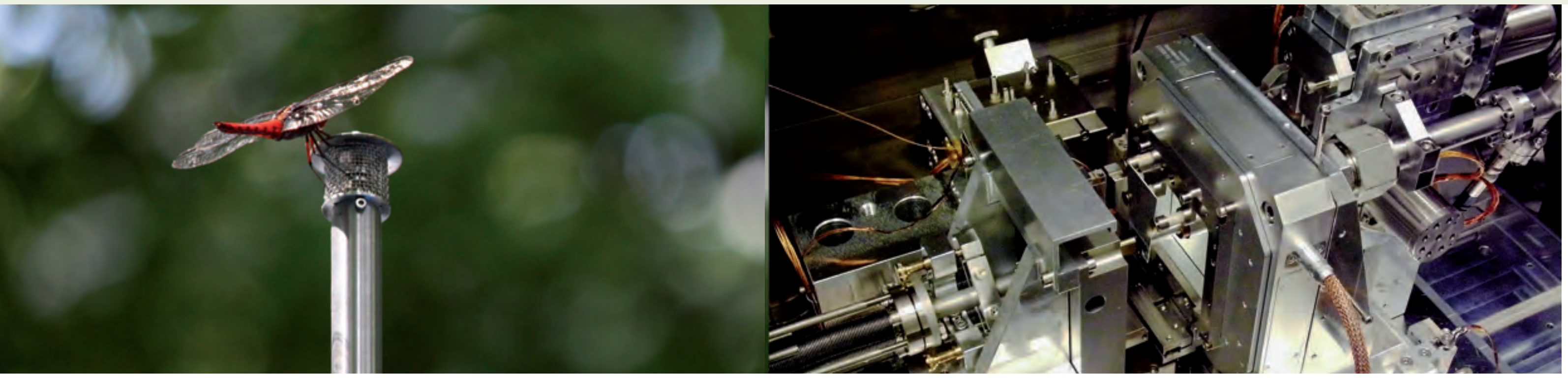

Figure 1: Aerosol samples are collected in different environments (e.g., at the remote ATTO site in Brazil, left image) and analyzed by micro-spectroscopy (e.g., at the x-ray microscope at the synchrotron BESSY II in Berlin, right image).

Aerosol particles play a key role in atmospheric, hydrological, and biogeochemical cycling and thus represent a central topic in environmental science. The analysis of atmospheric aerosols can be challenging because of their highly diverse composition and dynamic life cycle in the atmosphere. We are using several types of microcopy as fruitful tools in aerosol analysis (Huffman et al., 2013; Pöhlker et al., 2013). Recent advances in modern microscopy techniques provide an unprecedented view of aerosol particles with high spatial and chemical resolution. X-ray microspectroscopy at synchrotron facilities is a particularly powerful tool in this regard. It allows quantification of the elemental composition, provides detailed chemical speciation, and helps to identify trace elements in highly heterogeneous samples at nanometer scales.

In 2012, we started systematic experiments applying scanning transmission x-ray microscopy with near-edge x-ray absorption fine structure (STXM-NEXAFS) analysis to aerosol samples using x-ray microscopes at the synchrotrons Advanced Light Source (ALS, Berkeley, CA, USA) and BESSY II (Helmholtz-Zentrum, Berlin, Germany). The accessible photon energy range covers the x-ray absorption edges of a variety of atmospherically relevant elements (i.e., carbon, nitrogen, oxygen, potassium, calcium, iron, and sodium). We conducted STXM-NEXAFS experiments on a variety of aerosol samples including tropical, boreal, alpine, and marine environments.

One focal point of our analysis is the aerosol cycling in the atmosphere over the Amazonian rainforest. The atmospheric conditions in this unique ecosystem oscillate between pristine natural conditions during the wet season and anthropogenically polluted conditions during the dry season. Thus, the Amazon can be seen as a natural laboratory to study the impact of anthropogenic aerosols on atmospheric processes. Our STXM-NEXAFS experiments provide detailed insights into the composition and morphology of Amazonian aerosols throughout the seasons. To our surprise we found that wet season aerosol particles in the cloud-active size range do not consist exclusively of organic matter. Instead, they comprise a significant fraction of inorganic elements such as potassium, chlorine, and calcium (Pöhlker et al., 2012). Regarding the absence of pollution in the wet season, this indicates that biogenic salts are emitted by the forest ecosystem with subsequent influence on the formation and evolution of aerosol particles and the aerosol-cloud interaction overall. However, how and to what extent the biosphere and atmosphere in the Amazon are mechanistically linked remains a key question in our continuous field and laboratory measurements.

Besides the analysis of particle morphology and composition, STXM-NEXAFS can also be used to mimic aspects of the dynamic evolution and aging of aerosol particles in the atmosphere. Therefore, we modified the x-ray microscope at BESSY II to monitor the hygroscopic response of ambient aerosol particles to relative humidity variation. We observed substantial changes in particle microstructure with multiple coexisting solid and liquid phases, particularly in intermediate humidity regimes (Pöhlker et al., 2014). These initial results underline how dynamically the microstructure, and thus the physical-chemical properties of aerosol particles, respond to fluctuations in atmospheric conditions.

An upcoming focus for our microscopy studies will be the analysis of a comprehensive set of aerosol samples from the recent aircraft campaign ACRIDICON-CHUVA, which was conducted in the Amazon and aims at a detailed understanding of aerosol-cloud interactions under contrasting atmospheric conditions, ranging from pristine to highly polluted scenarios. Moreover, we have extended the scope of our analysis from aerosols to other environmental samples, such as rock varnish, whose origin has remained enigmatic since its first description by von Humboldt in 1819. STXM-NEXAFS allows insights into the complex micro-architecture of rock varnish and may therefore provide clues about its genesis.

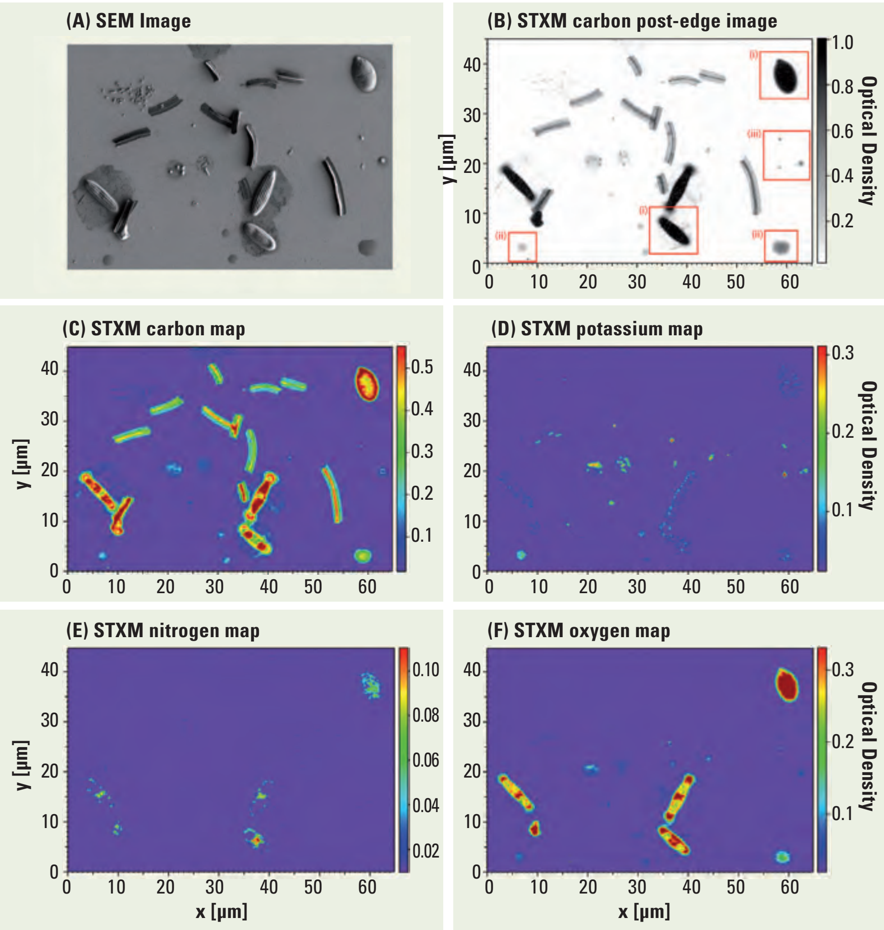

Figure 2: Microscopic images of Amazonian wet season aerosol particles. (A) SEM images of representative region. (B) STXM carbon post-edge image (293 eV) and (C-F) STXM elemental maps of same region.

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THE ATTO DATABASE – A TOOL TO MANAGE AND EXCHANGE DATA

BÄRBEL SARBAS

"Databases are essential for scientists to manage the constantly increasing amount of measured and published data."

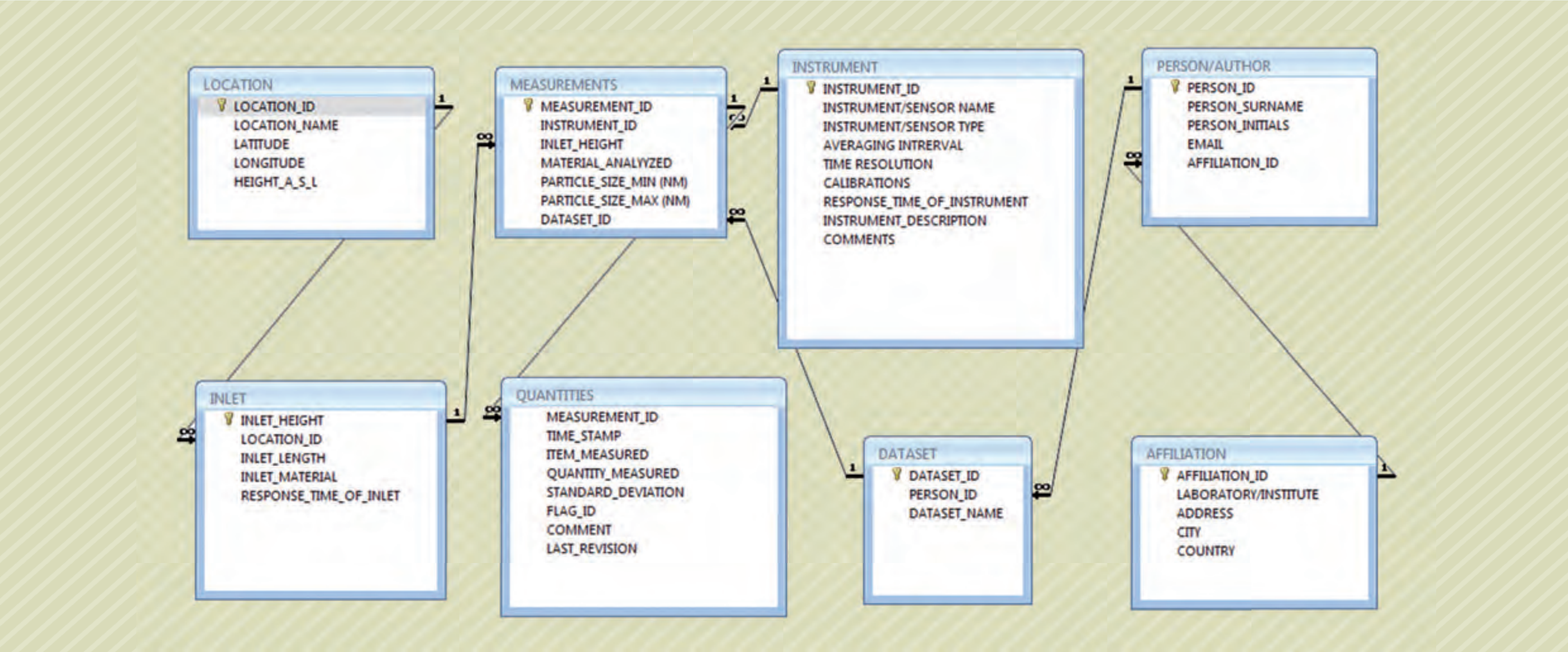

Figure 1: Structure of the ATTO database showing the respective columns and relationships.

Figure 2: The ATTO tower at about 150 meters (left). View from bottom to top of the Instant Walk-Up tower at the ATTO site (right).

The database group was started in the late nineties in the former Geochemistry Department of the Max Planck Institute for Chemistry to build up and manage GEOROC, an open-access geochemical database on volcanic rocks ranging in age from Archean to modern. This online database contains published data on the compositions of whole rocks as well as of volcanic glasses, rock-forming minerals and melt inclusions. The analyzed samples come from world-wide occurrences of different geological settings. Currently, the database contains about 775,000 analyses published in more than 12,700 papers. GEOROC became a frequently used tool, not only in hard-rock geochemistry, but also in paleoclimate, biogeochemical and atmospheric research. For instance, the source of dust in the atmosphere is determined by comparing its composition with that of rocks from possible source regions. 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 database is among the Earth Science databases recommended by Nature journals.

The new database project ATTO of the Biogeochemistry Department was started in 2014. This relational database uses a structure very similar to that of GEOROC (Figure 1). It will contain results of measurements done at various heights on the Amazon Tall Tower Observatories in the rainforest of Brazil (Figure 2). These measurements include concentrations of compounds like CO_2, CH_4, CO, ozone, N_2O, H_2O and black carbon but also meteorological data like temperature, humidity, wind speed and rainfall and data like particle scattering coefficient, particle number concentration and particle number size distribution. Metadata comprise 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 finally processed perfect data, raw data and data showing some noise.

To ensure that data can be entered into a database, a certain degree of standardization is necessary. In the case of the ATTO data, a defined time stamp (days since 30/12/1899) is crucial besides consistent units and abbreviations. Therefore we have developed a template that also distinguishes mandatory and optional information and should be used by the scientists to supply data.

The database will be accessible to all scientists working within the ATTO project. Actually, it is in a test phase and runs on a local machine in Mainz. As soon as a relevant amount of data is entered, it will be available online and run on a server at the Gesellschaft für wissenschaftliche Datenverarbeitung (GWDG) in Göttingen. It will be mirrored on a server in Brazil. It is planned to update the database every 4–6 months. The web interface allows selection of data by various criteria like measured item, quality of data, inlet height and/or scientist's name.

The main purpose of the database is a fast exchange of measurements between the working groups of the Max Planck Institute for Chemistry and the Brazilian National Institute for Space Research (INPE) in São José dos Campos. The raw data is already available. The above-mentioned flag system allows the differentiation between these raw data and finally processed data. Another advantage of the database is a long-term accessibility of data. Results of measurements are still available although the originating scientist might not be a member of the project anymore. And last but not least, the necessary formats lead to a certain degree of standardization of the data which enables a much easier comparison and evaluation.

SURFACE-ATMOSPHERE EXCHANGE OF REACTIVE NITROGEN

MATTHIAS SÖRGEL

> **"Reactive nitrogen is a nutrient and a pollutant. We want to track its pathways in the atmosphere and the biosphere to learn about the feedbacks between these two effects."**

Figure 1: Working 80 m above ground level and 40 m above the crowns of the trees of the Amazonian rain forest.

Molecular nitrogen (N_2) is the main constituent of the atmosphere (78 vol %) and very unreactive. Several processes are able to break the stable triple bond in N_2 and to create the so called reactive nitrogen (Nr). These processes are combustion, lighting strikes, catalytic conversion (Haber-Bosch), and enzymatic fixation by microorganisms. Once nitrogen has been converted to Nr, it is one of the key players in global biochemical cycles (an essential nutrient) and in atmospheric chemistry. In the troposphere, for example, nitrogen monoxide (NO) acts as a catalyst for ozone (O_3) formation and nitrous acid (HONO) as a primary source of OH radicals, the cleansing agent of the atmosphere.

Our group was founded in 2009 as a junior research group and was led by I.Trebs until September 2013. Since then the group has been led by M. Sörgel. We investigate the exchange of reactive nitrogen (Nr) species between the earth's surface (soil and vegetation) and the atmosphere. We apply micrometeorological methods to investigate the fluxes in the field and study the processes responsible for the uptake or emission of Nr in more detail in the laboratory. A special focus in recent years has been the investigation of HONO emissions from soil bacteria.

These investigations were started in a joint study with the research group of U. Pöschl and provided a proof of concept for the idea of H. Su that nitrite can be protonated in soil solutions and emitted from soils according to Henrys-law partitioning. The protonation strongly depends on pH, and therefore acidic soils were expected to favor HONO emissions. Nevertheless, our follow up study found the highest HONO emissions from neutral to alkaline arable and arid soils. An interesting consequence of the relatively high HONO emissions from arid soils is that HONO might be an unaccounted NO_x source that would explain the differences between the NO_2 values retrieved from satellites and those predicted by emission models (Oswald et al., 2013). Furthermore, the study showed that ammonium oxidizing bacteria are able to emit HONO in large quantities. A novel method for measuring isotopically labeled HONO was developed in collaboration with the Multiphase Chemistry Department (Wu et al., 2014). By applying ^{15}N-labeled urea to a natural soil sample, the fast conversion of reduced nitrogen to HONO by microorganisms was proved. The measurements for these studies have all been conducted by applying HONO-free air to the measurement system, but HONO can also be taken up (by soils) which would cause reverse fluxes. That HONO fluxes can be bi-directional at the ground surface has also been found in a recent field study in the Fichtelgebirge Mountains, Germany, in a joint project with the University of Bayreuth.

Therefore, the current research of our group consists of two major topics. A) What are the metabolic pathways (nitrification, denitrification) that are responsible for HONO (and NO) formation and consumption in soils? B) What are the physicochemical factors influencing HONO uptake and emission from soils?

For these studies we conduct fumigation experiments in Teflon chambers, measurements of HONO emissions from many different soil samples, genetic analysis of the microbial communities, and even studies with mutants that are deficit in genes encoding for certain enzymes.

Currently, we are also measuring the exchange of HONO and NO_x at the forest floor at a remote site in the Amazonian rain forest (ATTO site). Future studies will focus on the influence of Nr compounds (e.g., HONO and NO_x) on the oxidation chemistry in such remote forest environments.

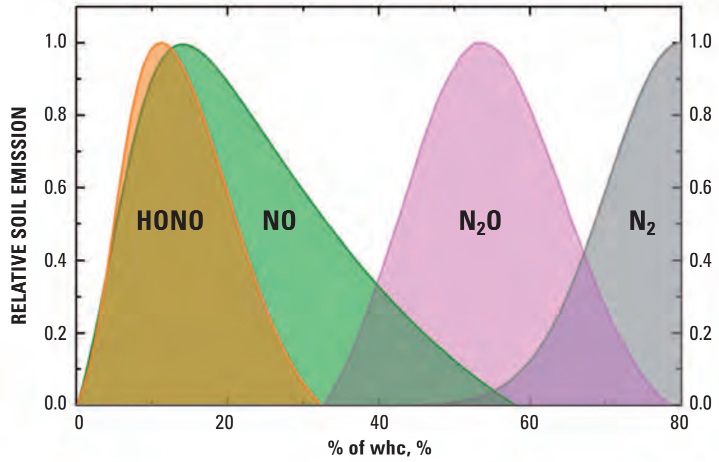

Figure 2: Conceptual model of emissions of reactive nitrogen from soils. From Oswald et al. (2013).

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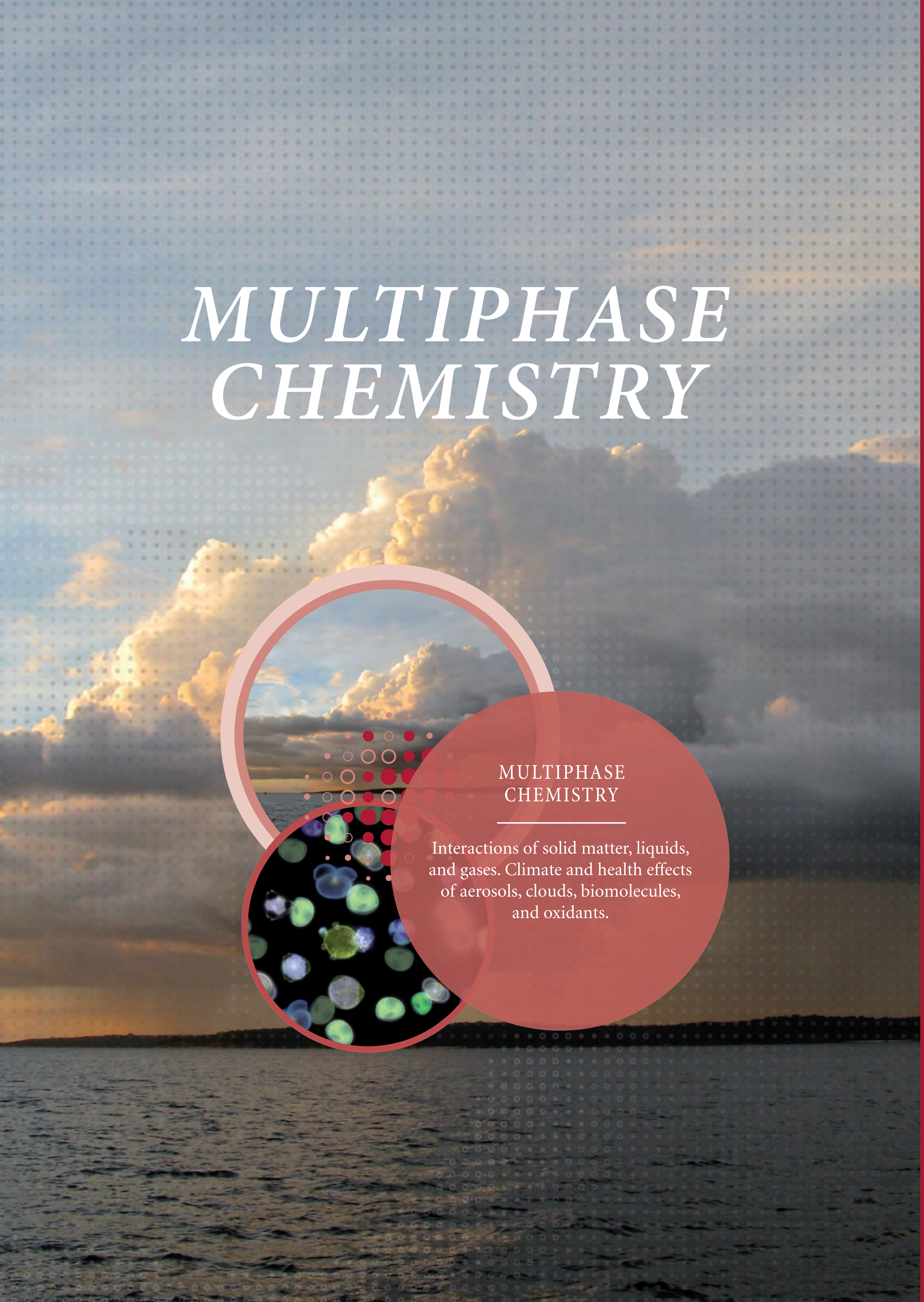

MULTIPHASE CHEMISTRY

MULTIPHASE CHEMISTRY

Interactions of solid matter, liquids, and gases. Climate and health effects of aerosols, clouds, biomolecules, and oxidants.

Born on 9 October 1969 in Klagenfurt, Austria. Studies in technical chemistry and doctorate in organometallic chemistry at the Technical University of Graz (1988-1995). Schrödinger fellow and postdoctoral researcher at the Massachusetts Institute of Technology (1996-1997). Research scientist at the Max Planck Institute for Chemistry (1997-1998). Research group leader and habilitation in chemistry at the Technical University of Munich (1999-2005). Research group leader at the Max Planck Institute for Chemistry and lecturer at the University of Mainz (2005-2012). Director and Scientific Member at the Max Planck Institute for Chemistry (since 2012). Professor at the Johannes Gutenberg University of Mainz.

ULRICH PÖSCHL

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 AND CLIMATE AS WELL AS FOR LIFE AND 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 involving gases like air, oxygen, and carbon dioxide; liquids like water, blood, lymph and plant sap; and solid or semi-solid substances like bone, tissue, skin, wood and cellular membranes. The global biogeochemical cycling of chemical elements and compounds, which can be regarded as the metabolism of planet Earth, also involves multiphase chemical reactions, mass transport and phase transitions within and between the atmosphere, biosphere, hydrosphere, and solid Earth.

The overarching aim of the department is to elucidate the role of multiphase processes in the Earth System and life from molecular to global scales, especially in the interplay of the atmosphere, biosphere, climate, the immune system and public health. Key issues are: the influence of natural and anthropogenic aerosols on clouds, precipitation & climate; the role of biological aerosols in the co-evolution of climate, life & ecosystems; the effects of air contaminants on public health; and the chemical causes and mechanisms of allergic reactions & chronic inflammation.

To explore and resolve these issues, we combine physical, chemical and biological 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 chromatography, spectrometry and microscopy; bioassays and DNA analyses; kinetic process models and regional atmospheric models.

The Multiphase Chemistry Department was established in 2012, and the current main areas of research are broadly reflected by the group structure as follows: Aerosol, Cloud & Biosphere Interactions (*Su et al.*), Bioaerosols & Microbiology (*Fröhlich et al.*), Cryptogamic Covers (*Weber et al.*), Inflammatory Processes (*Lucas et al.*), Organic Aerosols & Oxidants (*Shiraiwa et al.*), Semivolatile Organic Compounds (*Lammel et al.*), and Multiscale Integration (*Pöschl et al.*). The Minerva group on Aerosols and Regional Air Quality (*Cheng et al.*) is also closely associated with the department.

