

SCIENTIFIC REPORT 2009-2011



MAX-PLANCK-GESELLSCHAFT

	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
• • • • • • • • • • • • • • • • • • •	
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	000000000000000000000000000000000000000
000000000000000000	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	000000000000000000000000000000000000000
	• • • • • • • • • • • • • • • • • • •



FOR CHEMISTRY

Atmospheric Chemistry · Biogeochemistry · Particle Chemistry

SCIENTIFIC REPORT

2009-2011



CONTENT

6 GENERAL INFORMATION

- 7 Organization and governance
- 9 Publication impact of the institute
- 10 History of the institute
- 11 Location and buildings
- 12 Research and education
- 14 Major collaborations

16 DEPARTMENT OF ATMOSPHERIC CHEMISTRY

- 18 Stability of the atmospheric oxidation capacity (J. Lelieveld)
- 20 Global atmospheric measurements by a flying observatory (C. Brenninkmeijer)
- 22 Photochemistry and kinetics in the laboratory and in the field (J. N. Crowley)
- 24 Chemical processes related to ozone production in remote areas (H. Fischer)
- 26 Model studies of the chemistry and physics of the atmosphere (M. Lawrence, H. Tost)
- 28 Organic reactive species: understanding and measurements (J. Williams)
- 30 Radical measurements (H. Harder)

32 DEPARTMENT OF BIOGEOCHEMISTRY

- 34 Searching for the world before the anthropocene (*M. O. Andreae*)
- 36 Ecophysiology and trace gas exchange of the Amazonian rainforest (J. Kesselmeier)
- 38 Vegetation fire emissions, human health, and human security (J. G. Goldammer)
- 40 Multiscale trace gas flux measurement methodologies for semiarid, arid, and hyperarid ecosystems (F. X. Meixner)
- 42 The role of biogenic aerosols and multiphase chemistry in the earth system and in public health (U. Pöschl)
- 44 GEOROC and GEOREM databases (B. Sarbas)
- Ostracod shells in lake sediments from Tibet as paleo-46 environmental archives of past climate (K. Jochum)

- 48 Stable isotopes in the modern oceans (S. Galer)
- 50 Cosmogenic noble gas isotopes in earth and space sciences (U. Ott)
- 52 Mantle geochemistry (A. V. Sobolev)
- 54 High pressure chemistry and physics (M. L. Eremets)

56 DEPARTMENT OF PARTICLE CHEMISTRY

- 58 Wind tunnel investigations of collection kernels during riming and graupel formation (S. Mitra, M. Szakáll)
- 60 Development and field deployment of a mobile laboratory for studies of urban pollution and emission sources (F. Drewnick)
- 62 Aircraft-based aerosol composition measurements in the middle and lower troposphere (J. Schneider)
- 64 Impact of aircraft emissions on the tropopause region - AEROTROP (C. Voigt)
- 66 In situ studies of aerosols and polar stratospheric clouds in the Arctic upper troposphere/lower stratosphere (R. Weigel)
- 68 Sources of submicron aerosol in the tropical upper troposphere (S. Borrmann)
- 70 Stardust in the laboratory (*P. Hoppe*)

72 INDEPENDENT RESEARCH GROUPS AND **JUNIOR RESEARCH GROUPS**

- 74 Satellite remote sensing (T. Wagner)
- 76 Surface-atmosphere exchange of reactive nitrogen compounds (I. Trebs)
- 78 Nonmicrobial methane formation in the biosphere (F. Keppler)
- 80 Theoretical analysis of oxidation mechanisms, reaction rates, and products (L. Vereecken)

82 CENTRAL SERVICES

- 86 Staff and Budget
- 87 Contact data and imprint

PREFACE

The year 2012 is a very special year for our institute. On October 23rd, we will celebrate the 100th anniversary since the opening of the Kaiser Wilhelm Institute for Chemistry, our predecessor. But before looking back on a long and successful research history we celebrated another highlight. The institute moved into a new building that wholly meets the needs of modern research. The new building is unique in that it houses all departments, research groups and central services under one roof, thus facilitating interactions between staff and reinforcing team spirit.

Nevertheless, moving also has meant leaving behind the old and familiar. Some pieces of equipment or furniture may remind us of the good old days. But science does not conserve, it is a constant search invoking change and progress. The 19th century chemist Justus von Liebig stated that science starts to become interesting where it ends. But where does science end? Every elucidated question typically generates new ones. It is hoped and expected that the new environment will inspire creative questions.

In planning for the future development of the institute foresight is needed. Modern research in the area of Earth system chemistry is highly competitive – among other reasons – because the massive human influence on the Earth system, including global air pollution and climate change, has led

to the launch of numerous excellent research programs worldwide. However, the topics are often very application-oriented, whereas the goal of the Max Planck Institute for Chemistry is to supply the basic knowledge and methods needed for these applications, in support of the sustainable use of natural resources and environmental protection.

This research agenda was developed and implemented in the 1970s, when the chemistry of the Earth, its atmosphere and its planetary environment became a central theme. The institute plans to continue along this avenue, in accord with the joint strategy of the Earth System Research Partnership (ESRP) with the Max Planck Institutes for Meteorology (Hamburg) and Biogeochemistry (Jena). Our institute plans to increase the emphasis on studies of atmospheric aerosol particles and their interactions with gas-phase chemistry and cloud processes in a new department of Multiphase Chemistry.

board.