Common themes across the research areas and groups include water uptake & phase changes; molecular diffusion & reaction; reactive oxygen & nitrogen species; primary biological & secondary organic aerosols; soot & biomass burning aerosols; aromatic compounds & proteins. Focal points and highlights of recent and ongoing research projects are detailed in the following group reports. They comprise the role of bioparticles and smoke in the formation of cloud droplets, ice crystals and precipitation; molecular corridors and kinetic regimes in the chemical evolution of secondary organic aerosols; size-effects on the phase state of nanoparticles; protein nitration and pattern recognition receptors in allergic reactions and chronic inflammation; and global circulation of persistent organic pollutants.

MULTIPHASE CHEMISTRY FROM MOLECULAR TO GLOBAL SCALES

ULRICH PÖSCHL

"Multiphase processes on various scales play a vital role in the co-evolution of climate, life and health throughout Earth history and the Anthropocene."

Figure 1: ACRIDICON-CHUVA measurement campaign: instruments and operators on the HALO aircraft (left), convective clouds over the Amazon (right).

Multiphase chemical reactions, mass transport and phase transitions between gaseous, liquid and solid matter relevant for the Earth System, climate, life and health are bridging a wide range of spatial and temporal scales from below nanometers to thousands of kilometers and from less than nanoseconds to millennia.

Particularly important for the co-evolution of life and climate are the exchange and cycling of gases and particles between the biosphere and atmosphere. Anthropogenic air pollution has led to a massive increase of aerosol and oxidant concentrations in the lower atmosphere, i.e., at the atmosphere-biosphere interface. For example, the average mixing ratios of ozone in continental background air have increased by factors of 2-4 from the 19th century to the 21st century, and the number and mass concentrations of aerosol particles in polluted urban air are typically by 1-2 orders of magnitude higher than in pristine air of remote continental regions. The strong anthropogenic increase of these and other air contaminants like reactive nitrogen species is a characteristic feature of global environmental change in the Anthropocene, i.e., in the present era of globally pervasive human influence on the Earth System.

Over vegetated continental regions, biogenic particles are key elements of the unperturbed climate system. We found that the diversity and abundance of primary biological aerosol particles serving as ice nuclei (IN) are higher than previously known, and that atmospheric bioaerosol and IN concentrations exhibit close correlations and can increase strongly during rain. Our findings suggest that atmospheric bioaerosols, IN, and precipitation are more tightly coupled than previously assumed. Accordingly, a bioprecipitation feedback cycle appears likely to have influenced the co-evolution of life and climate in Earth history. Further research shall elucidate if anthropogenic alterations in bioaerosol emissions from terrestrial vegetation and microflora due to land-use change may influence regional and global climate change in the Anthropocene.

To capture the development of convective clouds and precipitation quantitatively, we develop and apply advanced methods for the determination of cloud condensation nuclei and water vapor peak supersaturations in ground-based and airborne experiments. Besides long-term measurements and intensive campaigns at various mountain observatories (Feldberg, Zugspitze, Jungfraujoch), we have recently performed an aircraft mission contrasting clean and polluted conditions over the Amazon rainforest in Brazil using the new German research aircraft HALO (ACRIDICON-CHUVA).

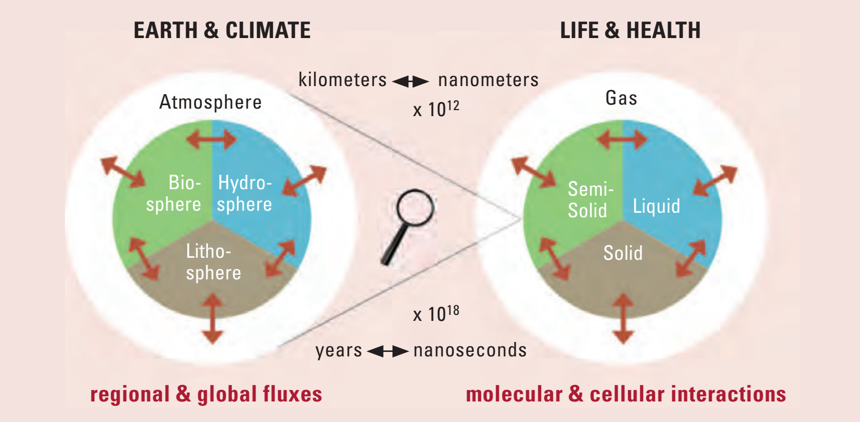

Figure 2: Multiphase processes on molecular to global scales affecting the Earth System, climate, life, and public health.

Air pollution is a potential key factor in the increasing prevalence of allergic and inflammatory diseases. The molecular interactions and mechanisms by which air pollutants may influence allergic and inflammatory immune responses, however, are complex and elusive. We found that long-lived reactive oxygen intermediates (ROI) formed upon interaction of ozone with aerosol particles may play a central role in the adverse health effects of air particulate matter. For example, ROI are involved in the nitration and cross-linking of proteins by polluted air, which can strongly enhance the allergenic potential of proteins.

We investigate the chemical mechanisms and kinetics of protein modification by reactive oxygen and nitrogen species (ROS/RNS) using state-of-the-art analytical techniques like nano-scale liquid chromatography and high-resolution mass spectrometry. For the birch pollen allergen Bet v 1 we found that the preferred nitration sites include tyrosine residues in structural elements that are particularly relevant for epitope binding and immune reactions. In collaboration with biomedical partners we continue to explore the role of ROS/RNS, proteins and multiphase chemical reactions in the coupling of environmental and physiological processes.

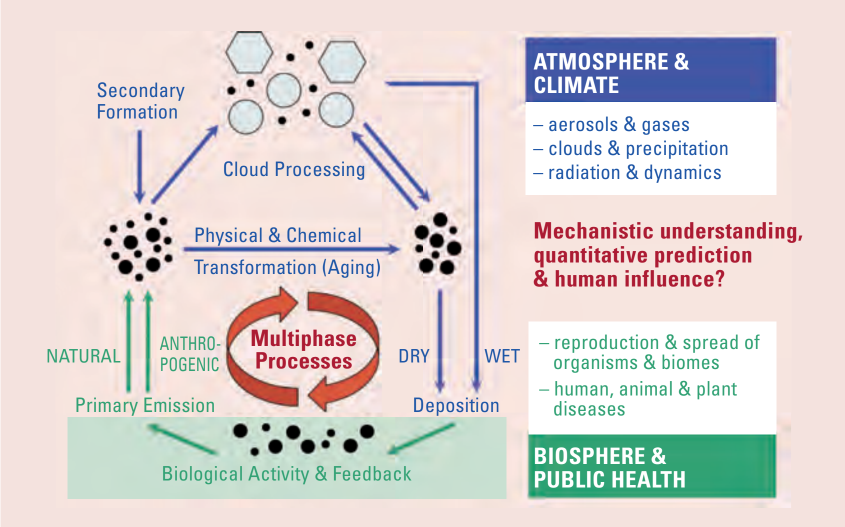

Figure 3: Atmosphere-biosphere exchange and multiphase processing of atmospheric particles and gases (adapted from Pöschl 2005 & 2011).

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BIOGEOGRAPHY, DIVERSITY AND EFFECTS OF AIRBORNE MICROORGANISMS

JANINE FRÖHLICH

> **"Knowing the properties and effects of airborne microorganisms and other bioaerosols is essential for understanding the interplay of life and climate."**

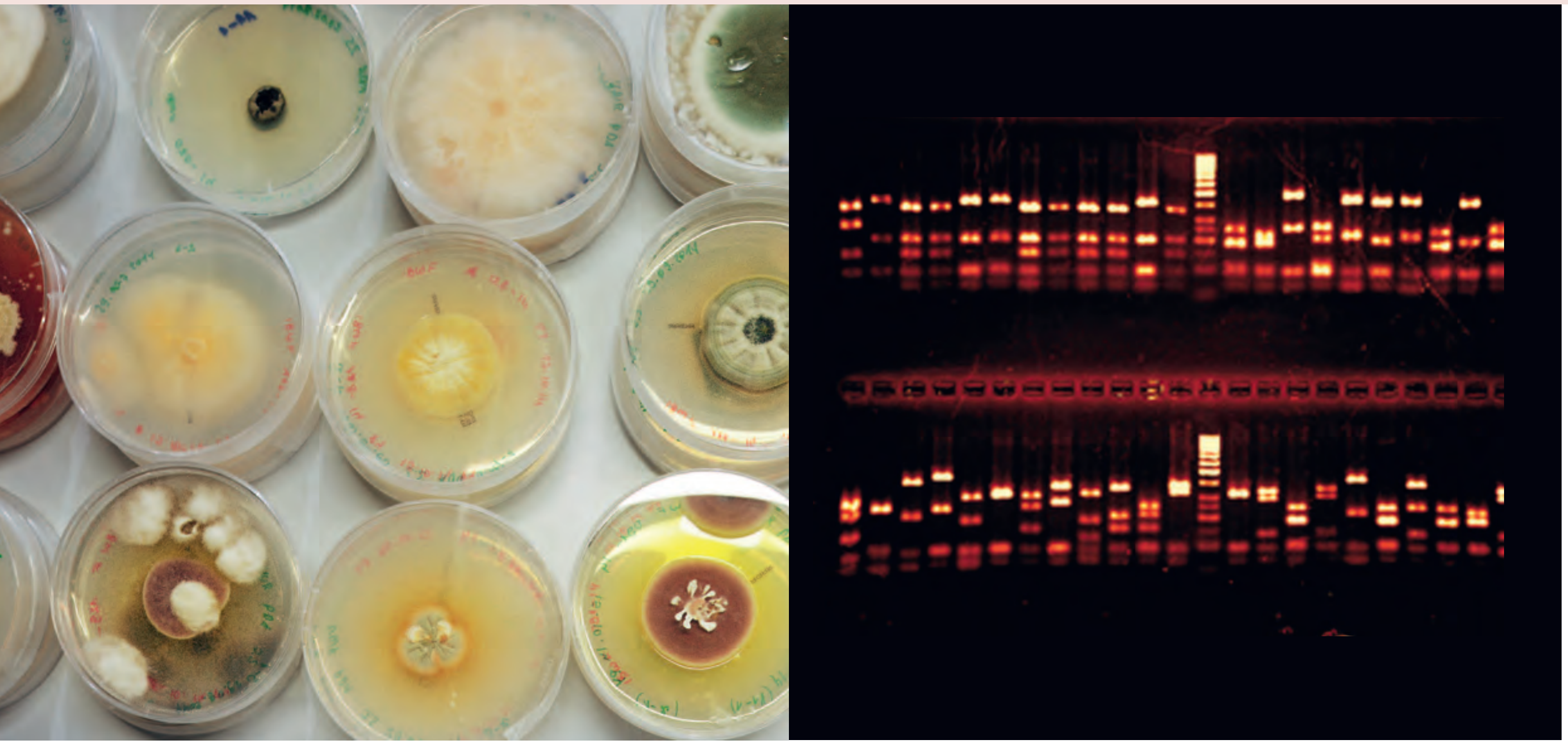

Figure 1: Fungal colonies (left), agarose gel electrophoresis of a DNA restriction digest used to select clones for sequencing (right).

Biological aerosol particles play a vital role in the Earth System, particularly in the interactions between atmosphere, biosphere, climate, and public health. They 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. The abundance, composition, and effects of biological aerosols are, however, not yet well characterized and constitute a large gap in the scientific understanding of the interaction and co-evolution of life and climate in the Earth System.

Primary biological aerosol particles are emitted directly from the biosphere into the atmosphere and include e.g., bacteria, fungal spores, pollen, or fragments of organisms. Our research focuses on the identification of airborne fungi and their effects in the atmosphere. To identify them on air filter samples we apply molecular genetic techniques. By extraction, amplification, and sequencing of deoxyribonucleic acid (DNA) we analyzed air filter samples collected at different locations and climatic zones around the world. We found a high diversity, seasonal cycles of various groups of fungi, and a higher species richness in samples collected during rain events than in samples collected under dry conditions. Most of the fungi belong to the phyla Ascomycota and Basidiomycota, and include various human and plant pathogens (molds, mildew, smut and rust fungi).

We found pronounced biogeographic patterns and provide first insights into the global atmospheric distribution of fungal diversity. In particular, we found that the ratio of species richness between Basidiomycota and Ascomycota is much higher in continental air than in marine air. The results clearly demonstrate the presence of geographic boundaries in the global distribution of microbial taxa in air, and indicate that regional differences may be important for the effects of microorganisms on climate and public health. This may be an important difference between the "blue ocean" and "green ocean" regimes in the formation of clouds and precipitation.

Only a handful of fungal species is reported to posses ice nucleation activity and the importance and sources of biological ice nucleating particles in the atmosphere are generally poorly understood. Therefore, we developed a freezing assay for a screening of many fungal cultures for ice nucleation activity. By determination of the freezing ability of more than 1200 fungal colonies obtained from air and soil samples we found three species of ice nucleation active fungi that were not previously known as ice nucleation active.

The initial freezing temperatures are between -4 and -9°C. By DNA-sequencing they were identified as *Acremonium implicatum, Isaria farinosa,* and *Mortierella alpina. A. implicatum* is an endophyte, *I. farinosa* an insect pathogen fungus, and *M. alpina* is known to be saprobic and widespread in soil. The ice nucleating macromolecules (INM) of these fungi are proteinaceous and not anchored in the fungal cell wall as they can be easily washed off. These small, cell-free INM might contribute to the as yet unknown pool of atmospheric ice nuclei and the ice nucleation activity itself may provide an ecological advantage for the fungi. In collaboration with the Max Planck Institute for Polymer Research we are investigating the interaction of these biological INM with water on molecule level.

We will continue to explore the role of biological aerosol particles and search for more unknown ice nucleating microorganisms and other materials that are released from plants or soils.

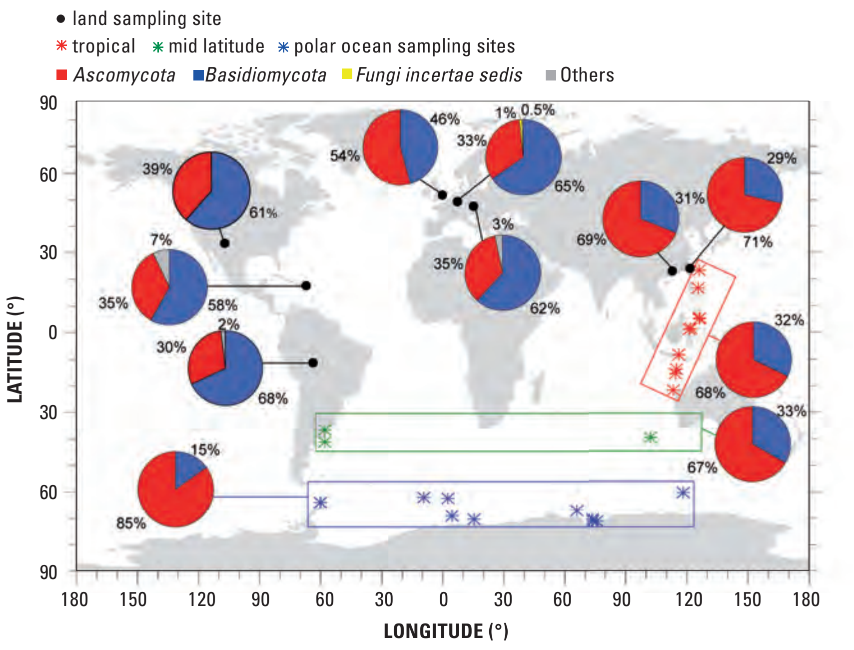

Figure 2: Geographical location and relative proportions of different phyla in continental, coastal, and marine (ocean) sampling locations (adapted from Fröhlich-Nowoisky et al. 2012).

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SEMIVOLATILE ORGANIC COMPOUNDS

GERHARD LAMMEL

"Understanding the global distribution and exposure of persistent chemicals cycling across atmosphere, ocean, cryosphere, soils and vegetation."

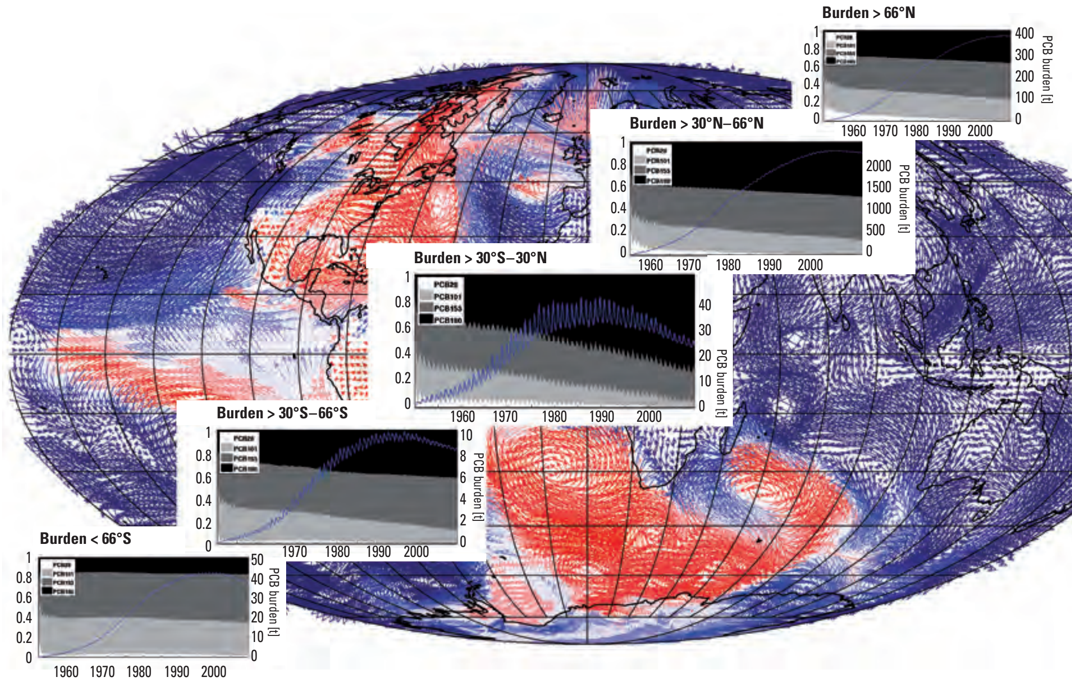

Figure 1: Global fractionation of PCB congeners with 3–7 chlorine atoms 1950–2010.

The cycling of long-lived (persistent) semivolatile organic compounds in the Earth System is particularly complex: in atmospheric aerosols they partition between the gaseous and particulate phases, upon deposition to soil, vegetation and sea surfaces they may re-volatilize to the atmosphere (multihopping). The total environmental residence time typically exceeds the atmospheric residence time by several orders of magnitude.

Global cycling is studied using an Earth System model extended to the study of multicompartmental chemicals i.e., the multicompartment chemistry-transport model, MPI-MCTM, which is based on the coupled atmosphere-ocean general circulation model (AOGCM), ECHAM5-MPIOM1 and includes a dynamic marine biogeochemistry submodel (HAMOCC5), a dynamic atmospheric aerosol sub-model (HAM), and two-dimensional surface compartments (top soil, vegetation surfaces, cryosphere). The model is currently integrated in the Modular Earth Submodel System (MESSy).

By means of atmospheric and the aforementioned surface exchange processes different substance properties translate into different regional and global distributions. Global fractionation in meridional direction of substances with historically and geographically very similar emissions is observed and predicted by the model.

Following peak of polychlorinated biphenyls (PCB) emissions in 1970 the total environmental burden has been increasing until 2000, or a few years before in the southern hemisphere (peak burden). The environmental compartments respond with varying delay (dominated by compartmental lifetime and intercompartmental mass transfers), with a different pace in different climate zones, with a tendency of faster response in warmer climates, and also in different regions or continents. Globally, secondary emissions (re-volatilization from surfaces) are, on the long term, increasingly gaining importance over primary emissions. They are most important for congeners of medium hydrophobicity (5-6 chlorine atoms). Their levels are predicted to decrease slowest. Negative PCB trends in high latitudes are in general weaker than in low latitudes. In the Arctic even still small positive trends are found for PCB153 and -180 in soil. The long-term trend of the substance pattern is dominated by the decline of the lighter PCBs at the expense of the fraction of the heavier ones in the mixture. In high latitudes (in southern somewhat more pronounced than in northern) this trend is partly compensated for by a trend to higher shares of the lighter PCBs, which is strongly influenced by advection.

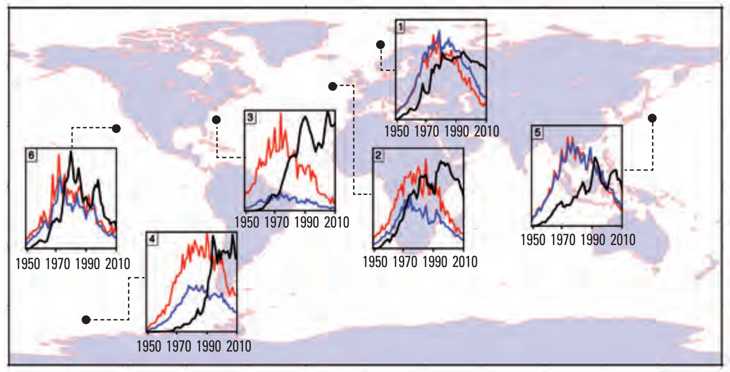

Figure 2: Trends of PCB153 depositions (red, ng m^{-2} a^{-1}), surface layer (0-100 m; blue) and deep water layer (depths at locations 1-6: 500-1,000 m, 700-1,200 m, 1,000-1,500 m, 1,000-1,500 m, 700-1,200 m, and 200-500 m, respectively; black) concentrations (ng m^{-3}) at 6 locations in the world oceans.

A delayed response to declining emissions in high latitudes was hypothesized as resulting from higher persistency in the cold regions and on-going 'global distillation' for organics which undergo multiple deposition - re-volatilization cycles (multihoppers). However, the geographic pattern of trend reversal from increasing to declining burdens is complex, as resulting from the combination of emission, transport and physical (deposition, sedimentation) and chemical (degradation) sink patterns. More features of this chemodynamics than in previous research could be captured in this study.

The results clearly indicate that the effectiveness of emission control measures may significantly vary among substances: trends of decline in abiotic environmental media do not only vary with latitude (slow in high latitudes), but do also show longitudinal gradients.

The long-term trends of distribution of persistent chemicals, PCBs and DDT, in the global deep ocean were studied for the first time. Exposure of the deep sea results from the combination of propagating downward transports (due to deepwater formation and sinking particulate matter) and advection with sea currents in lower levels, which had been contaminated by downward transports in some other sea region in the past. In this modeling study, the translation of a unimodal temporal emission profile (on the global scale, typically peaking during the 1960-70s) into bimodal and higher modal temporal exposure profiles in certain sea regions and depths (with first maximum delayed by typically 5-10 years) was found for the first time, not only for the exposure of the sea, but for the total environment.

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MOLECULAR AND IONIC PROCESSES OF INFLAMMATION

KURT LUCAS

"Understanding the chemical mechanisms of chronic inflammation and allergies will open up new perspectives for the treatment of related diseases."

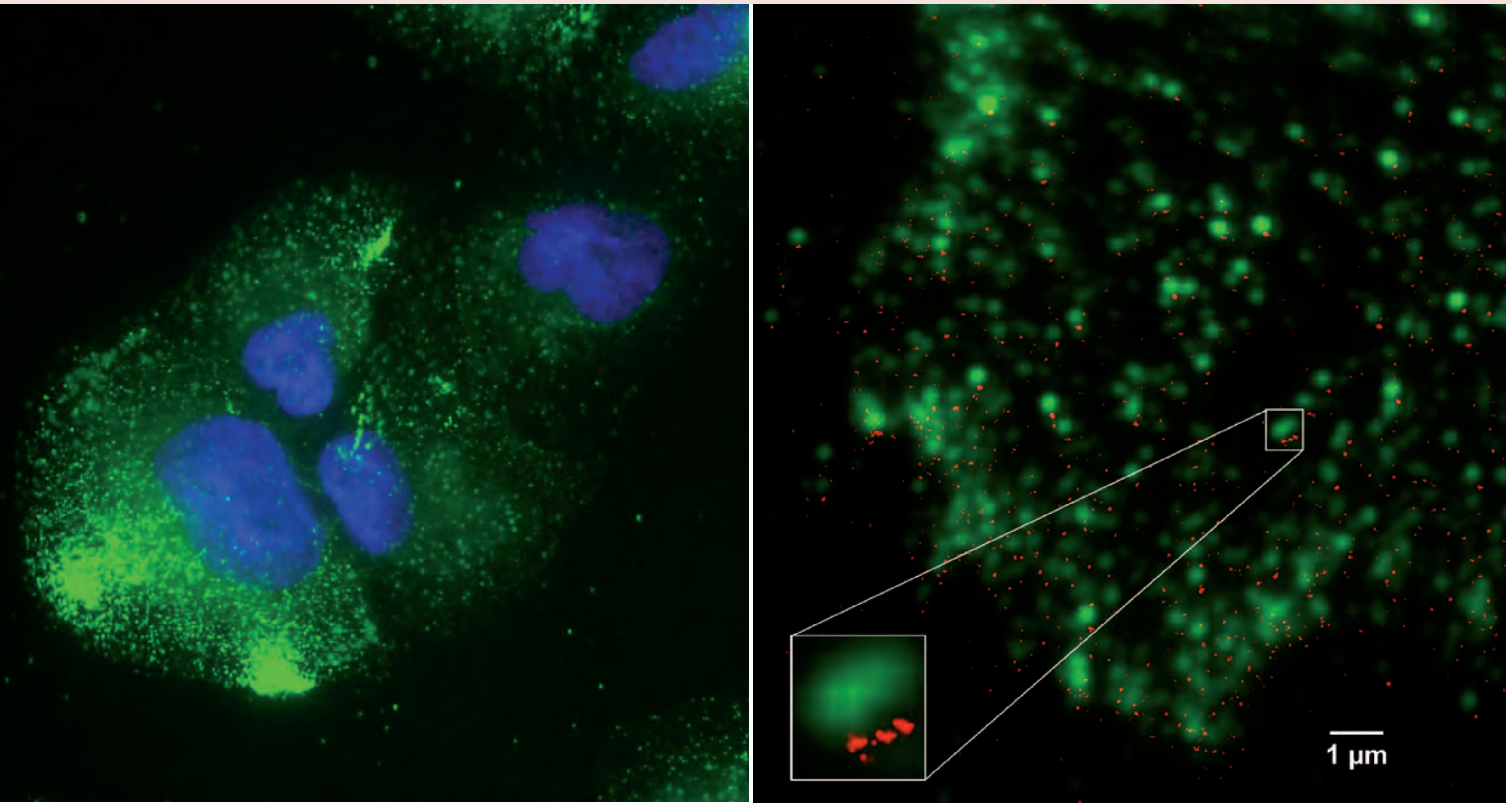

Figure 1: Microscopic images from cell culture experiments. (a) Lung cell line A549 with nuclei colored blue (DAPI) and TLR4 receptors colored green (Alexa 488). (b) Fibroblast cell line Vero-B1 with TLR 4 receptors colored green (Alexa 488) and red localization image.

Inflammation is a key element of immune response. We work on the elucidation of the molecular mechanism of chronic inflammatory processes and allergies. Focal points are the interaction of pattern recognition receptors with pathogen, damage associated molecular patterns, electrophysiological modulations, and adjuvant effects.

We perform cell culture experiments and use quantitative polymerase chain reaction, immunoassays, and fluorescence microscopy to measure the expression of genes involved in inflammation at the messenger-RNA and protein level. Moreover, we quantify reactive oxygen species (ROS) released upon the stimulation of relevant receptors.

Another approach we utilize is to investigate the translocation and clustering of relevant proteins using super-resolution microscopy which allows the localization of individual macromolecules and molecular clusters with spatial resolutions of the order of some 10 nm. For this work we closely collaborate with the group of Prof. C. Cremer at the University Heidelberg and the Institute of Molecular Biology in Mainz.

In addition to molecular interactions, we also investigate ionic signals in the cascade of inflammatory reactions. By measuring intracellular concentration changes of calcium, sodium and potassium ions, we follow the electrophysiological response to inflammatory stimuli and after treatment with anti-inflammatory agents. The investigated stimuli comprise lipopolysaccharides, nanoparticles, transition metals, semivolatile organic compounds, and ozone. With regard to anti-inflammatory agents, we investigate molecular hydrogen, hydrogen sulfide, and active compounds in herbal extracts (*Cinnamomum verum, Curcuma longa, Salvia officinalis, etc.*). Tests for clinical application are conducted in close collaboration with Prof. D. Schuppan at the University Medicine in Mainz and Harvard Medical School. Focal points of this collaboration are Ulcerative colitis (bowel disease) and Parkinson's disease.

Our studies on allergies address primarily the role of the innate immune system in the reaction to native and chemically modified allergens and adjuvants. We investigate similarities in structure, function, and reactivity of allergenic proteins, and we explore the effects of pro- and anti-inflammatory modulators of the innate immune system that may serve as adjuvant triggers for the development of allergies. In particular, we aim at elucidating the chemical reaction mechanisms by which air pollutants may influence the response of the innate immune system to aeroallergens and contribute to the increasing prevalence of allergic diseases.

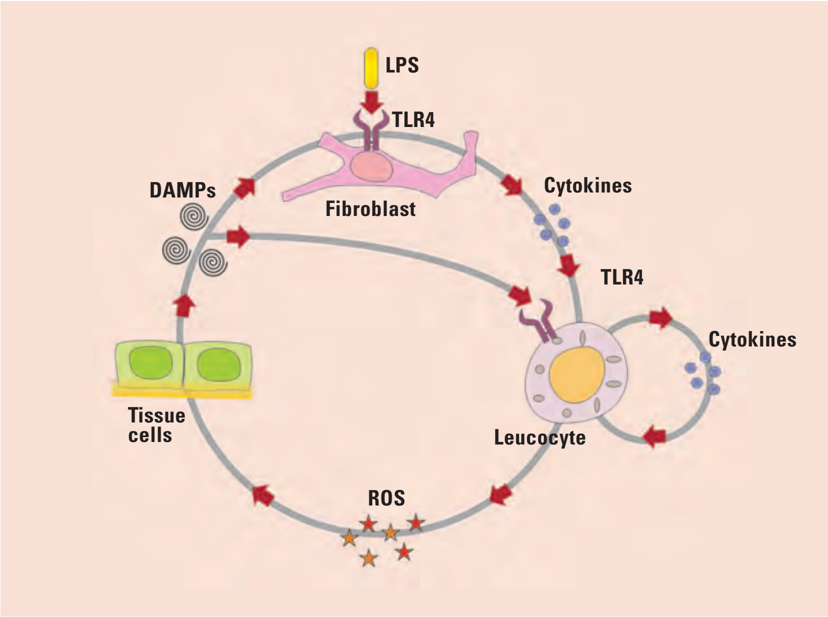

Figure 2: Activation of Pattern Recognition Receptors (PRRs) like TLR4 leads to the release of pro-inflammatory cytokines. These prompt leucocytes to release Reactive Oxygen and Nitrogen Species (ROS/RNS). This highly reactive chemical cocktail kills bacteria, viruses and cancer cells. But it also causes collateral damage. Some of the damaged molecules (DAMPs) can trigger PRRs, closing a feedback and amplification loop that can lead to self-sustained chronic inflammation. The chronic inflammation cycle can be interrupted by a blocking of receptors (e.g., with herbal extracts) or by a quenching of radicals (e.g., with molecular hydrogen).

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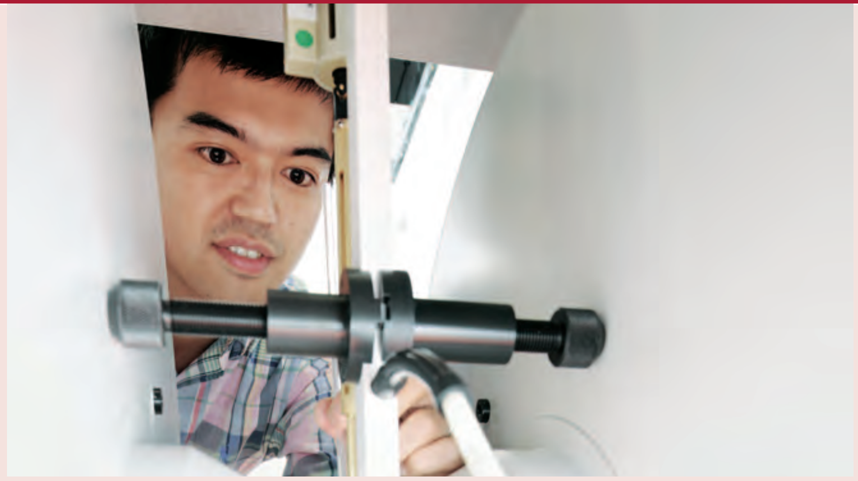
ORGANIC AEROSOLS & REACTIVE OXYGEN SPECIES

MANABU SHIRAIWA



> **"Gas-particle interactions and multiphase reactions of organic aerosols and reactive oxygen species are of central importance for air quality and public health."**

Picture: Creative Commons; Steven Buss

Figure 1: Organic aerosols and reactive oxygen species are important components of smog in megacities like Los Angeles.

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. For describing multiphase processes in aerosols and clouds, we have developed a novel kinetic multi-layer model for gas-particle interactions (KM-GAP) that treats explicitly all steps of mass transport and chemical reaction of semi-volatile species partitioning between gas phase, particle surface and particle bulk. KM-GAP shall help to bridge gaps in the understanding and quantification of multiphase chemistry and microphysics in atmospheric aerosols and clouds.

Secondary organic aerosol (SOA) is derived from the oxidation of volatile organic compounds emitted from various biogenic and anthropogenic sources. Formation and evolution of SOA is a complex process involving coupled chemical reaction and mass transport in the gas and particle phases. Based on molecular identification of SOA oxidation products, we have shown that the chemical evolution of SOA from a variety of VOC precursors adheres to characteristic "molecular corridors" with a tight inverse correlation between volatility and molar mass. Sequential and parallel reaction pathways of oxidation and dimerization progressing along these corridors pass through characteristic regimes of reaction-, diffusion-, or accommodation-limited multiphase chemical kinetics. The molecular corridors and kinetic regimes help to constrain and describe the properties of the products, pathways, and rates of SOA evolution.

Until recently, organic aerosol particles in the atmosphere were thought to be liquid and internally well-mixed. Depending on temperature and relative humidity, however, organic particles can adopt amorphous solid or semi-solid states. Bulk diffusion can limit the kinetics of mass-transport and reaction in amorphous organic aerosol particles and determine if chemical transformation proceeds only at the surface or throughout the particle. Through KM-GAP modeling and laboratory experiments, we have demonstrated that formation and chemical transformation of organic particles can be significantly affected by phase state. Moreover, hygroscopic growth and CCN activation can be inhibited and activation pathways of homogeneous or heterogeneous ice nucleation can be influenced substantially.

Reactive oxygen and nitrogen species (ROS/RNS) are key species of both atmospheric and physiological chemistry and their coupling through the atmosphere-biosphere interface is illustrated in Figure 2. ROS play a central role in the adverse health effects of air pollution, as they can cause oxidative stress and diseases. We found that the multiphase reactions of ozone with aerosols particles lead to the formation of long-lived reactive oxygen intermediates (ROI). ROI play a key role in formation and chemical transformation of hazardous components such as soot, polycyclic aromatic hydrocarbons, and allergenic proteins. The coupling and exchange of atmospheric and physiological ROS can proceed through various biosurfaces like the human respiratory tract, skins, and plant leaves. We detect ROS using an electron paramagnetic resonance technique (EPR) and investigate the role of ROS in the Earth System and public health.

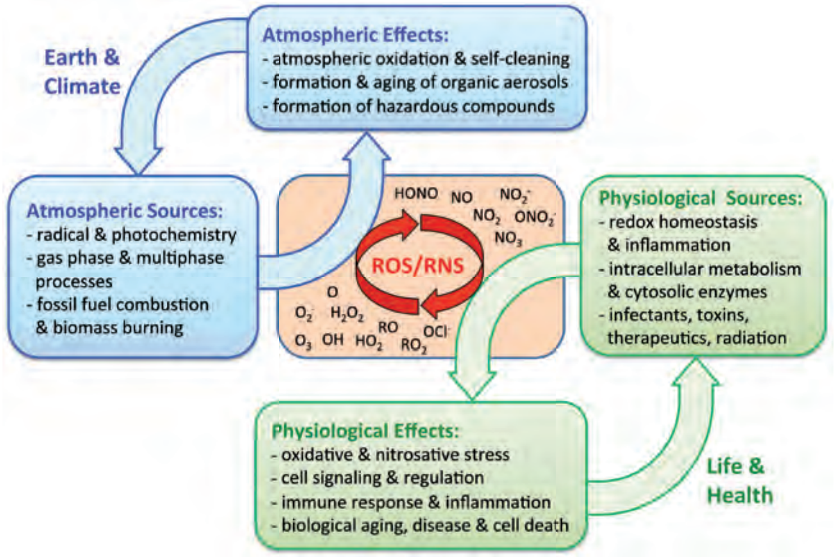


Figure 2: Reactive oxygen & nitrogen species (ROS, RNS): Sources, effects and interactions at the interface of atmospheric and physiological chemistry, with feedback loops involving the Earth System, climate, life, and health (adapted from Shiraiwa et al. 2012).

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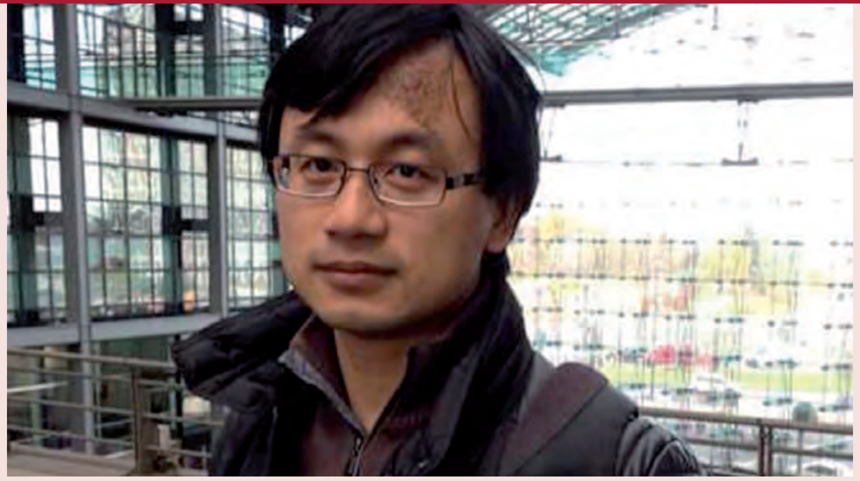
AEROSOL, CLOUD & BIOSPHERE INTERACTIONS

HANG SU



> **"The focus of our group is the investigation of aerosol-cloud interactions and atmosphere-biosphere exchange and their effects on the climate and the Earth System."**

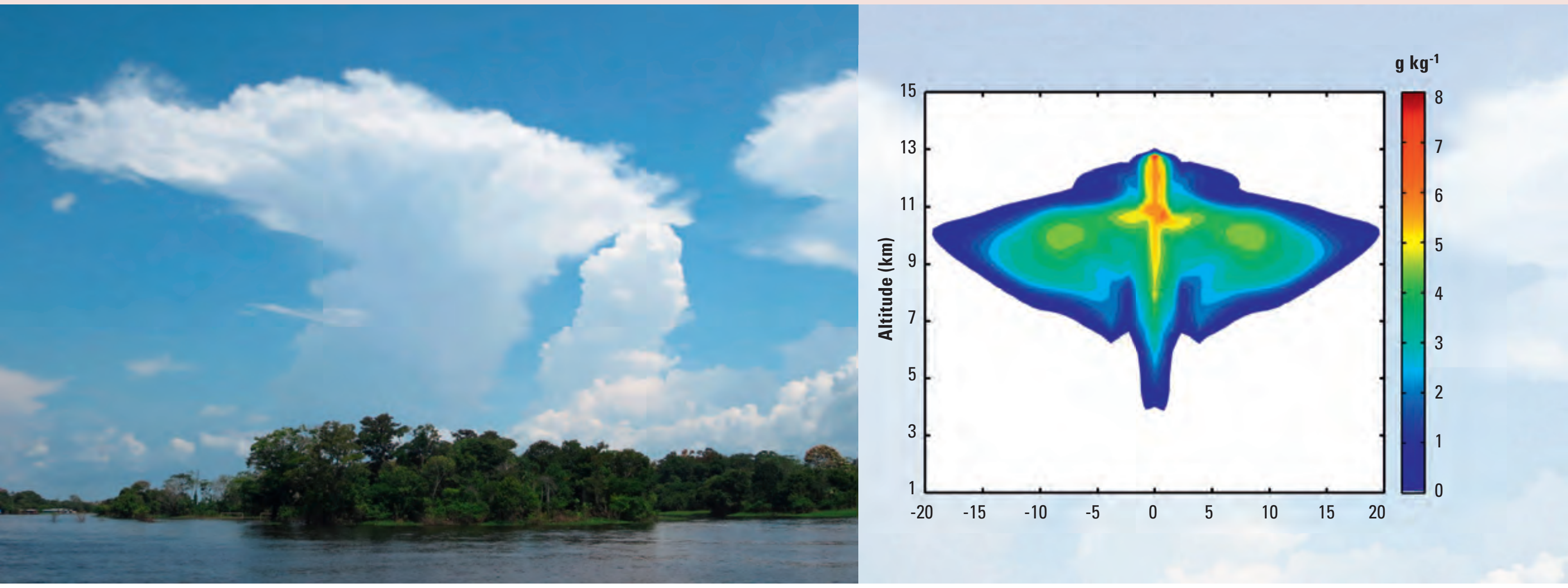


Figure 1: Convective clouds as observed over the Amazon (left) and simulated with a numerical model (right).

AEROSOL EFFECTS ON CONVECTIVE CLOUDS AND PRECIPITATION

Our previous parcel model study shows three deterministic regimes of initial cloud droplet formation, characterized by different ratios of aerosol concentrations to updraft velocities. That study, however, did not reveal how these regimes evolve during the subsequent cloud development. To address this issue, we employed the ATHAM model with full microphysics and extended the simulation from the cloud base to the entire column of a single pyro-convective mixed-phase cloud. A series of simulations (over 3000) were performed over a wide range of CCN (cloud condensation nuclei), IN (ice nuclei) and dynamic conditions. Our results show that: (1) the amount of liquid clouds is mainly controlled by the CCN rather than IN and exhibit three regimes (namely aerosol-limited regime, updraft-limited regime and transition regime) similar to those in the parcel model study. (2) The production of both raindrops and surface precipitation is within the updraft-limited regime, and the CCN effect is stronger than the IN effect. (3) The concentration of frozen clouds is nearly independent of aerosol concentration. This is because the negative effect of IN on the formation of frozen clouds counteracts the positive CCN effect.

ATMOSPHERE-SURFACE EXCHANGE OF NITROUS ACID AND FORMALDEHYDE

In the lower atmosphere, up to ~50% of the primary OH radical production is attributed to the photolysis of nitrous acid (HONO), and field observations suggest a large missing source of HONO. We showed that soil nitrite can release HONO and explain the reported strength and diurnal variation of the missing source. Our model calculation also shows that soil HONO emission can be comparable to the soil NO emission, which was considered as the only form of important reactive nitrogen from soil. We are now (1) performing additional experiments towards a better understanding of the soil water-content dependence of HONO emission (Figure 1); and (2) developing a model for the prediction of biogenic HONO emission from soil. Additionally, we are also investigating the HONO formation and formaldehyde exchange on different kinds of surfaces through flow tube and chamber experiments.

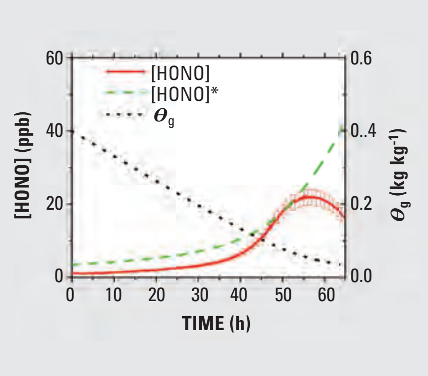


Figure 2: Chamber measurements of HONO emission from soil. [HONO] represents the measured gas phase HONO concentration (red solid line) and θ_g represents the gravimetric soil water content (black dots) (adapted from Su et al. 2011).

EMISSION AND CHARACTERIZATION OF PRIMARY BIOLOGICAL AEROSOLS PARTICLES

The formation and transportation of primary biological aerosol particles (PBAP) are important in understanding its climate, ecological and health effects. However, their explicit description in models is difficult due to the lack of understanding in the emission mechanisms. In the Beachon-RoMBAS campaign, PBAP were intensively characterized by various techniques. Elevated PBAP concentrations during and after rain have been found and attributed to particle bursts in the beginning of several rain events and active biota growing on wetted surfaces (e.g. spores from fungi, cryptogamic covers). In the present study we use both Eulerian and Lagrangian models to derive emission rates of PBAP for the campaign period covering both precipitation and non-precipitation conditions. Based on the retrieved emissions, our model could largely reproduce the measured PBAP results (Figure 3).

Besides the modeling study, we also carried out bioaerosol measurements with the Wideband Integrated Bioaerosol Spectrometer (WIBS) in several campaigns, from polluted megacities in China to clean rainforests (ATTO site) in Brazil. This technique measures the counts of fluorescent particles with much higher time and size resolutions. The big challenge for using WIBS data is how to interpret the bioaerosol information from the measured fluorescence signals. We are now testing different methodologies including cluster analysis and other statistical methods.

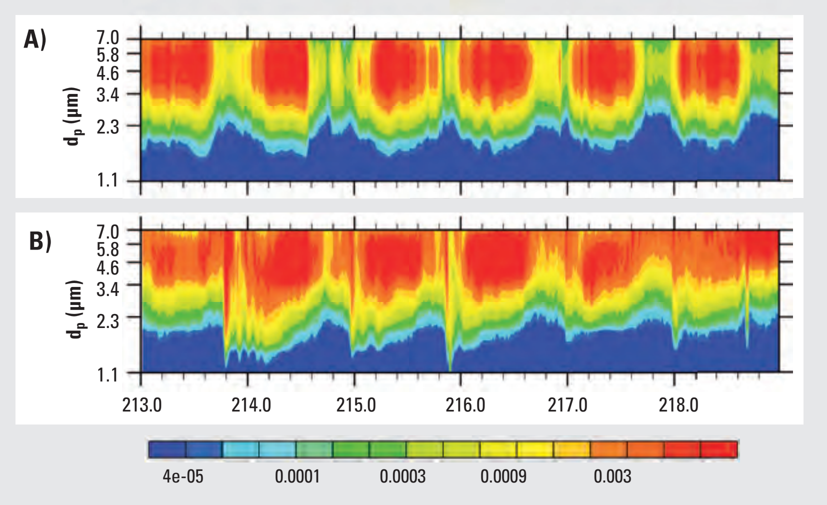


Figure 3: Mass size distributions of PBAP from model (A) and observation (B), Color bar: dM/dlogd$_p$.

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THE ROLE OF CRYPTOGAMIC COVERS IN THE EARTH SYSTEM

BETTINA WEBER

> **"We aim at understanding the effects of cryptogamic covers on climate processes and nutrient cycling depending on physiological and environmental conditions."**

Figure 1: Cryptogamic plant covers (growing on bushman's candle (Sarcocaulon patersonii)) and cryptogamic ground covers dominated by lichens in the southernmost Namib Desert in Alexander Bay, South Africa.

Many terrestrial surfaces including soils, rocks, and plants, are not bare, but covered by communities consisting of small plants and microorganisms. These cryptogamic covers comprise cyanobacteria, algae, lichens, fungi, bryophytes, other bacteria, and archaea in varying composition. They form cryptogamic ground covers, including biological soil and rock crusts as well as bryophyte and lichen carpets, which occur on many terrestrial ground surfaces. As cryptogamic plant covers they spread over the stems, branches, and even the evergreen leaves of trees and shrubs. Whereas these cryptogamic covers are often inconspicuous and sometimes small in size, they may strongly affect their surrounding environment and even global processes.

As biological soil crusts they cover the soil surface widely in dry regions throughout the world. With cyanobacteria comprising gelatinous sheaths and filamentous organisms they agglutinate the soil, thereby greatly reducing soil erodibility. They passively store water and change water infiltration and runoff patterns thus affecting the water balance on a local and catchment scale. The photoautotrophic organisms within cryptogamic covers sequester atmospheric CO_2 and many of them include nitrogen-fixing cyanobacteria, utilizing atmospheric N_2 to form ammonium which can be readily used by vascular plants.

In a large-scale data analysis approach, we compiled all available data on the physiological properties of cryptogamic covers and developed a model to calculate their annual nitrogen fixation and net primary production. Here, we obtained a total value of 3.9 Pg a^{-1} for the global net uptake of carbon by cryptogamic covers, corresponding to approximately 7% of the estimated global net primary production of terrestrial vegetation and being in the same range as the annually burned fossil carbon fuels. Calculation of the nitrogen assimilation of cryptogamic covers revealed a global estimate of ~49 Tg a^{-1}, accounting for as much as about half of the maximum value estimated for the total terrestrial biological nitrogen fixation.

Whereas there are still some uncertainties in these budgets, they clearly reveal the key role of cryptogamic covers, especially in the global terrestrial nitrogen cycle, which is now being studied by us in greater detail.

As this data analysis approach had shown a severe deficiency in long-term carbon balance data, we developed a new method to obtain carbon balances for cryptogamic covers at high spatiotemporal accuracy. We combine long-term microclimatic soil crust data with CO_2 gas exchange factorial analyses, assigning potential CO_2 gas exchange rates to each of the microclimate readings. Integration of these rates allows calculation of annual rates for different types of cryptogamic covers. These different cover types are characterized in a combined morphological and molecular species determination approach. Finally, the physiological data are combined with hyperspectral remote sensing mapping data for biological soil crusts to obtain the carbon balance of biological soil crusts on a habitat scale.

In a theoretical approach, we calculate the impact of lichens and bryophytes on global processes, e.g. their global carbon uptake, by means of a process-based model. In this model, we use gridded climate data combined with key habitat properties (e.g. disturbance intervals) to predict the processes which control net carbon uptake, i.e. photosynthesis, respiration, water uptake and evaporation. The model relies on equations frequently used in dynamic vegetation models, which are combined with concepts specific to lichens and bryophytes. Quantifying the physiological activity of the organisms, this model is also suited to quantify the effects of lichens and mosses on other global biogeochemical cycles.

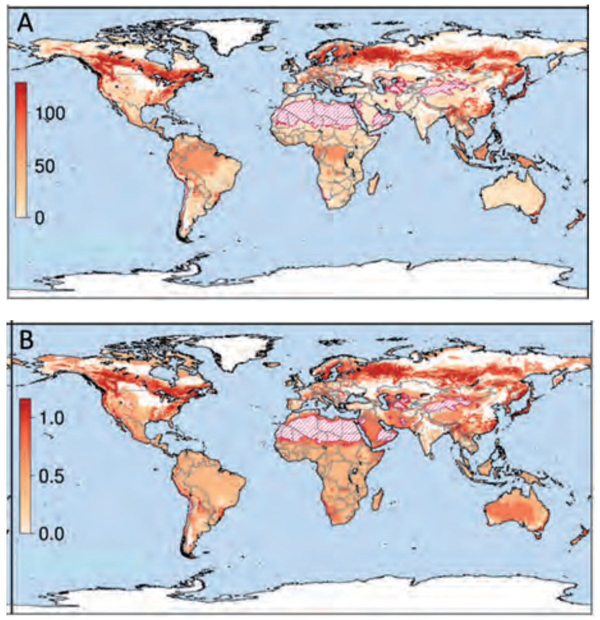

Figure 2: Global maps of N_2 fixation (A) and CO_2 uptake (B) by cryptogamic covers. The flux units are g m^{-2} a^{-1}. White areas indicate ecosystems for which no data are available; hashed areas are excluded from calculations due to low precipitation amounts (adapted from Elbert et al. 2012).

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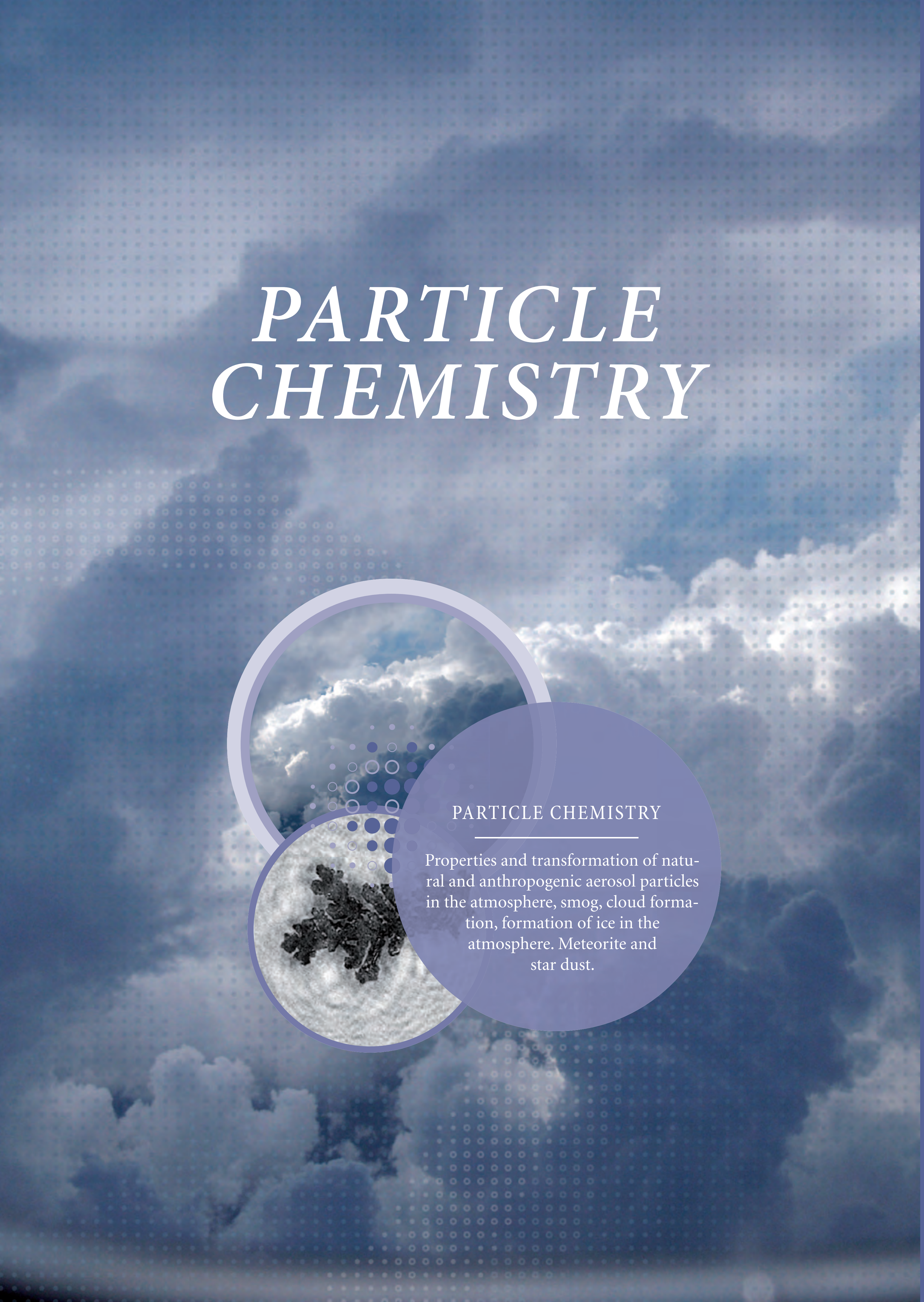
PARTICLE CHEMISTRY



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.

Born on 18 January 1959 in Mainz. Study of Physics and Biology Johannes Gutenberg University Mainz (1977–1984), Adjunct Research Instructor at the Naval Postgraduate School in Monterey/CA/USA (1985–1986), PhD in Physics (1991), Postdoctoral Fellow of the Advanced Study Program (University Corporation of Atmos-pheric Research, UCAR) at the National Center for Atmospheric Research (NCAR) in Boulder/CO/USA (1991–1993), German Habilitation in meteorology (1999), head of the Aerosol Research Group at the Institute for Chemistry and Dynamics of the Geosphere at the Research Center Jülich Ltd. (1998–2000), Professor Johannes Gutenberg University Mainz (since 2000), Director (part-time) and Scientific Member at the Max Planck Institute for Chemistry (since 2001).

STEPHAN BORRMANN

In 2001 the Particle Chemistry Department (PCD) was established as a shared structure between the Johannes Gutenberg University of Mainz (JGU) and the MPI for Chemistry. Its director, Prof. Dr. Stephan Borrmann, is full professor at the JGU Institute for Physics of the Atmosphere (IPA) and holds a formal part time ("Direktor im Nebenamt") position at the MPIC.

The scientific activities of the PCD are dedicated to fundamental processes concerning atmospheric aerosols, clouds, large hydrometeors, pollution and its sources, and cosmic particulate matter. The experimental activities are centered on ground based, mobile, and aircraft-borne field measurements, as well as detailed laboratory studies. This includes industry and application related research projects which in the past were focused on automotive vehicle and aircraft exhausts, waste incineration plant emissions, on inhalable pharmaceutical sprays, as well as the development of technology for aerosol and droplet measurements. Between 2012 and 2014 there have been research contracts with industry addressing emissions from large European steel manufacturing plants, fugitive particle emissions from construction sites, the prevention of riming and ice-accretion on wind energy turbine blades, and for measurements of gaseous and particulate emissions from biomass community boilers.

The PCD uses the large facilities of the worldwide unique Mainz Vertical Wind Tunnel (MAVERT, see report by Miklós Szakáll and Karoline Diehl), the Mobile Laboratory for Atmospheric research (MoLa, see report by Frank Drewnick), and the NanoSIMS laboratory of the NAMIP group (see report by Peter Hoppe). For field research five state of the art aerosol mass spectrometers are avilable (including two instruments certified for implementation on four different European research aircraft), as well as eleven sophisticated instruments for aircraft borne experiments on cloud and aerosol microphysics in the upper troposphere/lower stratosphere (see reports by Johannes Schneider and Ralf Weigel).

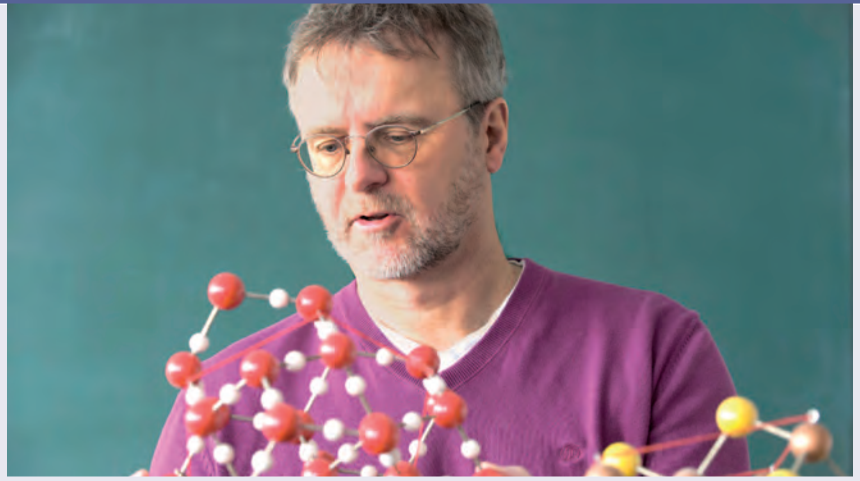
Several of the instruments have been and currently are developed completely in-house like the Airborne Laser ABlation Aerosol MAss spectrometer (ALABAMA), the Single Particle Laser Ablation Mass Spectrometer (SPLAT), the HALOHOLO holographic imaging probe, as well as the ERC Instrument for Chemical composition of Aerosols (ERICA).

Following the European "Bologna-Process" the teaching at IPA/JGU had to be redesigned for the transition of the previous "Diplom Meteorologie" curriculum to the new "Bachelor/Master in Meteorology" schemes. The external evaluation of the new Master curriculum was successfully completed in 2013. From 2012 to 2014 eleven Ph.D., nine diploma and two Bachelor theses have been completed at PCD; a further nine Ph.D. and three diploma theses are in progress. Four of the eleven Ph.D. candidates graduated with "summa cum laude" and received various prizes. Since 2001 altogether 43 Ph.D., 35 diploma and two Bachelor theses were – or presently are being – conducted within the department. Of these 80 graduates 46% are female.

Several million Euros of external funds were raised since 2001 through more than 30 research or technology development contracts. The ERC Advanced Grant for the period from 2012 until 2017 is 2.75 million Euros.
For the period between January 2012 and October 2014 the number of peer reviewed papers published from PCD is 76 with an additional 3 currently under review.

CLOUDS IN THE ARCTIC: FROM LOW LEVEL STRATUS TO POLAR STRATOSPHERIC CLOUDS

STEPHAN BORRMANN



> **"The Arctic is most sensitive to climate change and clouds from near the surface to the stratosphere play key roles in the radiative budget and chemistry."**

Figure 1: The research aircrafts: Left: Basler BT-67modified DC-3 "Polar 5" of the Alfred-Wegener-Institut Helmholtz-Zentrum für Polar- und Meeresforschung during VERDI. Right: MDB high altitude aircraft M-55 Geophysica (ceiling of 21 km) during RECONCILE.

The Arctic is most susceptible to the effects of climate change as a variety of complex, interacting processes causes the "Arctic amplification" leading to a faster increase of the near-surface air temperatures than in other regions. The wide spread low level stratus decks and stratocumuli act here as "iris" for visible and infrared radiation, an effect which is highly dependent on the sizes, number densities and microphysical properties of the liquid and glaciated cloud hydrometeors. Polar stratospheric clouds (PSC) occur at altitudes of roughly 16 km to 25 km inside the polar vortex. They are key players for the ozone-related chemistry because the particles are involved in heterogeneous processing of gaseous compounds and also cause the vertical redistribution of trace substances by dehydration and denitrification. Also, the microphysical and chemical properties of the clouds determine the efficiency of the relevant processes.

ARCTIC BOUNDARY LAYER CLOUDS: Aircraft borne optical in-situ measurements were performed within the top layers of low level stratocumuli and stratus clouds during the springtime VERDI (2012) and RACEPAC (2014) campaigns. The AWI Polar 5 research aircraft (a modified DC-3, Figure 1) operated over the Mackenzie River delta and the Beaufort Sea in Canada. Inside predominantly liquid-phase Arctic stratocumuli narrow monomodal droplet size distributions were observed with altitude-dependent mean diameters between 10 µm and 20 µm. In the cloud top transition zone adjacent to the cloud-free air changes from monomodal to bimodal droplet size distributions were frequently encountered where droplets of both modes co-exist in the same (small) air volumes at spatial scales down to 10 cm (Figure 2). The formation of this second size mode can be explained by (a) activation of freshly entrained aerosol particles, or (b) by differential evaporation processes occurring in the mixing zone. Model simulations revealed that turbulent mixing induced by the evaporative cooling of the larger droplets together with (b) most likely is the cause for the formation of the second mode in the uppermost cloud layer. As the "iris effect" strongly depends on the processes in the transition zone from cloudy-air to clear-air further detailed studies will be conducted in the coming years.

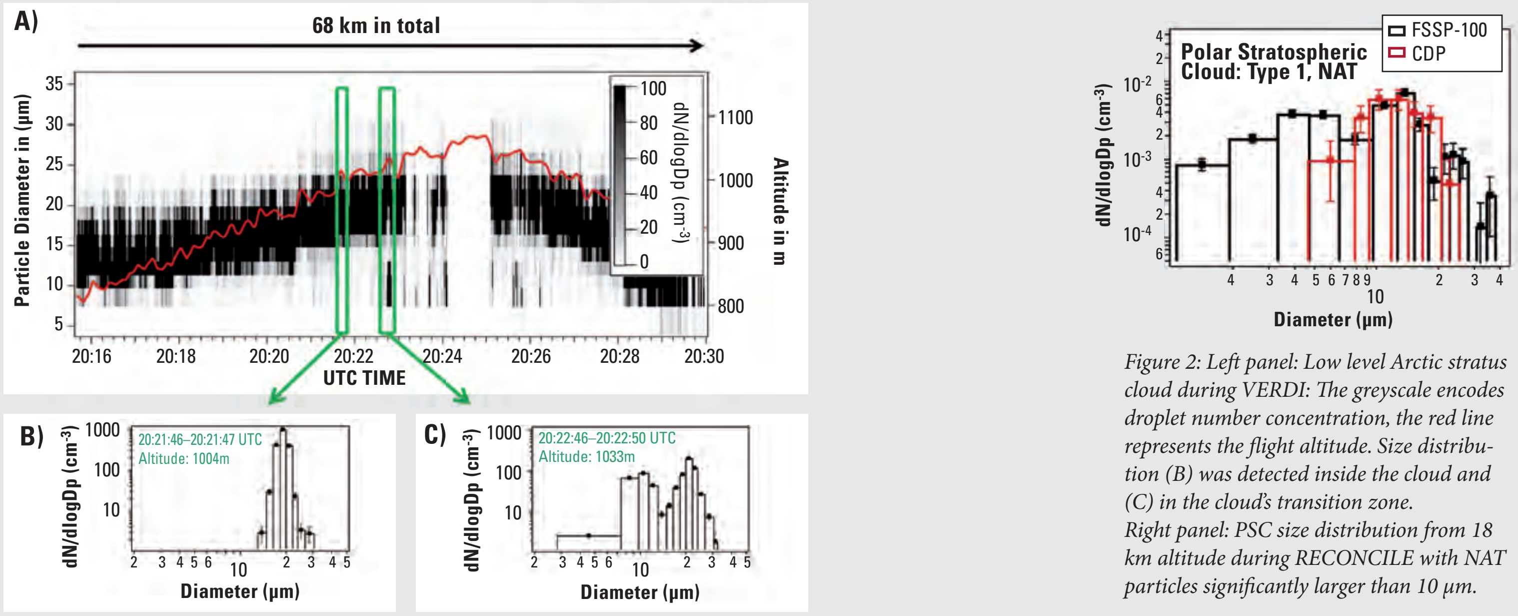


Figure 2: Left panel: Low level Arctic stratus cloud during VERDI: The greyscale encodes droplet number concentration, the red line represents the flight altitude. Size distribution (B) was detected inside the cloud and (C) in the cloud's transition zone.
Right panel: PSC size distribution from 18 km altitude during RECONCILE with NAT particles significantly larger than 10 µm.

POLAR STRATOSPHERIC CLOUDS: In the winters of 2009/2010 and 2011/2012 research flights were performed inside Arctic synoptic scale PSCs utilizing the Russian high altitude research aircraft M-55 Geophysica (Figure 1) during the RECONCILE and the ESSenCe projects. Particle size distributions between 0.46 µm and 40 µm (diameter) were measured by three different optical in-situ cloud particle counters and a single particle imaging instrument. A size mode below 2 µm was identified as supercooled ternary solution droplets (STS) and for the larger PSC particles a high HNO$_3$ content was found by an in-situ NO$_y$ instrument. If these PSC particles consist of nitric acid trihydrate (NAT), the optically measured size distributions yield geometric diameters up to 20 to 35 µm (Figure 2). This is unexpectedly large as such "NAT-rocks" would result in HNO$_3$ mixing ratios by far exceeding the levels available in the stratosphere. Also, the numerical simulations of particle growth and sedimentation along air parcel trajectories show that the particles fall too fast and have insufficient time to grow from their nucleation to the large detected sizes. These particles, however, do exist as the first visual evidence for the "NAT-rocks" was provided by a shadow cast imaging technique. We hypothesize that either a strong asphericity or an alternate particle structure (like NAT coated water-ice leaving behind hollow, large NAT shells after evaporation) could explain our observations. Concerning denitrification by sedimentation of large NAT particles our new measurements raise questions about composition, shape and nucleation pathways of PSCs in general. These are important for the numerical simulation of PSC processes to predict future polar ozone losses, especially under changing global climate conditions with the inherent stratospheric cooling.

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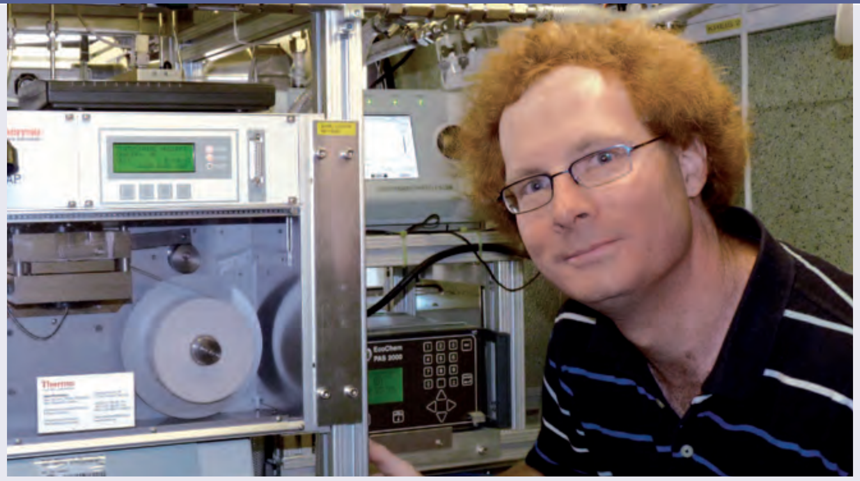
ACRONYMS:

NAT *= Nitric Acid Trihydrate*
RECONCILE *= Project: Reconciliation of Essential process parameters for an enhanced predictability of Arctic stratospheric ozone loss and its climate interaction*
VERDI *= Project: VERtical Distribution of Ice in Arctic Clouds*
ESSENCE *= Project: ESA Sounder Campaign*
PSC *= Polar Stratospheric Clouds*
RACEPAC *= Project: Radiation – Aerosol – Cloud Experiment in the Arctic Circle*
AWI *= Alfred-Wegener-Institut Helmholtz-Zentrum für Polar- und Meeresforschung*
MDB *= Myasishchev Design Bureau*
STS *= Supercooled Ternary Solution droplets*

INVESTIGATION OF COMMON AND EXOTIC PARTICLE EMISSION SOURCES USING A MOBILE LABORATORY

FRANK DREWNICK



> **"Locally, exotic particle sources can tremendously affect air quality. We want to learn more about their physical and chemical properties and the dynamics of their emissions."**

Figure 1: Measurement of emissions from "exotic" particle sources: Bengal fires, logwood combustion, sea-going ships, construction work. Photos: von der Weiden-Reinmüller, Freutel, Drewnick, Faber.

The major anthropogenic sources of particulate matter in central Europe are traffic, domestic heating and industrial processes, often associated with combustion of fossil fuels. Thanks to a multitude of studies, particulate emissions from these sources are reasonably well known, both in terms of quantity as well as of physical and chemical properties of the aerosols. On small scales, other – more "exotic" – sources of particulate matter can dominate the ambient aerosol and significantly affect air quality. Due to their minor contribution to the overall particulate matter load of the atmosphere, knowledge on characteristics and dynamics of such emissions is often sparse.

The recently developed mobile aerosol research laboratory MoLa (Drewnick et al., 2012) is well suited to investigate source emissions. MoLa is based on a common delivery vehicle and equipped with on-board electrical power generation and an exhaust removal system. It provides a comprehensive set of aerosol and trace gas measurement instrumentation which can flexibly be used to probe emissions with high temporal resolution. Parallel online measurement of particle number and mass concentrations, size distributions and composition as well as of concentrations of various trace gases provides a broad picture of the ambient aerosol. Highly time-resolved (1–60 s) measurements allow the separation of emissions and background under typical meteorological conditions as well as the study of the dynamic behavior of the individual sources.

MoLa has been applied to the investigation of a large range of common and uncommon particle sources, extending from an individual smoker, a single deep fryer, or individual ships over construction sites and integrated steel plants up to a whole megacity (Figure 1).
In order to determine the emissions from such sources, MoLa was parked downwind of the emission locations and set up to measure ambient air over an appropriate time interval. In case of larger sources, mobile measurements when driving across or along the emission plume can be used to determine the extension of the plume and to investigate aerosol aging processes. In several cases limitations of the instruments surfaced when measuring unusual aerosol, e.g. with uncommon chemical composition like metal-dominated particles. Additional laboratory experiments with particles of known physical and chemical properties helped interpreting these measurements and pushed the limits of the instruments.

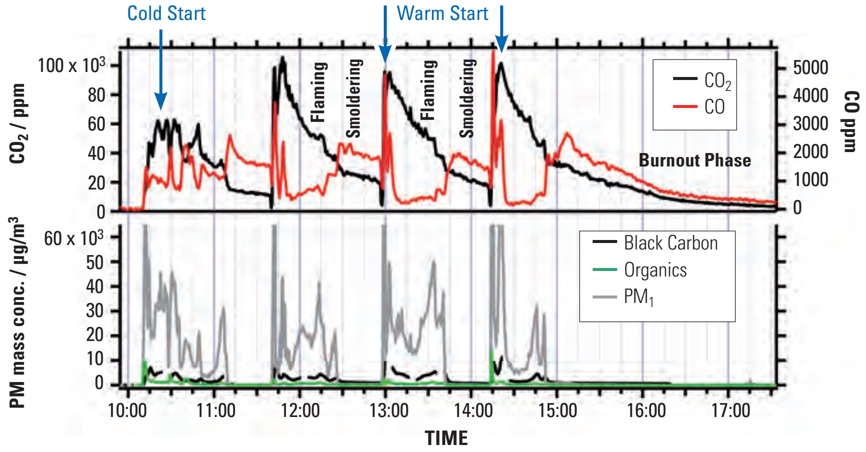


Figure 2: Temporal trends of concentrations of trace gases (CO, CO_2) and particle components (PM_1, black carbon, particulate organics) during four consecutive wood burning experiments.

Measurements in the emission plume of the megacity of Paris (von der Weiden-Reinmüller et al., 2014) have provided insight into the composition of the plume and its spatial distribution up to several tens of kilometers downwind of the city. Also organic aerosol aging could be observed in this plume, which was shown to occur much faster in summer than during winter.

Deployment of MoLa at the banks of the Elbe River yielded detailed information on the particulate and some gas phase emissions from approximately 140 sea-going ships that passed the site (Diesch et al., 2013). The combination of measurements allowed determining emission factors for various pollutants within the plumes. It was found that generally PM_1 emission factors increase with increasing fuel sulfur content and ship size.

Also for other uncommon sources emission factors have been determined using MoLa measurements downwind of these emitters. Fugitive emissions from a steel plant are generally very hard to measure. Probing these aerosols in ambient air close to the point of release, provided the information needed to determine emission fingerprints for the various processes on such a plant. Measurements at road construction sites yielded emission factors and typical aerosol characteristics for various construction work processes. Finally, laboratory measurements, using MoLa as a stationary laboratory setup, provided emission factors and aerosol characteristics for wood combustion for a large variety of biofuel types and combustion conditions (Figure 2).

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NANOANALYTICAL STUDIES OF DUST FROM SPACE AND EARTH

PETER HOPPE

"Studying isotopic fingerprints of dust: A tool to trace chemical and physical processes in Space and on Earth."

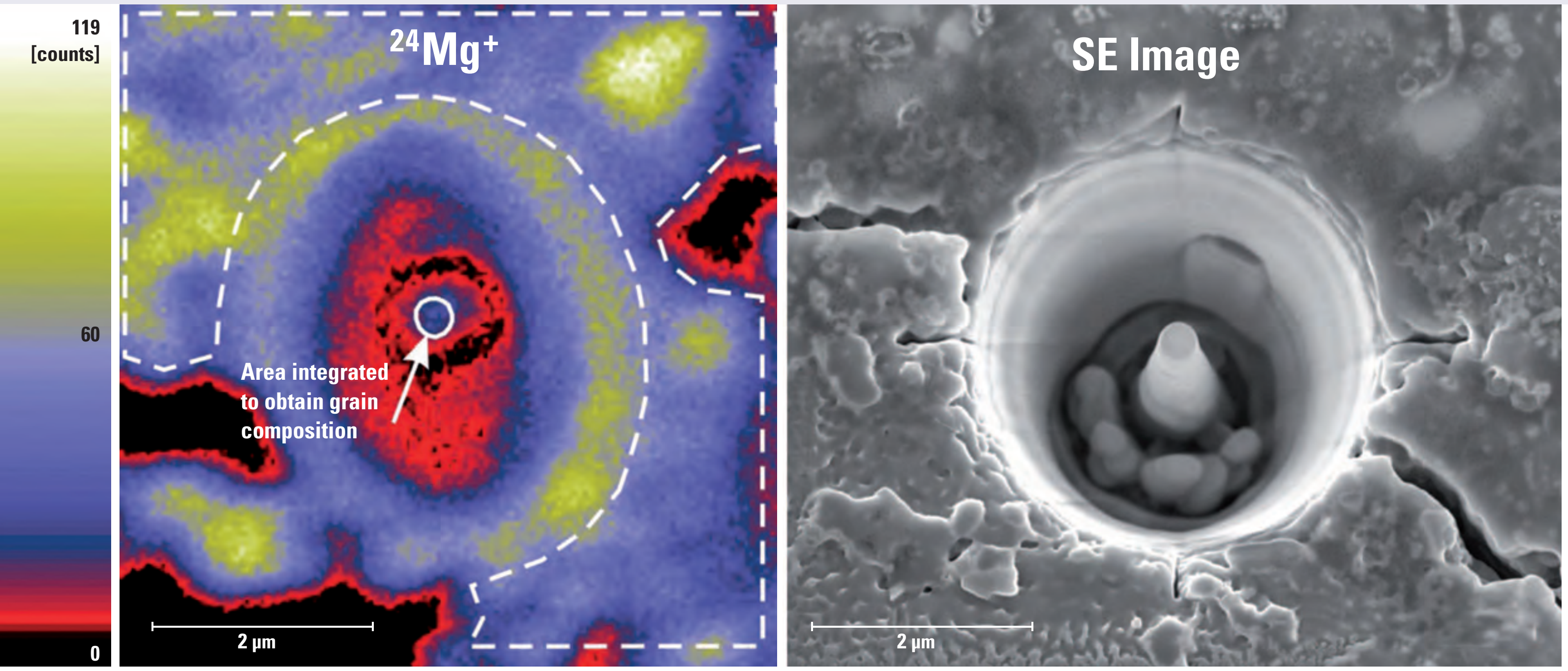
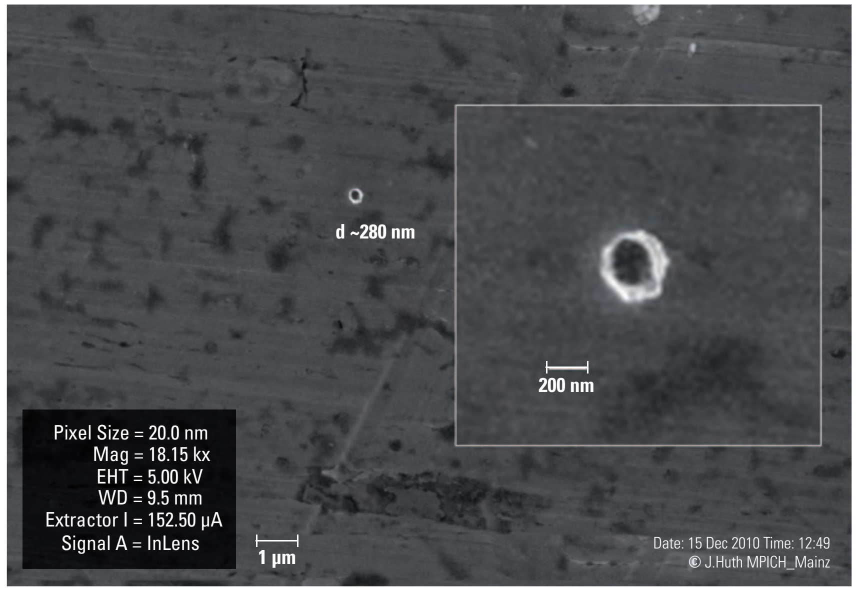


Figure 1: Magnesium-24 isotope image acquired with the NanoSIMS ion probe (left) after FIB preparation (right) of a stardust silicate from the Acfer 094 meteorite. The stardust grain sits on top of the tip prepared by FIB.

Dust plays an important role in Space and on Earth. It is found in a variety of environments, e.g., around evolved stars, in interstellar clouds, in planetary materials, and in the atmosphere on Earth. Dust carries specific isotopic signatures which can be used to trace chemical and physical processes at the sites of dust formation or processing. We have studied a variety of extraterrestrial materials and terrestrial aerosols with different nanoanalytical analysis techniques, in particular secondary ion mass spectrometry (NanoSIMS; Hoppe et al., 2013) and electron microscopy (SEM/EDX, TEM, Auger spectroscopy) in conjunction with sample preparation by the FIB technique (Figure 1). These studies allowed us (i) to get new insights into all stages in the life cycle of interstellar dust, from the formation in circumstellar environments to the incorporation into planetary bodies, and (ii) to investigate SO_2 oxidation pathways involving dust catalysis in terrestrial environments.

THE EXTRATERRESTRIAL PERSPECTIVE: Most of the chemical elements, from carbon to uranium, are produced in the interior of stars by nuclear reactions. 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 Solar System materials, it is possible to get detailed insights into stellar nucleosynthesis and dust formation. We have used the technique of ion imaging, specifically developed for the NanoSIMS ion probe at our department, to study thousands of individual submicrometer-sized presolar SiC grains chemically separated from meteorites. In this way dozens of rare types of grains were identified by specific isotopic fingerprints and subsequently analyzed in more detail. These studies were complemented by in-situ searches for various stardust minerals in meteoritic thin sections and cometary matter. This allowed us to get new insights into the nucleosynthetic production mechanisms of the important rock-forming element magnesium and volatile sulfur and how these elements were carried into the Solar System (e.g., Kodolanyi et al., 2014). To investigate the distribution and survival of presolar matter in the solar nebula we have studied its abundance and nature in different types of primitive meteorites which can be used to constrain the degree of thermal and aqueous processing of small planetary bodies (e.g., Leitner et al., 2012). Furthermore, our group was part of the ISPE team that carried out the first studies of contemporary interstellar dust collected by NASA's Stardust mission. With our SEM we identified five impact craters on two Al foil targets, one of which is likely of interstellar origin (Figure 2; a Mg-Fe-rich silicate based on EDX analysis of the impact residue). Overall, ISPE identified seven dust grains of likely interstellar origin which are surprisingly diverse in chemical composition, crystal structure, and size in view of existing models and astronomical observations of interstellar dust (Westphal et al., 2014).

THE TERRESTRIAL PERSPECTIVE: Global sulfate production plays a key role in aerosol radiative forcing; more than half of this production occurs in clouds. We participated in the HCCT 2010 campaign and collected SO_2 and aerosols from upwind, downwind, and in-cloud sampling sites. Sulfur-isotopic analysis by NanoSIMS of single particles, in combination with isotopic measurements of gas-phase sulfur, allowed the major sulfate addition pathways to be resolved. It was found that SO_2 oxidation catalyzed by natural transition metal ions is the dominant in-cloud oxidation pathway. The pathway was observed to occur primarily on coarse mineral dust, so the sulfate produced will have a short lifetime and little direct or indirect climatic effect. Taking this into account will lead to large changes in estimates of the magnitude and spatial distribution of aerosol forcing (Harris et al., 2013).



Pixel Size = 20.0 nm
Mag = 18.15 kx
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Figure 2: SEM image of a 280 nm-sized impact crater on an Al foil target from NASA's Stardust mission. The impactor was likely an interstellar Mg-Fe-rich silicate grain.

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ACRONYMS:

SIMS: *Secondary Ion Mass Spectrometry*
SEM: *Scanning Electron Microscopy*
EDX: *Energy-dispersive X-Ray Spectroscopy*
TEM: *Transmission Electron Microscopy*
FIB: *Focused Ion Beam*
ISPE: *Interstellar Preliminary Examination*
HCCT: *Hill Cap Cloud Thuringia*

RESIDUAL PARTICLES FROM LIQUID CLOUD DROPLETS AND ICE CRYSTALS

JOHANNES SCHNEIDER

"Experimental investigation of aerosol-cloud interactions is key to understanding the role of aerosol and clouds in the atmosphere."

Figure 1: Cloud measurements: The picture shows the tower at the HCCT2010 field site "Schmücke". On the tower several instruments were installed to collect cloud water and to measure cloud droplet size distributions.

Clouds play an essential role in the radiation budget and chemistry of the Earth's atmosphere and are thus an important subject in climate research. Especially the indirect aerosol-cloud effect (or Twomey effect), describing the changes of cloud properties by additional anthropogenic aerosol production, is one of the major uncertainties in current climate predictions. Also the phase state of cloud particles (liquid droplets or ice crystals) influences the lifetime and the radiative properties of clouds. Cloud droplets or ice crystals can only form when pre-existing aerosol particles are available as cloud condensation nuclei (CCN) or ice nucleating particles (INP). For correct modeling and prediction of cloud properties the knowledge of CCN and INP properties is therefore required. Another aspect in aerosol-cloud interaction is cloud processing of aerosol particles. Most clouds evaporate before their droplets grow large enough to initiate precipitation. Upon evaporation of the cloud water, the aerosol particles that initiated cloud formation are released again, but due to the cloud processing the properties of the aerosol have changed. This has to be taken into account when predicting cloud formation from initial aerosol properties inferred from emission data bases.

In recent years the research group "Aerosol and Cloud Chemistry" conducted several field experiments to investigate these effects. The general concept of these experiments was sampling of cloud particles from ambient clouds, evaporating the cloud water/ice, and analyzing the residual particles online by different direct-reading aerosol mass spectrometers.

Cloud particles can be sampled by accelerating the particles towards the inlet and applying a counterflow in the inlet tube, such that only large droplets or crystals have sufficient inertia to overcome the counterflow and pass into the inlet tube. There the dry counterflow air is also utilized to evaporate the water or ice from the droplets/crystals. Two types of aerosol mass spectrometers were used: The thermal desorption technique instrument C-ToF-AMS (Compact Time-of-Flight Aerosol Mass Spectrometer) and the single particle laser ablation instrument ALABAMA (Aircraft-based Laser ABlation Aerosol MAss spectrometer), which was developed and built at MPIC (Brands et al., 2011).

The experiments conducted between 2010 and 2013 include: HCCT, 2010, at the central German mountain Schmücke (10°46'15''E, 50°39'19''N, 937 m a.s.l.); PRADACS, 2011, on the Puerto Rican mountain Pico del Este (65°45'33''W, 18°16'07''N, 1039 m a.s.l.); ACRIDICON-Zugspitze, 2012, on the German alpine mountain Zugspitze (10°59'11'' E, 47°25'16''N, 2650 m a.s.l.); and INUIT-JFJ/CLACE2013, at the Swiss High Alpine Research Station Jungfraujoch (7°59'2''E, 46°32'53''N, 3580 m a.s.l.).

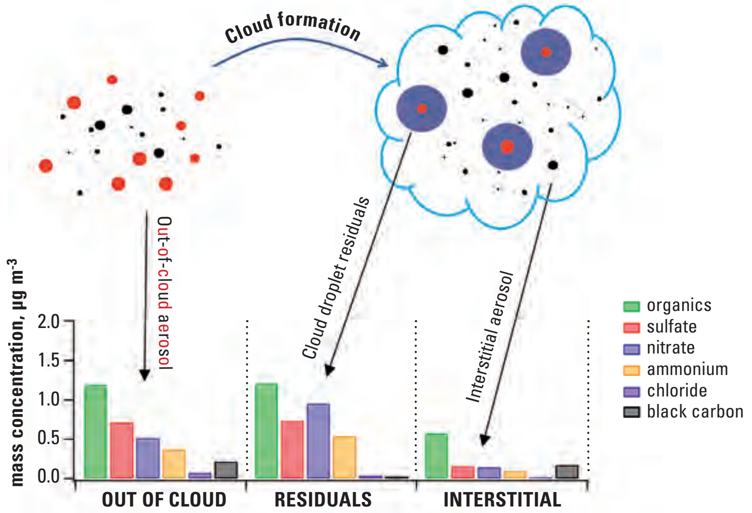

Figure 2: Aerosol composition before and during cloud occurrence. The absolute amount of nitrate increases in the cloud due to uptake of nitric acid from the gas phase by the cloud droplets. Black carbon remains mainly in the unactivated interstitial aerosol.

Our results from the liquid cloud sampling experiments confirm the importance of nitric acid uptake in aqueous cloud droplets: In all data sets obtained at the very different stations the relative amount of nitrate in the cloud droplets was elevated compared to the non-cloud aerosol (Figure 2). Sulfate production by SO_2 oxidation in the aqueous phase was also observed (Harris et al., 2013), but the mass addition by sulfate oxidation is less than that by nitrate. However, results from a downwind station during the HCCT 2010 experiment suggest that the nitrate addition is reversible: after cloud evaporation the nitric acid can also partition back to the gas phase.

The ice particle residuals reveal different chemical composition compared to the liquid cloud residuals. Insoluble compounds like mineral dust are known to be well suited as ice nucleating particles, but primary biological particles and organic particles play a more important role at higher cloud forming temperatures. This effect has been previously observed in laboratory studies and was confirmed by the data obtained during the Jungfraujoch measurements in 2013.

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WIND TUNNEL INVESTIGATIONS ON THE RETENTION OF CARBOXYLIC ACIDS DURING RIMING

MIKLÓS SZAKÁLL, KAROLINE DIEHL

“Retention of trace substances by cloud ice is fundamental to atmospheric chemistry and only laboratory experiments yield the essential parameters for numerical cloud chemistry modeling.”

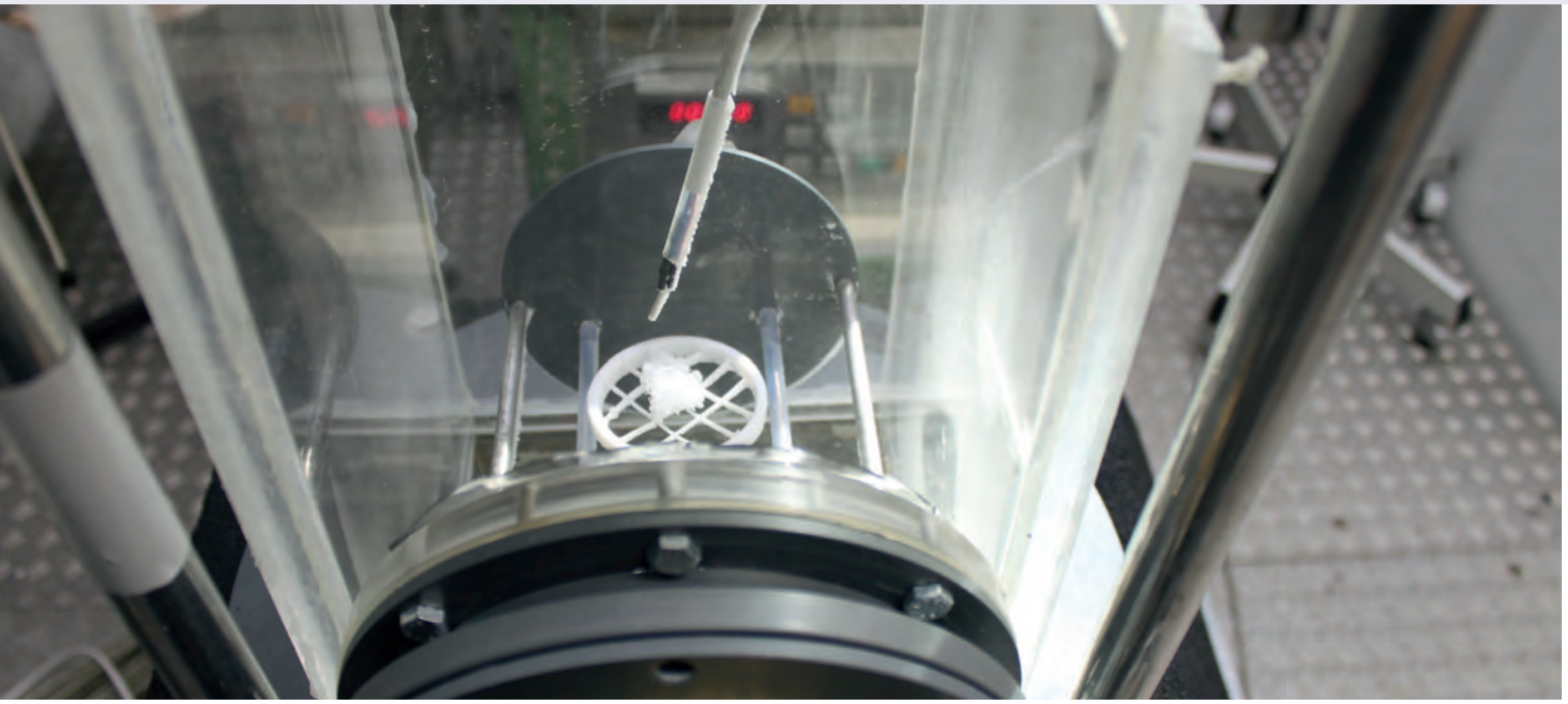

Figure 1: Shown is the insulated box which is fixed at the wall of the experimental section of the wind tunnel. The rime collector is exposed in the center of the section and, thus, in the cloud of supercooled droplets. The air flow enters from below the picture.

In mid- and high-latitudes precipitation is mainly initiated by the ice phase, so that mixed phase clouds play a major role in the formation of precipitation. In such clouds the ice particles grow fast to precipitation sizes at the expense of liquid drops through the process of riming where supercooled droplets collide with and freeze onto glaciated hydrometeors. The droplets, however, always contain – depending on the circumstances – more or less water-soluble trace substances. During riming a fraction of these solutes remains in the ice phase which ultimately becomes amenable for scavenging. This effect is called “retention” and it is an important process which determines the partitioning of atmospheric trace substances between the phases.

The Mainz vertical wind tunnel (Diehl et al., 2011) allows free levitation of various hydrometeors such as droplets, ice particles and crystals, snowflakes, graupels, and hailstones from tens of micrometers to centimeter sizes. Experiments are conducted under controlled air conditions for temperature (from -30°C to +30°C), humidity (dew points from -40°C to saturation), and velocities (from 10 cm s^{-1} up to 40 m s^{-1}) in laminar or slightly turbulent flows.

Extending our previous series of measurements with inorganic substances particular wind tunnel experiments were performed to determine the retention of formic acid (HCOOH), acetic acid (CH_3COOH), oxalic acid ($(COOH)_2$) and malonic acid ($CH_2(COOH)_2$). The droplets containing well-defined concentrations (5 mg/l) of the respective trace substance were injected into the wind tunnel via two sprayer nozzles. Their mean volume radius was 14 µm, the measured liquid water content ranged from 0.9 to 1.6 g m^{-3} with temperatures extending from -16 to -7°C. In the experiments two types of rime collectors were examined: ice particles (as graupels) and snowflakes. The ice particles were captively floated, i.e. they were hung up on a thin nylon fiber (80 µm in diameter) where they could move in the airstream at their terminal settling velocity with a realistic flow field around them. The snowflakes were placed on a coarse meshed net out of the same fine nylon fibers. The diameters of the ice particles were 6 mm and the diameters of the snowflakes ranged from 10 to 15 mm.

The rime collectors were positioned in the center of the experimental section of the wind tunnel within the airstream containing the supercooled droplets. After riming the melt water of the rime collectors was analyzed by ion chromatography. From the concentrations of the trace substances in the ice phase after riming and the initial liquid droplet’s retention coefficients could be calculated for each trace substance.

The retention coefficients for all four acids were found to be independent of temperature. Their mean values were 73 ± 7% for formic acid, 69 ± 5% for acetic acid, 98 ± 3% for oxalic acid, and 98 ± 4% for malonic acid. This means, for example, that 73% of the formic acid initially carried by the liquid droplets in the end was retained within the rimed hydrometeor. The present results were compared to earlier wind tunnel studies (v. Blohn et al., 2011; 2013) and related to the effective Henry’s law constant (H*) which accounts for solubility and dissociation. Figure 2 indicates that high H* values are correlated with high retention coefficients. This is the case for the di-carboxylic acids ($(COOH)_2$) and $CH_2(COOH)_2$), as well as for hydrochloric and nitric acid (HCl and HNO_3) where the retention coefficients were measured to be 1. Their retention is dominated by strong solubility and dissociation so that the ions are hardly able to leave the liquid phase. The mono-carboxylic acids (HCOOH, CH_3COOH) are characterized by lower H* values and, thus, their retention coefficients are smaller. Because these substances are less dissociated they are more easily released back to the gas phase than incorporated into the ice. Here the retention is more sensitive to other factors such as ambient temperature, liquid phase concentration, and shape of the rime collector which affect the rate of latent heat removal from the rimed surface.

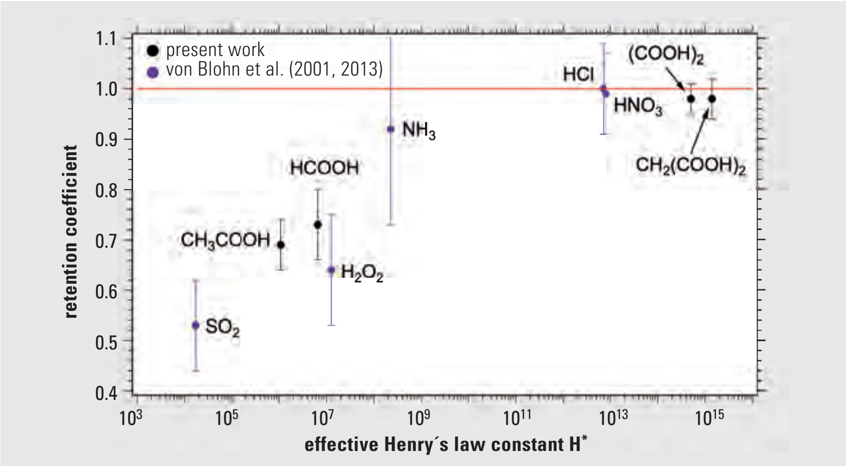

Figure 2: Measured retention coefficients as a function of effective Henry’s law constant (H). Black dots: present work. Blue dots: experimental work of v. Blohn et al. (2011, 2013). All H* values were calculated at 0°C and pH of 4.*

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VOLATILE AND REFRACTORY SUBMICRON AEROSOLS IN THE ARCTIC STRATOSPHERIC WINTER VORTEX

RALF WEIGEL

> **"The Arctic vortex is a temporary stratospheric reservoir of refractory particulate matter which is regularly imported from aloft during polar winters."**

Figure 1: The instrumented Russian high altitude research aircraft M-55 Geophysica launched from Kiruna.

The Earth's upper stratosphere and mesosphere (i.e. the middle atmosphere) is continuously burdened with ablation material of evaporating micrometeorites on the order of 10 – 100 tons per day (Plane, 2012). The deposited material forms ultrafine smoke particles with size diameters smaller than 10 nm in the mesosphere. Such ultrafine refractory aerosols originating from space have residence times of several months to years at these altitudes. The middle atmosphere may also contain aerosol from anthropogenic activities, e.g., components from space debris, rocket launches, and exhaust from high flying aircraft. The anthropogenic contribution to the overall aerosol load in the middle atmosphere is not yet well quantified and understood. Soil materials, continuously released by sub-Pinatubo volcanism (e.g. Souffriere Hills, Nabro, etc.) and other ground sources, such as biomass burning, may also contribute to the refractory aerosol in the middle atmosphere.

The polar winter vortices probably are the most efficient pathways to drain mesospheric aerosol due to the inherent large scale subsidence, which causes a downward transport of air from aloft including aerosols and trace gases. During the Northern hemisphere winter the downwelling reaches ~ 500 K (i.e., roughly 25 km) of potential temperature altitude. Until late March further import from high altitudes extends towards the vortex bottom (at ~ 400 K), and is distributed mainly by diabatic dispersion (Weigel et al., 2014). Once the aerosol enters regions with saturated vapors, for example of sulfuric acid, nitric acid, or water, the refractory particles provide surfaces for heterogeneous condensation. In this way the formation of noctilucent clouds, polar stratospheric clouds, and ultimately cirrus is supported.

In-situ measurements with a 4-channel stratospheric condensation particle counter of the aerosol vertical distribution were conducted at up to 20 km altitude on board the high-altitude research aircraft M-55 Geophysica (Figure 1) from Kiruna, Sweden, during the winters of 2003, 2010/11, and 2011/12. The measurements repeatedly revealed an increase of the mixing ratios of sub-micrometer sized particles with altitude inside the Arctic vortices. This monotonous rise of particle concentrations coincided with an increasing fraction of non-volatile (refractory) aerosol components. Up to 8 out of 11 particles per cm^3 were found to contain refractory residuals with sizes of 10 nm to 1 µm which resisted evaporation at 250 °C. Particle mixing ratios (N_{10}nv ~ 140 mg^{-1}, Figure 2) and fractions f of non-volatile (refractory) particles (75% of total detected) exhibited highest values in air masses having the lowest content of nitrous oxide (70 nmol mol^{-1} of N_2O). This strongly indicates that these particles originate from the middle atmosphere. The strength and extent of the downward transport inside the vortex varied between the years depending on the dynamical evolution of the vortex. The qualitative agreement of the observations from three independent field campaigns over eight years (Figure 2) leads to the conclusion that the import of refractory particles at the vortex lower stratosphere is a regular feature rather than exceptional (e.g. during a winter with extraordinarily strong inner vortex subsidence as in 2003). In December the transport from aloft appears to be developing; thereafter the abundance of refractory aerosol inside the vortex reaches its highest levels in March. A measurement-based estimate yields an enhancement of the refractory aerosol mass by a factor of 4.5 (in scales of kilotons) at the vortex bottom (100 – 67 hPa) over the course of a winter. Usually at the end of March the downward motion inside the Arctic vortex abates and later the vortex disintegrates releasing the ingested material for mixing towards mid-latitudes. The Arctic vortex can thus be understood as a temporary stratospheric reservoir of refractory aerosol material imported from aloft.

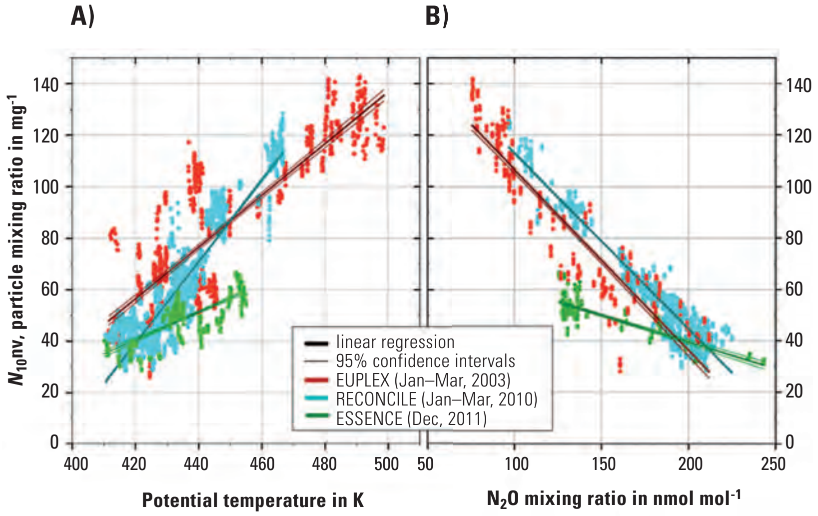

Figure 2: Dependence of the mixing ratio of non-volatile particles N_{10}nv as function of potential temperature (Panel a) and of N_2O mixing ratio (Panel b), linear regressions with 95% confidence intervals are shown. Results from measurements within the vortex are shown for the three Arctic missions: EUPLEX (2003), RECONCILE (2010) and ESSenCe (2011).

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FURTHER RESEARCH GROUPS

FURTHER RESEARCH GROUPS

Satellite data, air quality, theory and practice of the exchange of chemical compounds in biosphere and atmosphere, and high pressure chemistry and physics

The **AEROSOLS AND REGIONAL AIR QUALITY GROUP** led by Yafang Cheng deals with central questions of environmental research and Earth System science, such as the influence of soot particles and other aerosols on air quality and climate. In 2014, Yafang Cheng received an award from the Minerva women's advancement program of the Max Planck Society, which includes a W2 group leader position and further support for independent research and continuation of her scientific career.

The **HIGH PRESSURE CHEMISTRY AND PHYSICS GROUP** led by Mikhail Eremets studies matter under extremely high pressure. The group achieved record static pressures of 440 GPa, which equates to 4.4 million atmospheres and exceeds the pressure in the earth's inner core (360 GPa). At the heart of their work is a diamond anvil cell. Pressure is generated between the tips of two diamond anvils. This small device can be combined with heating lasers, cryostats, magnets and X-ray sources. The research is being supported from 2011 until 2016 by an Advanced Grant from the European Research Council.

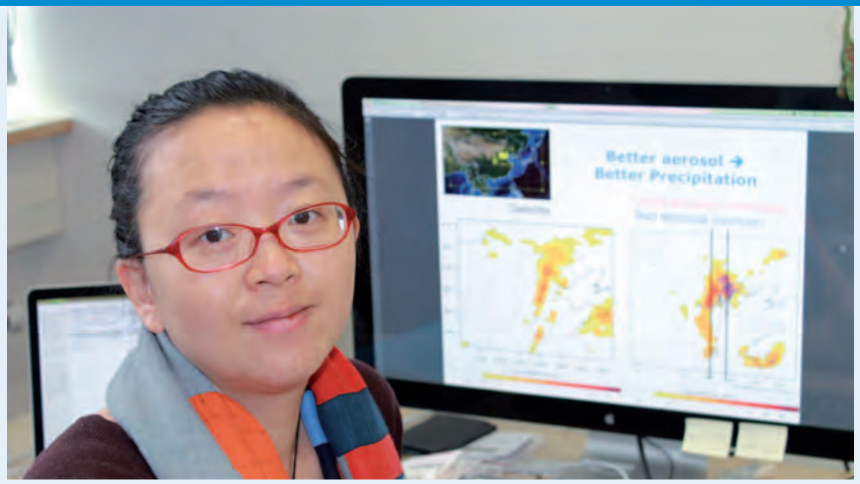
The **ORCAS RESEARCH GROUP** led by Frank Keppler, who in 2014 accepted a Heisenberg professorship and moved to the Ruprecht-Karls-University of Heidelberg, was funded through a European Young Investigator Award (EURYI) and investigated the production of climate-relevant volatile organic compounds and their life cycles. Emphasis was on the trace gases methane and halomethanes and their contributions to the greenhouse effect and ozone destruction.

The **THEORETICAL CHEMISTRY GROUP** led by Luc Vereecken is part of the Max Planck Graduate Centre and was established in 2011. It applies quantum chemical theories to relate the chemical structure of compounds to their reactivity, with a focus on atmospheric applications. The group advances kinetic theories to predict rate coefficients of volatile organic compounds in the atmosphere and their reaction products that contribute to aerosol formation.

The **SATELLITE REMOTE SENSING GROUP** led by Thomas Wagner was established in 2006 and analyses 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.

AEROSOLS AND REGIONAL AIR QUALITY

YAFANG CHENG



"Focus of our group is the investigation of aerosol optical properties, hygroscopicity and phase state, and their impact on air quality and climate."

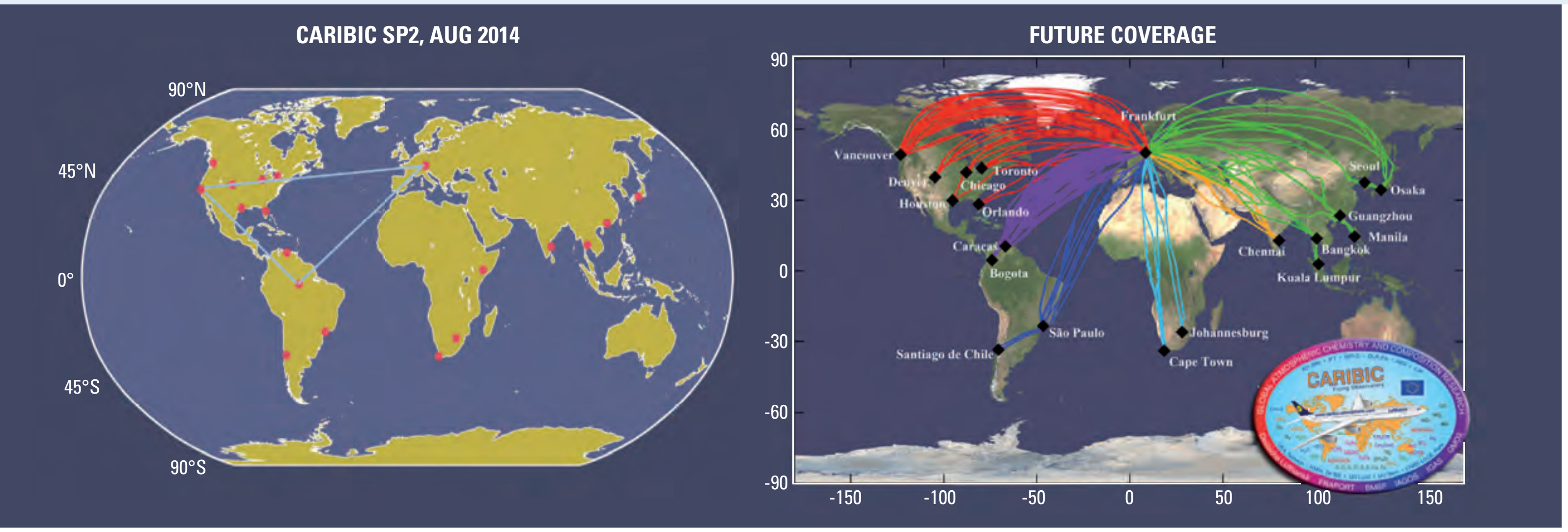


Figure 1: Current and future routes of CARIBIC-SP2 and for further information on CARIBIC, including all destinations, please see http://www.caribic-atmospheric.com.

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

Black carbon (BC) aerosols, also described as soot, play an important role in regulating the Earth climate due to their light absorbing properties. However, it is very difficult to determine the radiative forcing from BC. One reason for this is because the radiative forcing of BC shows a strong dependency on its vertical distribution. Model simulations show that when tropospheric BC exists at higher altitudes above a greater proportion of cloudy layers, its radiative forcing can be significantly enhanced. Different from tropospheric BC, BC in the stratosphere contributes negative shortwave radiative forcing (countered by induced positive longwave radiative forcing). Despite its importance, we still do not have enough information on the vertical distribution of BC, especially in the upper troposphere and lower stratosphere.

Together with Carl Brenninkmeijer's group and support from Lufthansa and Droplet Measurement Technologies company, we have started in August 2014, the first long-term characterization of black carbon using a single particle soot photometer (SP2) carried by a passenger aircraft in the CARIBIC project. The SP2 has flown from Munich, Germany to San Francisco, USA and Manaus, Brazil. The upcoming results will improve our knowledge about the BC global spatial distribution and mixing state, and toward a better understanding of its climate radiative forcing.

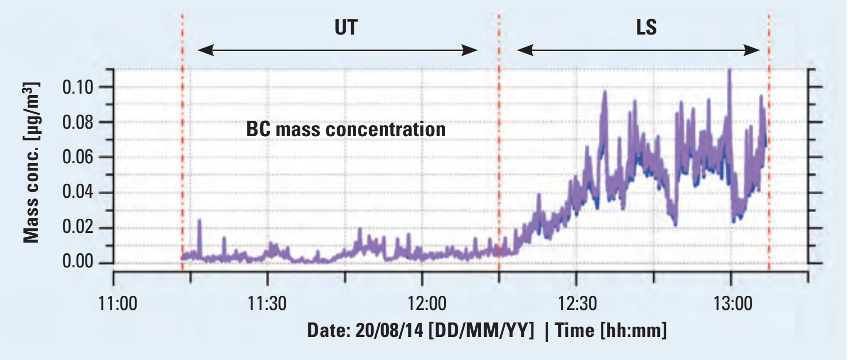


Figure 2: Preliminary results of BC mass concentration in the upper troposphere (UT) and lower stratosphere (LS) during the flight on Aug 14, 2014.

EVALUATION OF THE SOURCES AND LIGHT ABSORPTION OF BLACK CABON IN CENTRAL EUROPE

Besides aircraft measurements, we have also performed a modeling study to assess the source and light absorption properties of BC. In a case study over Central Europe we compared measurement data to modeling results by WRF-Chem. In addition to BC-related measurements, particle number concentrations within the German Ultrafine Aerosol Network, PM_{10} from 392 monitoring stations, and aerosol optical depth from MODIS and AERONET were also used to assist the assessment. The modeled BC concentrations were a factor of 2 lower than the observations while PM_{10} and AOD show good agreement with the modeled results. Together with back trajectories, detailed model bias analyses revealed that the current BC emission in countries to the east and south of Germany might be underestimated by a factor of 5 for the simulation period. On the contrary, the particle absorption coefficient was positively biased by about 20% even when the BC mass concentration was underestimated by around 50%. This indicates that the internal mixture treatment of BC in the WRF-Chem optical calculation over amplifies the light absorption.

DEVELOPMENT OF A NANO-CCN COUNTER FOR THE ANALYSIS OF NANOPARTICLES

Chemical composition is essential for understanding the formation and evolution of atmospheric aerosol particles. Due to analytical limitations, however, relatively little information is available for sub-10 nm particles. We present the design of a nano-cloud condensation nuclei counter (nano-CCNC) for measuring size-resolved hygroscopicity and inferring chemical composition of sub-10 nm aerosol particles. We extend the use of counting efficiency spectra from a water-based condensation particle counter (CPC) and link it to the analysis of CCN activation spectra, which provides a theoretical basis for the application of a scanning supersaturation CPC (SS-CPC) as a nano-CCNC. Measurement procedures and data analysis methods are demonstrated through laboratory experiments with monodisperse particles with diameter in the range of 2-10 nm, where sodium chloride, ammonium sulfate, sucrose and tungsten oxide can be easily discriminated by different characteristic supersaturations of water droplet formation. The design is not limited to the water CPC, but also applies to CPCs with other working fluids (e.g. butanol, perfluorotributylamine). We suggest that a combination of SS-CPCs with multiple working fluids may provide further insight into the chemical composition of nanoparticles and the role of organic and inorganic compounds in the initial steps of atmospheric new particle formation and growth.

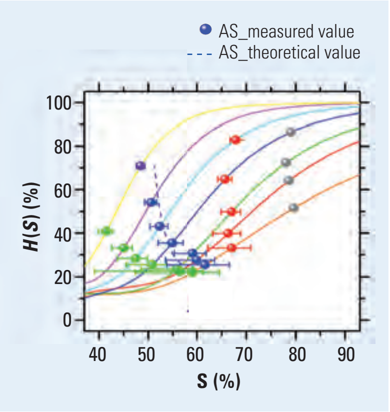


Figure 3: Supersaturations determined for particles of mobility diameter 2.5 nm sodium chloride (green), ammonium sulfate (AS, blue), sucrose (red) and tungsten oxide (gray) aerosols. Solid lines indicate different cumulative effective supersaturation distributions.

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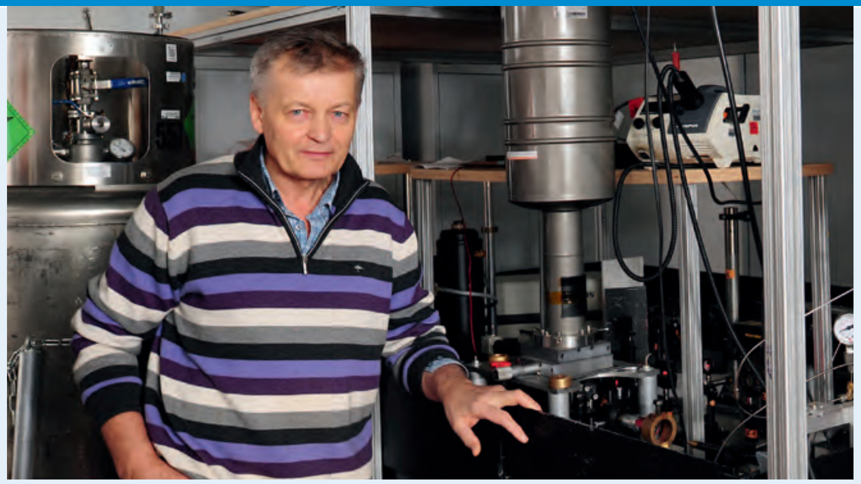
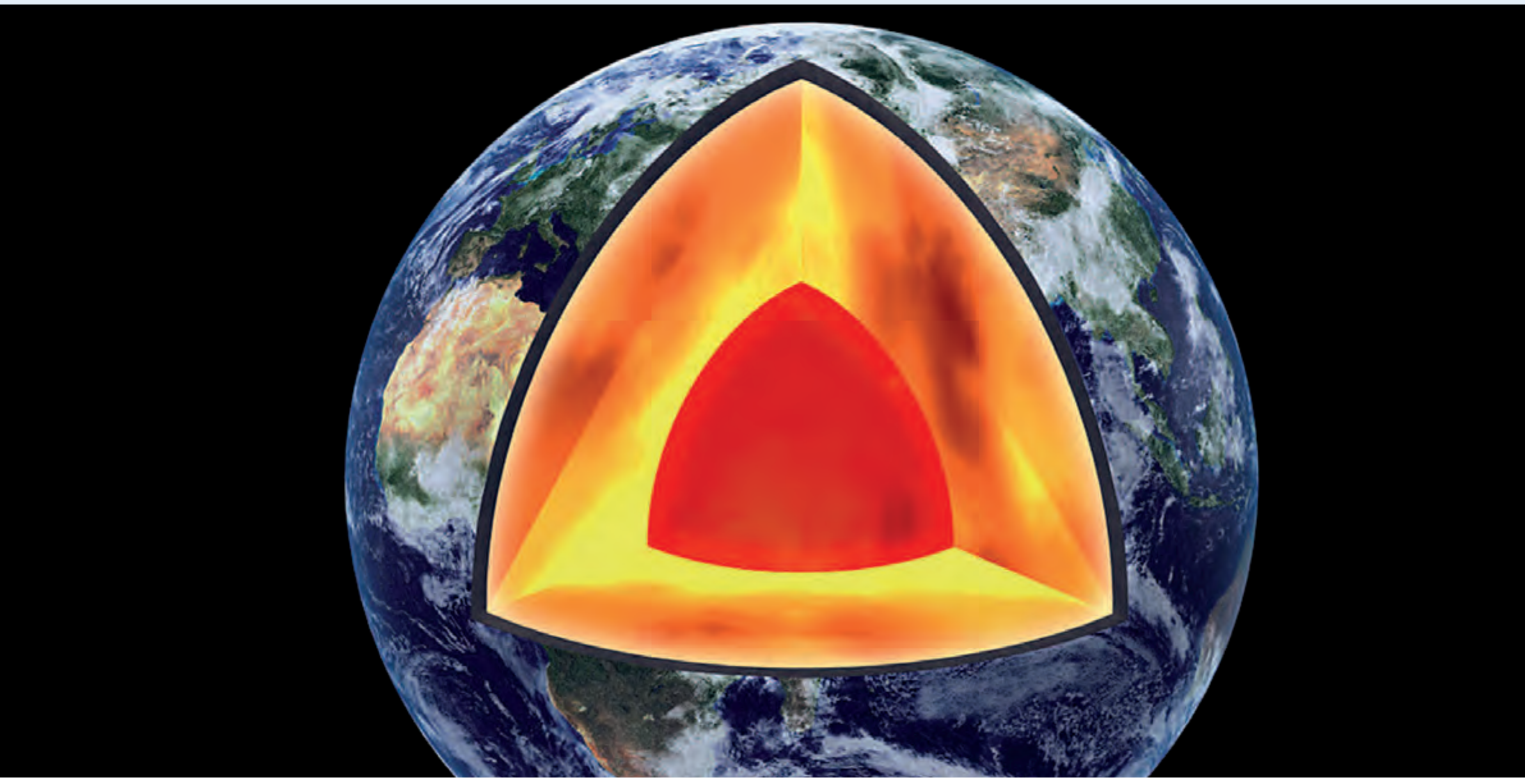
HIGH PRESSURE CHEMISTRY AND PHYSICS

MIKHAIL EREMETS



> **"Study of metallic hydrogen, search for high-temperature superconductivity in hydrogen-rich materials, and synthesis of new materials."**



Picture: Peter Egermann, Fotolia

The group has three main directions of study: 1) metallic hydrogen and related covalent hydrides as potential high temperature superconductors, 2) N-H compounds as highly energetic materials, and 3) synthesis of organic molecules from inorganic materials at pressure-temperature conditions of the Earth´s mantle relevant to prebiotic chemistry and the origin of life.

For metallic hydrogen *(1, 2)* we established the new phase diagram of hydrogen (Figure 1). In particular we found a new triple point at 208 GPa and 305 K. Another triple point is likely at ≈370 GPa and 200 K as follows from the minimum at the line between phases III and IV. At higher pressures and lower temperatures hydrogen might be in a metallic atomic state according to recent calculations (Azadi et al., 2014).

For N-H compounds we found that ammonia at a pressure of ~120 GPa forms an as yet experimentally unknown ionic compound - ammonium amide *(3)*. In contrast NF_3 remains in the molecular form *(4)*.

Polymeric nitrogen *(5)* is a highly energetic material with many potential uses, but it is synthesized at megabar pressures. To reduce the synthesis to low, practically achievable, pressures we have tried to stabilize nitrogen with hydrogen. We found that nitrogen and hydrogen react directly at room temperature and pressures of 35 GPa forming a mixture of nitrogen backbone oligomers which are seen as chains of single-bonded nitrogen atoms with the rest of the bonds terminated with hydrogen atoms (Figure 3) as identified by IR absorption, Raman, X-ray diffraction experiments and theoretical calculations. The pressure required for the synthesis strongly decreases with temperature to ~ 20 GPa at 550 K. At releasing pressures below 10 GPa, the product transforms into hydrazine. Our findings might open a way for the practical synthesis of these extremely high energetic materials as the formation of nitrogen-hydrogen compounds is favorable already at pressures above 2 GPa according to the calculations.

The aforementioned work inspired us to check if simple organic molecules (precursors of biological molecules) can be created at the pressure-temperature conditions of the Earth's mantle (pressure 1-3 GPa, temperature 300-800 K). These conditions are easily created with the diamond anvil cell technique. Reactions are monitored in-situ with Raman and infrared spectroscopy. The products are further analyzed with the aid of chromatography and mass spectrometry. In this endeavor we are working in close collaboration with J. Williams and his group, and over the past year have accumulated a lot of data. Figure 2 presents one example: reaction of carbon (graphite) with water at 1000°C and 3 GPa. Reaction of carbon with D_2O helps to unambiguously identify absorption peaks as C-H stretching modes belonging to methane and higher hydrocarbons. Gas chromatography provided further detailed analysis of the product. These results support the hypothesis that at least part of natural gas and probably oil have abiotic origins. We also synthesized more complex organic C-O-H molecules under conditions of the Earth´s mantle.

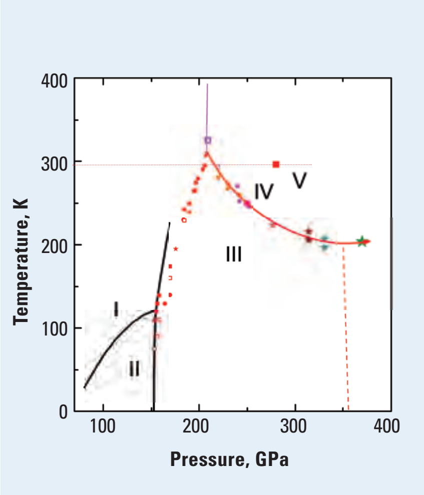


Figure 1: Phase diagram of hydrogen. Black lines are boundaries between phases I, II, and III established in previous works (Mao and Hemley, 1994). Our experimental data established borders of new phases.

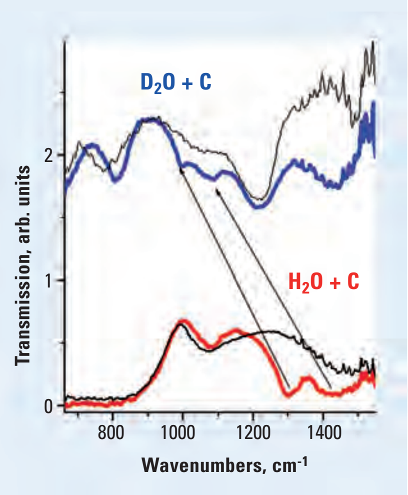


Figure 2: Synthesis of hydrocarbons from carbon and water at 3 GPa and 1000°C. Infrared transmission spectra. The peak at 1310 cm^{-1} is characteristic for methane, others to higher hydrocarbons.

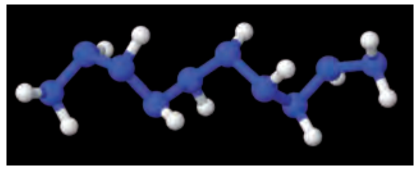


Figure 3: Ball and stick representation of $N_{10}H_{12}$, illustrating the low-energy spiral backbone structure.

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FORMATION OF METHANE IN EUKARYOTES

FRANK KEPPLER

"New evidence of methane formation under aerobic conditions."

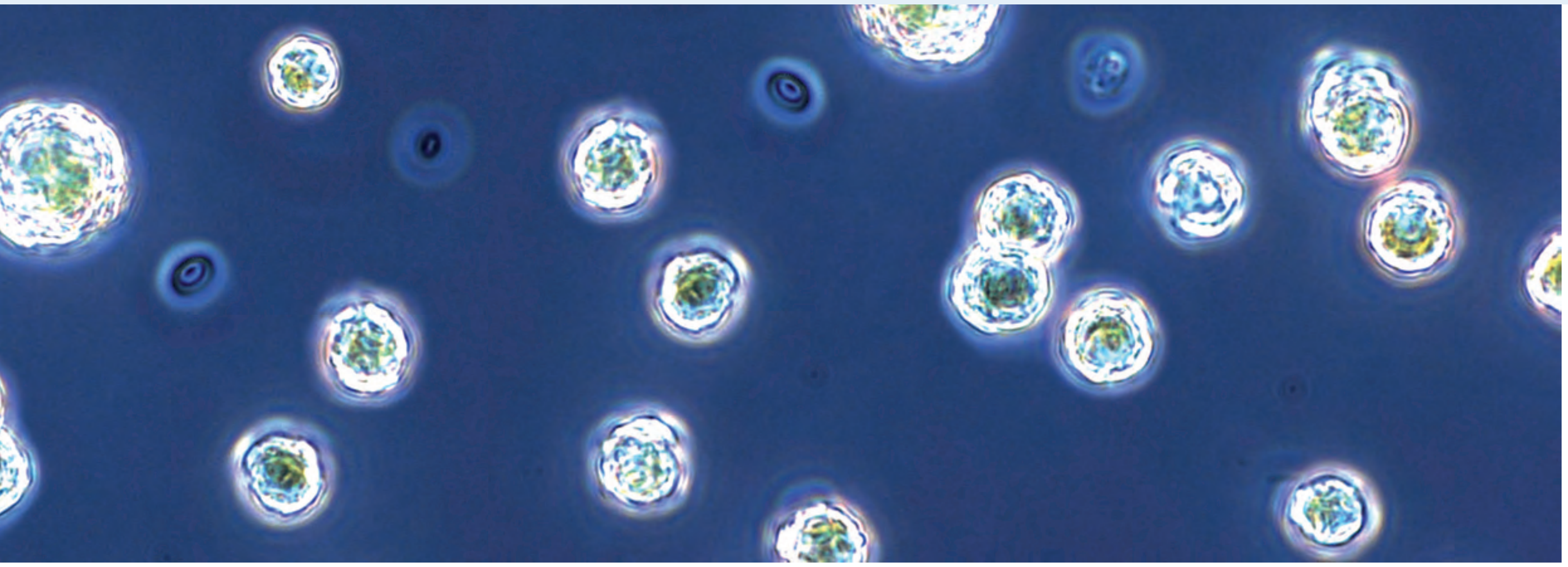

Figure1: Marine algae such as the coccolithophore Emiliania huxleyi produce methane, probably from organic sulfur compounds.

Methane (CH_4), the second most important anthropogenic greenhouse gas after CO_2, is the most abundant reduced organic compound in the atmosphere and plays a central role in atmospheric chemistry. A comprehensive understanding of the current global CH_4 budget including its sinks and the parameters that control emissions is a precondition for simulating past and future scenarios of its atmospheric concentration. Traditionally biogenic CH_4 was thought to be formed only from microorganisms (methanogens) under strictly anaerobic conditions in wetland soils and rice paddies, the intestines of termites and ruminants, and human and agricultural wastes. Until the recent discovery of direct CH_4 emissions from plants only combustion processes were considered to form it in the aerobic biosphere. But independent observations from several research fields now indicate that in addition to terrestrial plants, fungi, lichens, animals and marine algae also produce CH_4 under aerobic conditions. However, the mechanisms involved in its formation have not yet been delineated and thus are currently the subject of considerable debate and speculation. This is particularly true for the newly identified plant source whose global strength has been a topic hotly debated with as yet no agreed consensus. Nevertheless, the mounting evidence from unexpected research findings suggests that aerobic CH_4 formation may not be an exotic process, but could be widespread in nature. Such observations require essential new research to be undertaken to allow identification of CH_4 sources and a full understanding of the global biogeochemical cycling of CH_4.

In 2006 we provided first evidence that plants produce CH_4 without the aid of methanogens. Since then we have investigated other aerobic organisms such as fungi, lichens, mosses and marine algae and found that they all generate CH_4. In addition other research groups have identified animals as being another non-microbial CH_4 source. Thus combining recent observations in plant, animal and marine biology, it is now apparent that several reaction pathways exist by which CH_4 is generated by aerobic organisms. The newly discovered sources of CH_4 formation under different environmental conditions in the biosphere are schematically illustrated in Figure 2 (middle part). Whereas the biochemistry of methanogenesis in microbes (procaryotes) is well described, possible pathways of aerobic CH_4 generation from plants, fungi, animals and algae (eukaryotes) have yet to be determined.

One main focus of our research is the investigation of the reaction pathways and organic precursor compounds that lead to the formation of CH_4 by aerobic organisms and also the environmental factors affecting their fluxes. For example CH_4 is released from intact living plants at much higher rates when they are under physical stress. In this context it was suggested that reactive oxygen species (ROS) might play an important role in the formation of CH_4 in plants. All environmental stresses, both biotic and abiotic, as well as cellular signalling processes involve ROS formation. Thus CH_4 formation in aerobic organisms may be an integral part of cellular responses towards changes in oxidative status present in all eukaryotes. Furthermore, we established a chemical reaction showing that CH_4 can be readily formed from the amino acid methionine under oxidative conditions, ambient atmospheric pressure and temperature. We also found by using stable isotope studies that tobacco plants (Nicotiana tabacum) and several fungi (Basidiomycota) generate methane from methionine. These experiments provided the first evidence that the thio-methyl group of methionine is a parent compound of CH_4 in plants and fungi.

The observation that CH_4 formation under aerobic conditions occurs in many eco- and bio-systems is robust and prevalent, and opens new, interesting and very challenging options for future research in biochemical, medical and environmental sciences. We are particularly interested in exploring the reaction pathways involved in CH_4 formation from aerobic organisms employing a stable isotope measurement approach. Once major pathways (both abiotic and biotic) under different environmental conditions have been identified, emphasis will be placed on the recent prediction that biospheric emissions of CH_4 are expected to be significantly affected by climate change. This will require identification of all major sources of biospheric CH_4 and investigation of the environmental parameters affecting their fluxes before the prediction of future scenarios.

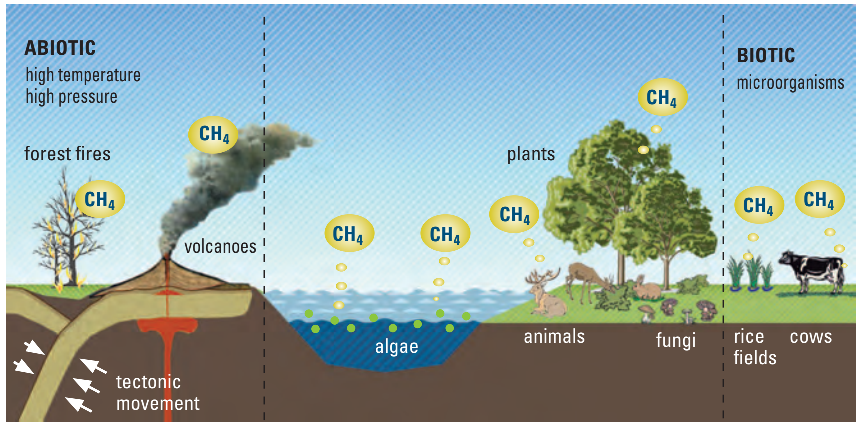

Figure 2: Sources of methane in the environment. For decades scientists only knew forest fires, fossil fuel use and geological processes such as volcano outgassing as abiotic methane sources. Microorganisms were considered as the only biotic source to produce methane without oxygen. We have found that aerobic organisms such as plants, fungi, lichens and algae also produce methane. Whether this is biotic, i.e. catalyzed by enzymes, or abiotic is currently being investigated.

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THEORETICAL STUDIES OF THE TROPOSPHERIC CHEMISTRY OF CRIEGEE INTERMEDIATES

LUC VEREECKEN

“Theoretical calculations connect laboratory investigations, field observations and modeling studies.”

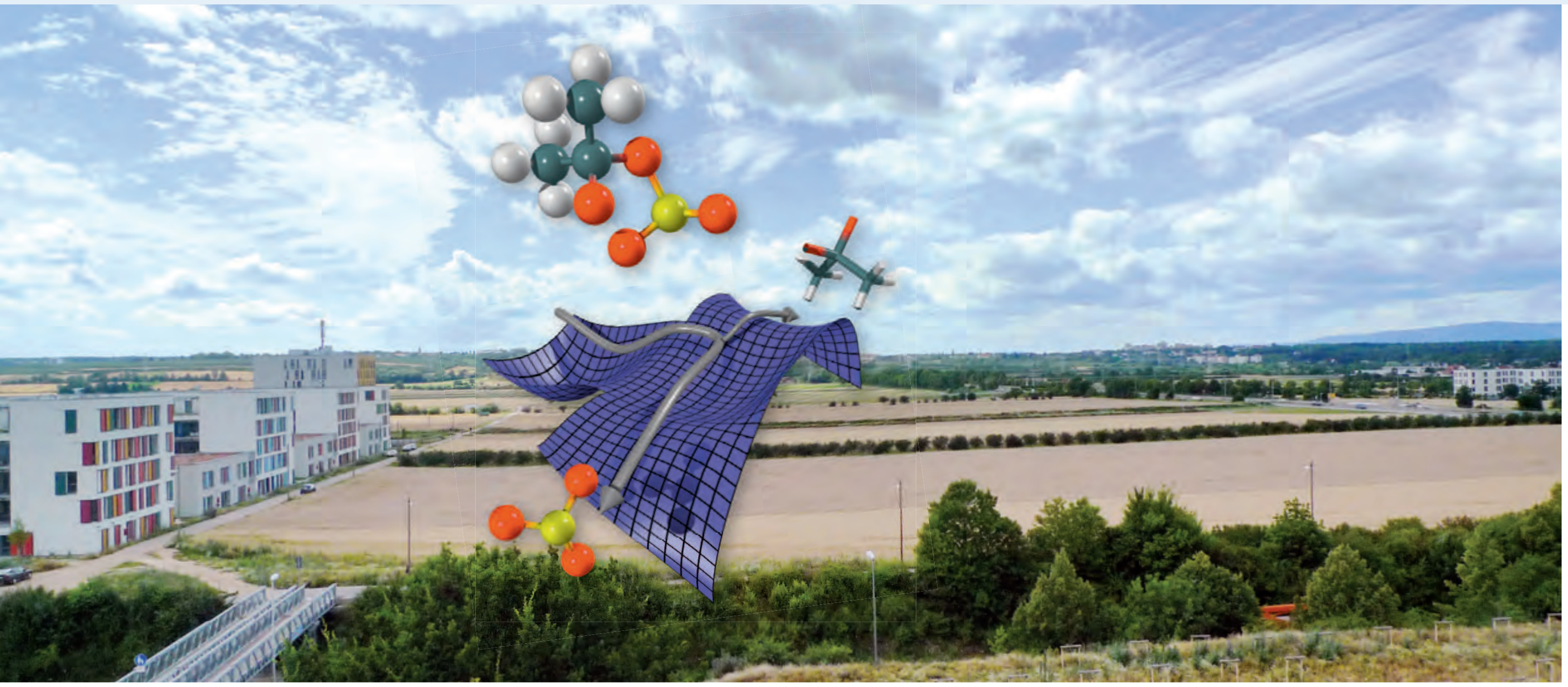

Figure 1: The dominant source of Criegee intermediates in the troposphere is the ozonolysis of biogenic VOCs emitted by vegetation. They contribute to the formation of low-volatility oxygenates and aerosol, and of oxidants.

The theoretical analysis of chemical processes, based on computer simulations, is a powerful method that can be applied to a wide range of questions allowing a deeper understanding of the physical chemistry of processes studied at the Institute. In addition to more general studies, the group aims to support ongoing research efforts by complementing laboratory experiments, studying the chemistry of compounds observed in the field, and by providing kinetic parameters for reactions needed in chemical models when insufficient empirical information is available.

In the atmosphere Criegee intermediates (CI) are formed predominantly from ozonolysis, one of the key oxidation initiation routes of volatile organic compounds (VOCs). They are known to generate OH radicals, also at night when the photolytic sources of this important oxidant are unavailable, as well as creating oxygenated species such as carboxylic acids and esters. These latter low-volatility VOCs play a role in the formation of aerosols in the atmosphere (Figure 1). Despite the pivotal role of CI in the atmosphere, they have only recently been directly observed in the laboratory, and have yet to be measured in the field. Complementing recent worldwide efforts to experimentally determine the kinetics of simple CI, theoretical work remains the most important source of information on CI chemistry, especially with regards to temperature and pressure dependence, the identification of critical co-reactants and more complex CI.

In collaboration with the Radical Measurements Group (Harder) we have investigated CI reactions theoretically and experimentally. Our theoretical analysis showed that the reaction with NO is slow, in agreement with experimental data. The rate of reaction with alkenes depends strongly on the combination of CI and alkene; our predictions are in reasonable agreement with later experimental work. The reaction of CI with RO_2 was found to be a source of oligomers, in agreement with earlier experimental results in the Atmospheric Chemistry Department. Likewise, the reaction with ROOH is a source of low-volatility oxygenates, but can also form ether-oxides (similar to oxy-water) that have yet to be observed and characterized experimentally. The CI + RO_2 and ROOH reactions play a role in aerosol formation, though mostly in an experimental setting at elevated concentrations. The reaction with O_3 was found to be moderately fast, and is expected to play a role as a CI sink in both experiments and the ambient atmosphere. Our predictions for the reaction of CI + SO_2 agree well with the experimental investigations available; this reaction is important for the atmospheric formation of H_2SO_4, and thus affects aerosol formation. The reaction of CI + CO was predicted to be slow, in disagreement with the scarce experimental data; the reason behind this discrepancy is unclear. Finally, the CI + CI reaction is found to be fast and important in laboratory experiments; while our predictions were significantly below earlier experimental work, later work found them to be accurate within a factor of 2-3.

These results have been used to create a kinetic computer code for CI chemistry, combined with the literature data (extensively reviewed by us in 2012) and newly available information, allowing modeling of the fate of CI in laboratory settings and the atmosphere. It appears to be critical that CI are not treated as a single pool, as the substituents and conformation of the CI have a large impact on the reaction kinetics with rate coefficients differing by up to 5 orders of magnitude. Figure 2 shows the impact of the different reactions in a laboratory setting; this model was used to determine the decay rate of *syn*-CH_3CHOO Criegees based on experiments (20±10 s^{-1}). In the atmosphere, some simple CI react predominantly with water, but most other CI will undergo uni- or bimolecular reactions affecting the chemistry in the troposphere.

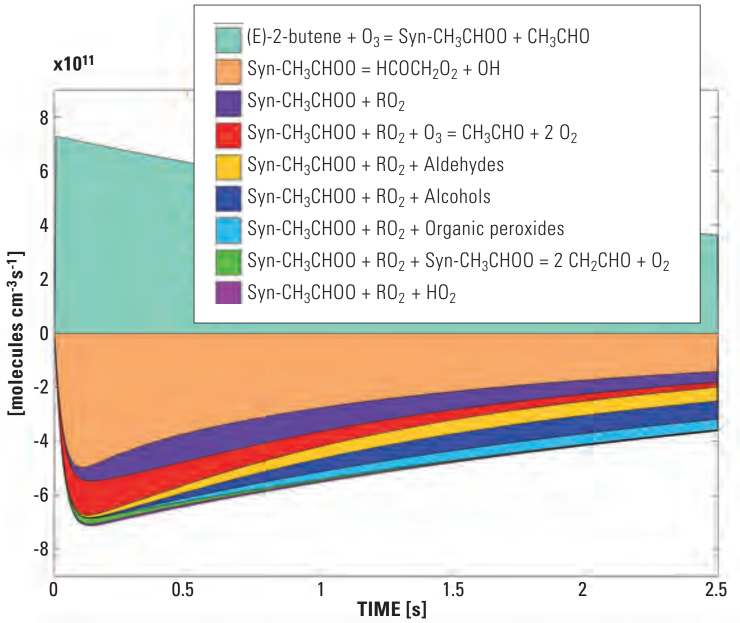

Figure 2: Criegee intermediates formed in the ozonolysis of propene react with the plethora of co-reactants available in such reaction mixtures, affecting their steady-state concentration.

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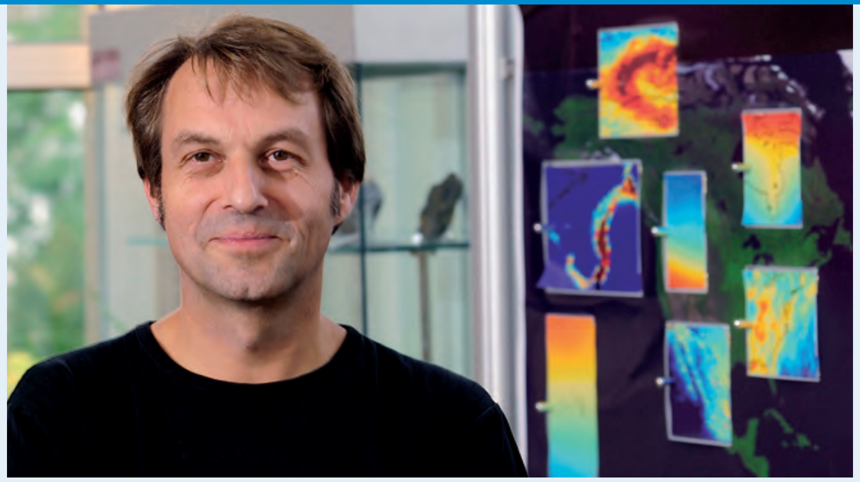
SATELLITE REMOTE SENSING

THOMAS WAGNER



“Volcano emissions of sulfur dioxide and sulfate aerosol formation measured from space.”

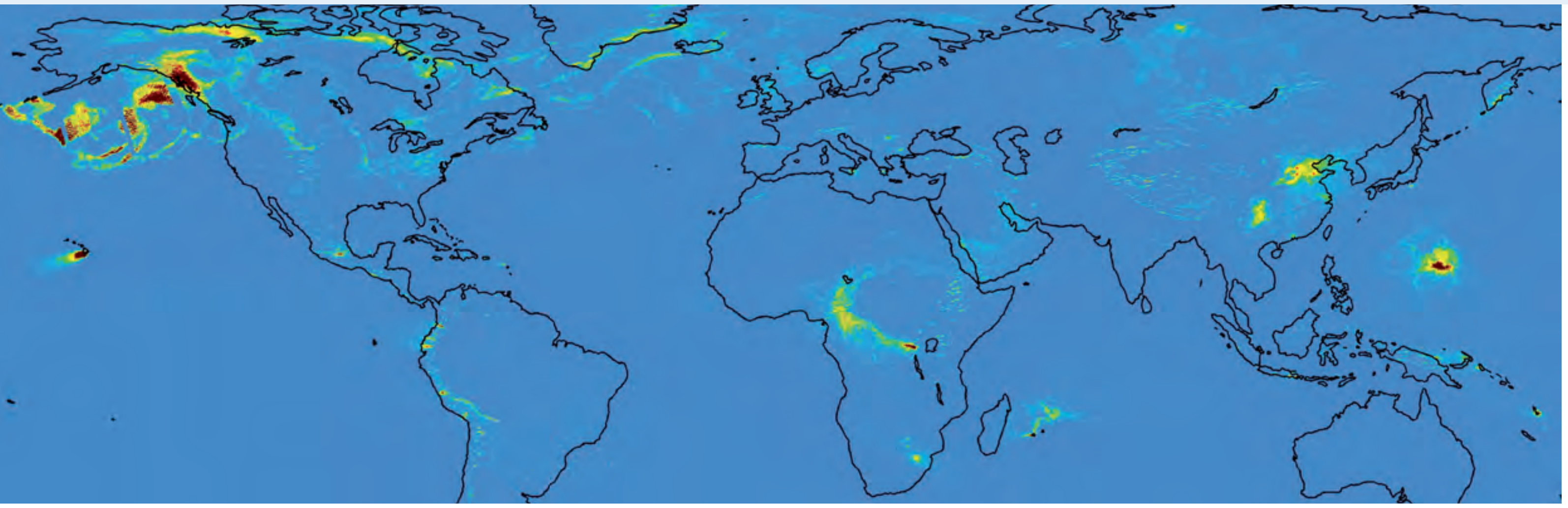


Figure 1: Composition of monthly averaged SO_2 vertical column densities as seen by the OMI satellite instrument. Besides anthropogenic and passively degassing volcanic sources, the picture shows volcanic plumes during major eruptions of Anatahan (2005), Nyamuragira (2006), Piton de la Fournaise (2007) and Kasatochi (2008).

The research activities of the Satellite Remote Sensing Group focus on the exploitation of the spectral information from UV/vis satellite instruments like GOME on ERS-2, SCIAMACHY on ENVISAT, OMI on AURA, and GOME-2 (A & B) on METOP. Besides trace gases, clouds, aerosols, and surface properties are also studied in our group.

One particular strength of satellite observations is that they yield information on the spatio-temporal variation of atmospheric constituents and thus allow us to identify and quantify natural and anthropogenic emission sources. From the observed downwind evolution of pollution plumes information on emissions and atmospheric conversion processes can be derived (see case study below). We also compare the satellite results with those from atmospheric models to test and improve our knowledge of the Earth System on a global scale.

Sulfur dioxide (SO_2) plays an important role in the earth’s climate, as it is an important precursor of aerosols, which affect the planet’s radiative budget both directly and indirectly. Volcanoes are a large natural source of SO_2 (Figure 2) with high temporal and spatial fluctuations, and still highly uncertain total emissions. Consequently, the impact of volcanic emissions on aerosol radiative forcing is one important uncertainty in climate models.

We developed a method for the simultaneous determination of SO_2 emissions and lifetime for the Kīlauea volcano (Hawai‘i) based on GOME-2 satellite measurements (Beirle et al., 2014). In addition we considered observations of the aerosol optical depth (AOD) from the MODIS instrument. The continuous emissions of the Kīlauea volcano, together with the steady trade winds, constitute an ideal ‘natural laboratory’ for the quantitative study of SO_2 emissions and subsequent oxidation to sulfate aerosols based on satellite observations. Clearly defined downwind plumes of SO_2 and aerosols are visible in the monthly averaged maps (Figure 2), but for both quantities important differences are also found: The spatial extent of the aerosol plume is much larger than that of the SO_2 plume, and the maximum AOD is found 2000 km downwind of the volcano. These findings indicate different time scales for decay and that the aerosols are not directly emitted from the volcano, but are subsequently formed from the primarily emitted SO_2. We use the satellite observations together with wind fields derived from the European Centre for Medium-Range Weather Forecasts (ECMWF) to estimate the emissions and atmospheric lifetimes of SO_2 and aerosols. Our method consists of three steps: First, the SO_2 vertical column density is integrated and the AOD is averaged over the latitude range, over which the respective plumes are distributed. Second, the average wind speed at the altitude range of the volcanic plume is determined (between 1.5 and 2.5 km, see Beirle et al., 2014). This wind speed is used to convert the spatial dependencies of the satellite observations into the corresponding time dependencies (see upper left part in Figure 2).

Finally, specific model functions are fitted to these time dependencies. For SO_2 the model function simply consists of an exponential decay with subsequent smoothing, which accounts for the spatial extension of the satellite ground pixels. The model function for the aerosols includes an additional production term, which is assumed to be proportional to the simultaneous loss of SO_2. Both model functions are individually fitted to the monthly averaged satellite data and yield both the respective total emissions and lifetimes. For SO_2 lifetimes between 1 and 2 days and for the aerosols lifetimes between 2 and 6 days are determined. The volcanic SO_2 emission rates are 9–21 kt per day, which is about 3 times higher than initially reported from ground-based monitoring systems. The aerosol production rate is determined relative to the oxidation of SO_2. For typical atmospheric sulfate aerosols, the observed temporal evolution of the AOD corresponds to a production of $3 \cdot 10^{-8}$ aerosol particles per SO_2 molecule. We have also used a similar method previously to determine emissions and conversion of NO_x from megacities. One particular advantage of our results is that they are fully independent of model simulations. Thus they are well suited for the testing of chemical conversion schemes in atmospheric models.

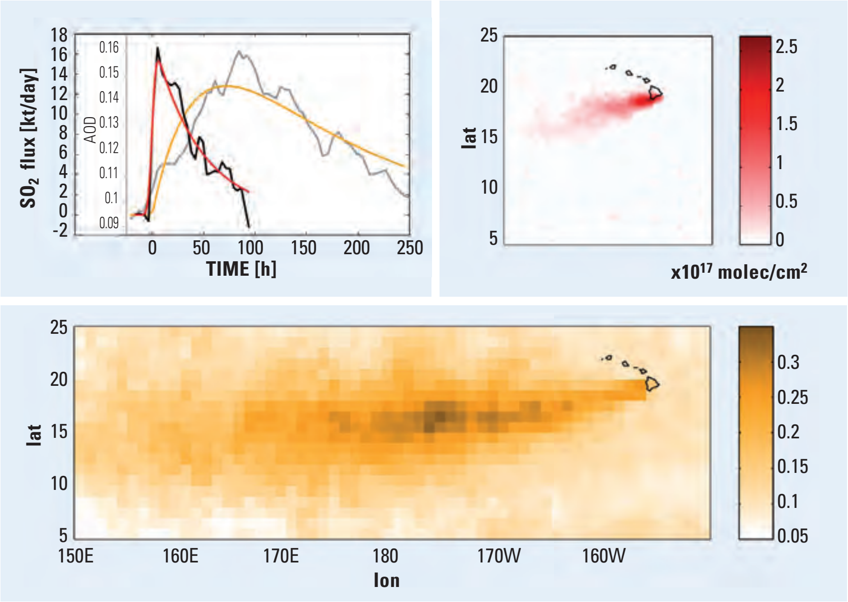


Figure 2: Top left: Temporal evolution of line densities of SO_2 (black: measured; red: fitted) and averaged AOD (grey: measured; orange: fitted); Top right: Monthly mean distribution of the SO_2 VCD; Bottom: Monthly mean distribution of the AOD (all results for August 2008).

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We acknowledge the free use of tropospheric MODIS AOD data from NASA/GSFC, MODIS Rapid Response, http://aeronet.gsfc.nasa.gov/cgi-bin/bamgomas_interactive. We thank the European Centre for Medium-Range Weather Forecasts for providing wind fields.

CENTRAL SERVICES

CENTRAL SERVICES

Administration, Instrument Development and Electronics, Information Technology, Workshops and Communications

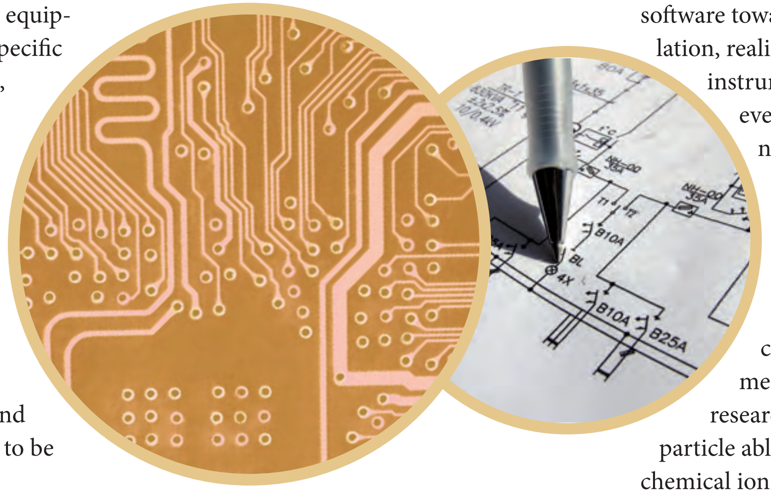
THE SCIENTIFIC WORK OF THE INSTITUTE IS SUPPORTED BY CENTRAL SERVICES:

The central services assist the scientific research departments and groups in practical matters such as administration, instrument development and electronics, information technologies (IT), mechanical workshops, and communications.

ADMINISTRATION

The Institute's administration is responsible for the overall economic, legal and organizational support of the research at the Max Planck Institute for Chemistry. This involves the personnel administration of approximately 300 employees, implementation and monitoring of procurement policies, the administrative execution of projects and third party funding, bookkeeping and accounting of the Institute's budget and accounting of travel expenses. In addition, it also includes the coordination of the graduate schools. Consequently, the administration is divided into the areas Human Resources, Purchasing, Accounting, and Graduate Schools. Affiliated to 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 is maintaining contact with those institutions and is collaborating through this network on a managing level to keep in touch with current science policy and general developments in science management.

INSTRUMENT DEVELOPMENT AND ELECTRONICS



Commercially available equipment rarely meets the specific needs of scientific work, especially for field measurements. To keep an instrument's local environment parameterscontrolled despite changing ambient conditions, sophisticated additional hardware for temperature, pressure and humidity control needs to be implemented.

Professional CAD software, the latest software development environments, and unique infrastructure like 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 continuously from development and manufacturing of electronic components, process controllers and system-to-application level software towards the full design, simulation, realization and verification of instrumentation subsystems and even complete instruments not available commercially, worldwide field campaign support included.

The latest projects realized include the setup of very compact airborne instruments deployed on the HALO research aircraft, namely a single particle ablation mass spectrometer, chemical ionization mass spectrometers, a fast gas chromatograph – mass spectrometer system and an aerosol measurement package comprised of a double column cloud condensation nuclei counter, a soot particle instrument and a completely, from scratch, newly designed multi impactor aerosol sampler.

INFORMATION TECHNOLOGIES (IT)

The IT Group provides the Institute's central information technology needs, data processing systems and ensures smooth operation of the servers, PCs and the network. Five staff members currently provide support to some 300 users, approximately 400 clients and network devices, about 30 servers and the operating systems Windows, Linux, Mac OS, Solaris 10 and Windows Server 2008 R2.

A network based on fiber optic and copper wiring ensures that data is available throughout the Institute. Both the backbone and Internet connection are designed redundantly and provide a data throughput of up to 10GbE, allowing for rapid data exchange with other research facilities. With its comprehensive WLAN, the Institute is also part of Eduroam (Education Roaming), allowing guests to easily access the Internet.

The Institute's application servers are virtualized using VMware. Several high performance host servers provide the stability our services need. In addition to the central IT services, several of the scientific working groups' application servers are virtually operated here.

A centralized software distribution supports MPIC employees in installing software and maintaining their computers. It also ensures automatic installation of security updates. Currently 135 devices are supported, with a rising trend.

Since 2013 the IT group has been supporting research at very remote locations such as in the middle of the Amazon rainforest near Manaus, Brazil. The Amazonian Tall Tower Observatory, ATTO, requires a stabile internet connection to ensure large and automated data transfer from the ATTO site to Germany and vice versa. For safety reasons and support, a satellite phone connection was established to enable fast exchange of information. Other tasks on the site included setting up a local network between the ATTO camp and the measurement towers and providing large data storage facilities for daily data transfer.

MECHANICAL WORKSHOPS

Many of the measurement devices needed for the Institute's research are not commercially available. Therefore, they must be produced by the Institute, requiring a well equipped workshop and highly qualified staff. In the workshop for fine mechanics, new and highly precise instruments are designed and built in co-operation with scientists. These instruments have to comply with stringent requirements, for usage on board of satellites, aircraft or ships. The workshop staff performs a wide range of operations, such as welding of high quality materials, bracing of special metals, and electroplating.

The Institute has been training apprentices since 1949. The training of mechanics is currently part of the mechanical workshop. The apprentices not only craft practice pieces, they also carry out practical machining tasks for the scientific departments. In addition, the apprentices are specially trained in CNC-techniques, pneumatics/hydraulic systems and welding technology, partly in inter-institutional courses. The apprentices have been highly successful in competitions and during their certification exams resulting in several prize winners at regional, state and federal level contests.

The electronics technicians, who train for their qualification in the electronics group, are provided with a basic education in metal techniques as well.

COMMUNICATIONS

Does the term 'Max Planck' mean anything to you? Are you familiar with a Max Planck Institute? What kind of employer would this kind of Institute be? In October 2013, these and other questions were posed to random shoppers in Mainz. The results were surprising: even if most of the 33 respondents weren't sure of the research focus of "the" Max Planck Institute in Mainz, or whether there were two such institutions, they nevertheless had a general positive impression. The associations ranged from 'innovative' and 'exciting' to 'important' and 'excellent.' It was clear that most of those interviewed couldn't clearly differentiate whether the Max Planck Institute was focused on applied or basic research. Even so, 90% answered positively to the question of what they would think if an acquaintance or relative were offered a job at a Max Planck Institute. Financing through public funds was also viewed as unproblematic.

The survey was intended to examine the existing image of the "Max Planck" brand, and where more public relations work might be useful. As the Institute is an active member of the "Mainzer Wissenschaftsallianz,“ an alliance of research institutes, universities, museums and researching companies, the Institute participated in the annual science market (Mainzer Wissenschaftsmarkt). Additionally, it hosted several visitor groups including school children, such as the nationwide Girls' Day which aims at motivating girls to enter natural science and technical professions.

In 2012 the three Max Planck Institutes involved in the Earth System Research Partnership participated in an interactive exhibition on the floating science center on board the ship "MS Wissenschaft" (Motor Ship Science) with an exhibit on the climate towers ZOTTO and ATTO. About 30 cities are visited each year, with the target group being primarily school classes.

From 2012 until today the Institute has published 36 press releases, often in close cooperation with the MPG central press department and with other institutions. These have resulted in numerous articles and reports in national and international newspapers, magazines, radio and television shows.

Communications highlights were the celebration of the 100th anniversary of the Institute in 2012 including a history of science colloquium, an historical exhibition, an open house day, and an anniversary publication and the the Anthropocene Symposium in 2013.

However, besides external audiences such journalists or, as in this case, inhabitants of Mainz, the Institute's employees are an important target group which needs to be addressed with specific communications measures. To cope with the need for information and exchange we have developed a quarterly newsletter and a new intranet including interactive functionalities. New employees are offered a newcomer event including a guided tour of the Institute and its facilities on a regular basis.

Organizationally the communications group comprises public relations, internal communications, support for scientific guests, the graphics office and the library.

GLOSSARY

ABA	Abscisic Acid
ACRIDICON-CHUVA	Aerosol, Cloud, Precipitation, and Radiation Interactions and Dynamics of Convective Cloud Systems; Chuva is Portuguese word for rain
AERONET	AErosol RObotic NETwork
AOD	Aerosol Optical Depth
ALABAMA	Airborne Laser ABlation Aerosol MAss Spectrometer
AOGCM	Atmosphere-Ocean General Circulation Model
ATHAM	Active Tracer High Resolution Atmospheric Model
ATTO	Amazonian Tall Tower Observatory
BC	Black Carbon
Beachon-RoMBAS	Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H_2O, Organics & Nitrogen – Rocky Mountain Biogenic Aerosol Study
BESSY	Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung
CAABA	Chemistry As A Box Model Application
CARIBIC	Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container
CBD	UN Convention on Biological Diversity
CCN	Cloud Condensation Nuclei
CI	Criegee Intermediates
CLRTAP	UNECE Convention on Long-Range Transboundary Air Pollution
COS	Carbonyl Sulfide
CPC	Condensation Particle Counter
C-ToF-AMS	Compact Time-of-Flight Aerosol Mass Spectrometer
DDT	Dichlorodiphenyltrichloroethane
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
ECMWF	European Centre for Medium-Range Weather Forecasts
EMAC model	The ECHAM/MESSy Atmospheric Chemistry model
Envisat	Environmental Satellite
EPR	Electron Paramagnetic Resonance
ERICA	ERC Instrument for Chemical Composition of Aerosols
ERS-2	European Remote Sensing Satellite 2
EURYI	European Young Investigator Award
FIB	Focused Ion Beam
FP	Framework Program
GC-MS	Gas Chromatography – Mass Spectrometry
GEOROC	GEOchemistry of Rocks of the Oceans and Continents
GFMC	Global Fire Monitoring Centre
GMXe Submodel	Global Modal-Aerosol Extension
GOME	Global Ozone Monitoring Experiment
GPP	Gross Primary Productivity
GWDG	Gesellschaft für Wissenschaftliche Datenverarbeitung Göttingen (Organization for Scientific Data Processing)
HALO Aircraft	High-Altitude Long Range Aircraft
HALOHOLO	Holographic Imaging Probe for Aircraft Application
HAMOCC5	HAMburg Ocean Carbon Cycle Model 5
HCHO	Formaldehyde
HCCT-2010	Hill-Cap Cloud Thuringia 2010
HNLC	High Nutrient Low Chlorophyll
HONO	Nitrous Acid
HPLC	High-Pressure Liquid Chromatography
IN	Ice Nuclei
INM	Ice Nucleating Macromolecules
INP	Ice Nucleating Particles
INPE	Brazilian National Institute for Space Research, Sao José dos Campos
IPA	Institute for Physics of the Atmosphere
ISPE	Interstellar Preliminary Examination
KM-GAP	Kinetic Multilayer Model for Gas-Particle Interactions
KWG	Kaiser Wilhelm-Gesellschaft (Kaiser Wilhelm Society)
MAVERT	Mainz Vertical Wind Tunnel
MESSy	Modular Earth Submodel System
METOP	Meteorological Operational Satellite
MoLa	Mobile Laboratory for Atmospheric Research
MODIS	Moderate Resolution Imaging Spectroradiometer
MPG	Max-Planck-Gesellschaft (Max Planck Society)
MPIC	Max Planck Institute for Chemistry
MPI-MCTM	MPI-Multicompartment Chemistry Transport Model
MXL	Mixed Layer Model
NAMIP	Nano and Microparticle Research Group
NanoCCNC	Nano-Cloud Condensation Nuclei Counter
NanoSIMS	Nano-scale Secondary-Ion Mass Spectrometry
NBS 28	National Bureau of Standards Reference Material 28, Quartz Sand
NIOZ	Royal Netherlands Institute for Sea Research
NO_x	Nitrogen Oxides (NO, NO_2)
OH	Hydroxyl Radical
HO_x	Hydrogen Oxide Radicals (OH, HO_2)
OMI on AURA	Ozone Monitoring Instrument on Aura (NASA atmospheric chemistry mission)
ORCAS	Origin, Fate and Impact of Biospheric Climate-relevant Trace Gases During Global Change
ORSUM	Organic Reactive Species Understanding and Measurement
PBAP	Primary Biological Aerosol Particles
PCB	Polychlorinated Biphenyl
PN (PAN)	Peroxy(acetyl) Nitrate
PRR	Pattern Recognition Receptors
PSC	Polar Stratospheric Clouds
PTR-MS	Proton Transfer Reaction Mass Spectrometry
PTR-TOF-MS	Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry
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
RNS	Reactive Nitrogen Species
ROI	Reactive Oxygen Intermediates
ROOH	Organic Peroxides
ROS	Reactive Oxygen Species
SCIAMACHY	SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY
SEM/EDX	Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy
SOA	Secondary Organic Aerosol
SPLAT	Single Particle Laser Ablation Mass Spectrometer
SS-CPC	Scanning Supersaturation Condensation Particle Counter
STXM-NEXAFS	Scanning Transmission X-Ray Microscopy with Near Edge X-Ray Absorption Fine Structure
SWC	Soil Water Content
TEM	Transmission Electron Microscopy
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
VOCs	Volatile Organic Compounds
WIBS	Wideband Integrated Bioaerosol Spectrometer
WRF Chem	Weather Research, Forecast and Chemistry
ZOTTO	Zotino Tall Tower Observatory
200 nm-fs-LA-MC-ICP-MS	200 Nanometer Femtosecond Laser Ablation Multi Collector Inductively Coupled Plasma Mass Spectrometry

STAFF AND BUDGET

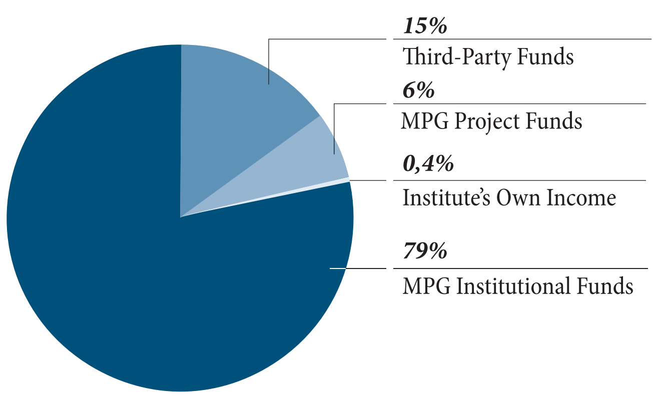
In early 2014, a total of about 300 persons were employed at the Institute, among them 77 scientists, 122 junior scientists, 3 scientific guests and 11 apprentices; 228 staff members were paid from institutional funds and 38 scientists were paid from third-party project funding.

The annual budget of the Institute is approximately € 20 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.

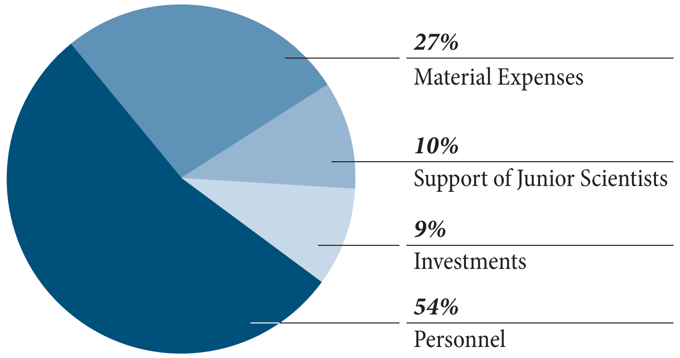
REVENUES 2013

Percentage distribution excluding construction activities.



EXPENDITURES 2013

Percentage distribution excluding construction activities.



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All others if not stated separately: authors of the article.

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For up-to-date information please see
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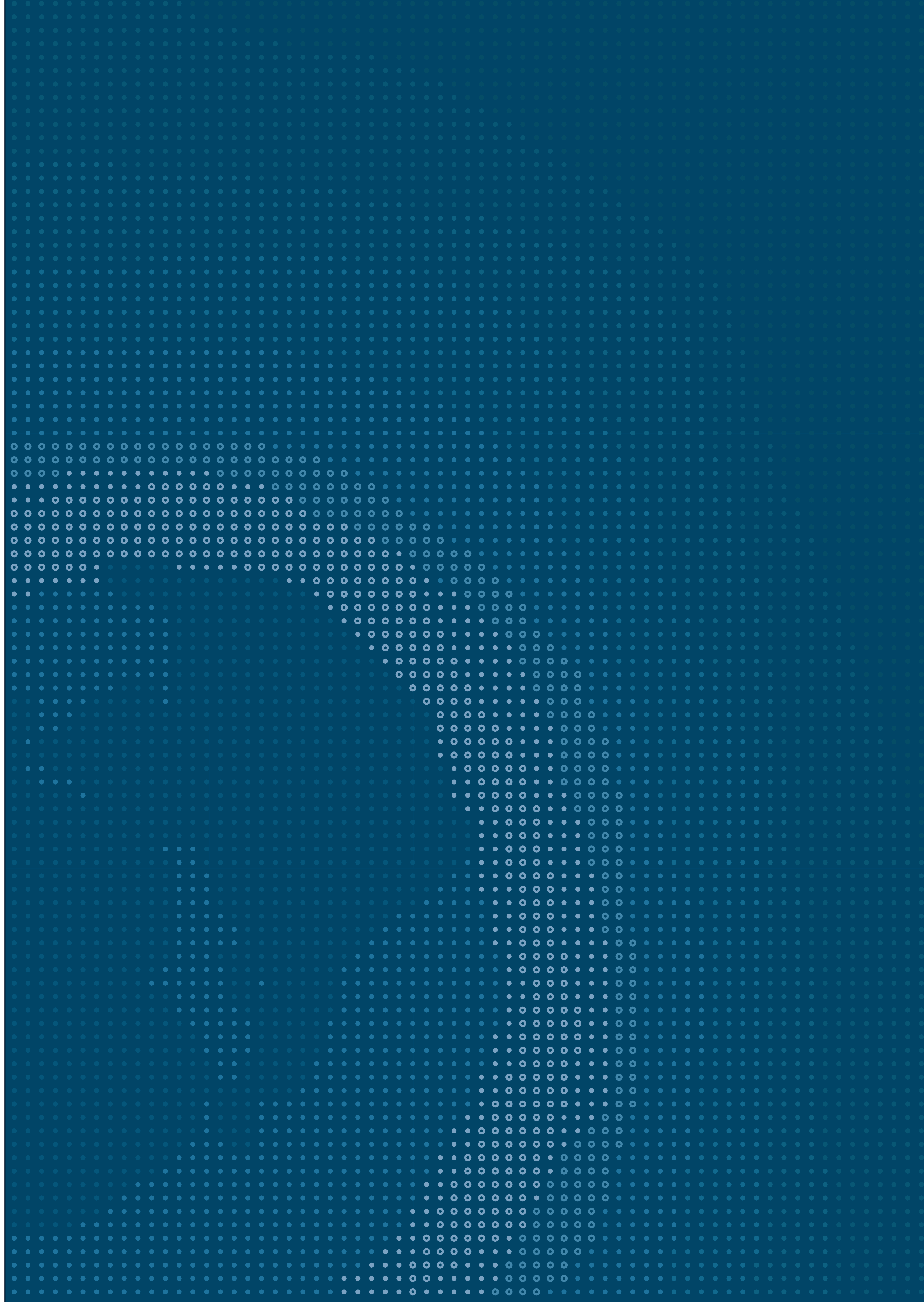

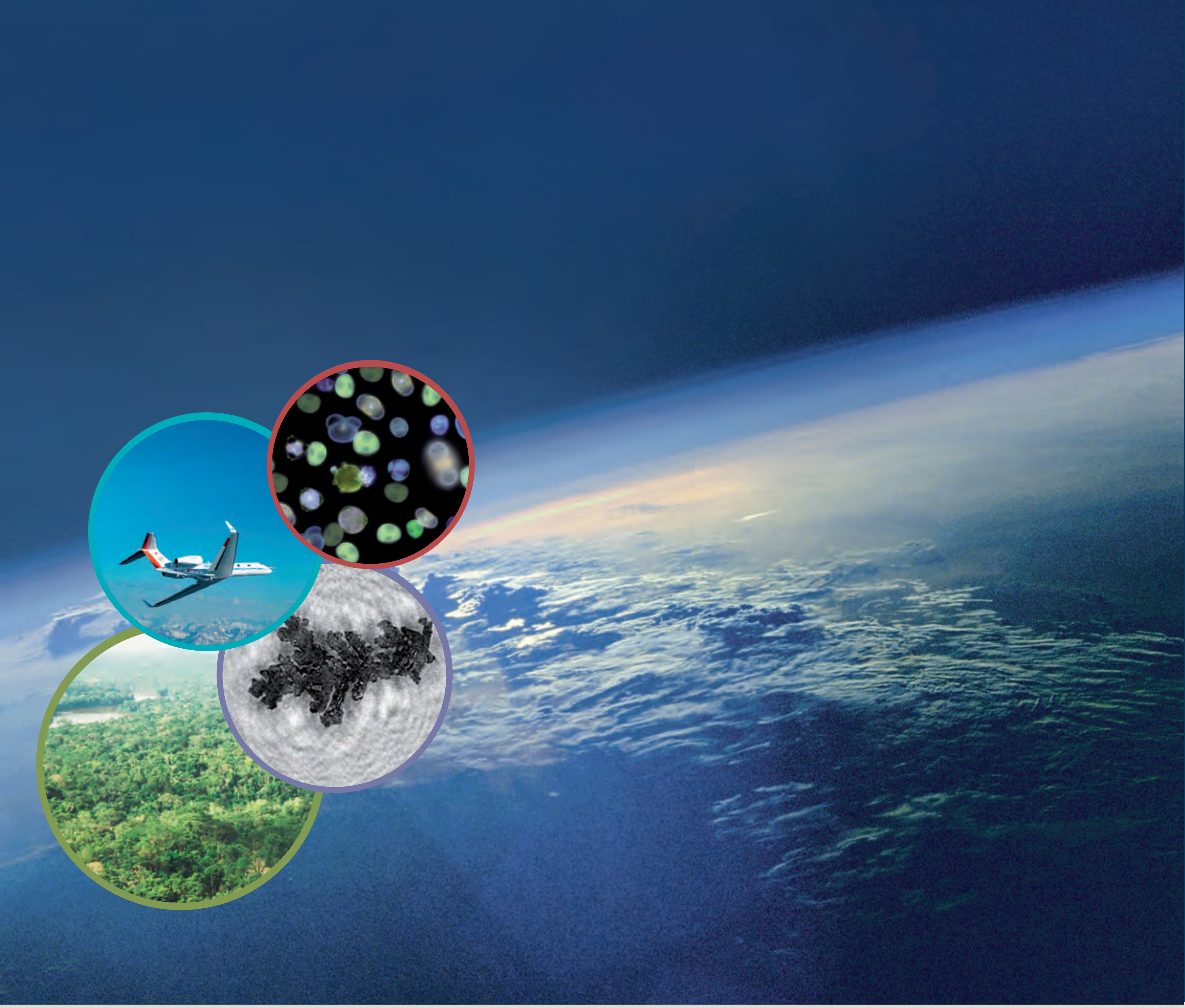

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