() hunded

Ianuary 2012

4 5

We hope you will enjoy reading this brochure, which includes sections on our current research and on what is programmed for the future. It focuses on the last three years, the period over which our research is to be evaluated by the internationally renowned experts of the institute's advisory

Jos Lelieveld (Managing Director)

GENERAL INFORMATION

00

00

00

0000

0000

000

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.

ORGANIZATION AND GOVERNANCE

The Max Planck Institute for Chemistry (MPIC) explores the Earth and its environment on a range of scales, from ecosystems to the solar system, and from nanoparticles to supernovae. It conducts field studies of natural phenomena as well as laboratory analyses and experiments under controlled conditions, and system interactions and feedback mechanisms are simulated through computer modeling.

At present the institute consists of three departments, two independent research groups and two junior research groups. Each of the departments is supervised by a director, who, as a scientific member of the Max Planck Society, has sole responsibility for the field of research. The directors decide jointly on the institute 's development and elect a managing director out of their circle every three years. Since 1 January 2010, this position has been held by Jos Lelieveld.

THE ATMOSPHERIC CHEMISTRY

DEPARTMENT (*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 DEPART-

MENT (*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 soilvegetation 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 PARTICLE CHEMISTRY DEPART-

MENT (Stephan Borrmann) has been established jointly by the MPIC and the University of Mainz. Its research focuses on the composition and physical properties of micro- and nanoparticles as well as cloud hydrometeors in the Earth's environment, and on interactions between aerosols and clouds. Methodologies include aerosol particle mass spectrometry in field measurements on mobile plattforms and laboratory experiments using a vertical wind tunnel facility. 6 **_ 7**

Until recently, the MPIC also included the departments of Cosmochemistry and Geochemistry. These departments have been reduced to single groups after the retirement of the directors (Günter Lugmair and Albrecht Hofmann) and have been successfully integrated into the departments of Particle Chemistry and Biogeochemistry, respectively.

The Max Planck Institute for Chemistry 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.

ORGANIZATION AND GOVERNANCE

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.

MARIA CRISTINA FACCHINI, Institute for Atmospheric and Climate Science, Italian National Research Council, Bologna, Italy

THORSTEN HOFFMANN, Institute for Anorganic and Analytic Chemistry, Johannes Gutenberg University, Mainz, Germany

ZEV LEVIN, Department of Geophysics and Planetary Sciences, University of Tel Aviv, Ramat Aviv, Israel

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

MARY SCHOLES, Animal, Plant and Environmental Sciences, University of the Witswaterrand, Johannesburg, South Africa

ORGANIZATION CHART

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

GEOROC database

Mantle Geochemistry

B. Sarbas

A. Sobolev

ATMOSPHERIC CHEMISTRY J. Lelieveld	BIOGEOCHEMISTRY M. O. Andreae	PARTICLE CHEMISTRY S. Borrmann	FURTHER RESEARCH GROUPS	CENTRAL SERVICES	
Global Atmospheric Observations	High Pressure Che- mistry and Physics	Instrumental Aerosol Analytics	ORCAS F. Keppler	Press and Public Relations S. Benner	
Kinetics and Photochemistry	Isotope Biogeochemistry S. Galer	Aerosol and Cloud Chemistry	Reactive Nitrogen Species I. Trebs	Electronics F. Helleis	
J. Crowley	Fire Ecology I. Goldammer	J. Schneider	AnnoceCentral Serv.Semivolatile OrganicAdministratiCompoundsU. MüllerG. Lammel- Internation	Central Services Administration II Müller	
H. Fischer	Paleoclimate Research K. Jochum Plant Physiology J. Kesselmeier Micrometeorology and Flux Measurement Methodology F. X. Meixner	Micro-Particle Research		- International Max	
Radical Measurements H. Harder		Plant Physiology Atmospherical	Atmospherical	Theoretical Atmospheric Chemistry	Planck Research School (IMPRS)
Atmospheric Modelling N.N.		Hydrometeors S. Mitra, M. Szakáll	L. Vereecken Satellite Research T. Wagner	E. Uherek - Workshops R. Wittkowski - Administration U. Müller - IT T. Disper	
Organic Reactive Species J. Williams		Aerosol and Cloud Physics Group R. Weigel (University Mainz)			
	Cosmochemistry U. Ott				
	Aerosol Research U. Pöschl				

The institute's research, as science in general, is covered well by the citation indexes accessible under the Web of Science (WoS) by Thomson Reuters. Between 2000 and October 2011 about 2,500 papers have been published with at least one author assigned to the address of the Max Planck Institute for Chemistry in Mainz giving an average rate of more than 200 papers per year. Many studies have shown that citation counts and research performance assessed by peers highly correlate, 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 strengths and weaknesses of a research institute. Since 2000 the institute's papers received altogether more than 52,000 citations with an average of 21 citations per paper.

INSTITUTE'S AVERAGE CITATION RATE VERSUS WORLD AVERAGE

The world average for the time period 2001–2011 is 11.1 citations per paper for chemistry, 8.6 citations per paper for physics, and 9.5 citations per paper for the geosciences. The MPIC papers published within that same time period were cited 19.8 times on average. The impact of the institute's papers is thus about twice that of the world average, a good performance in view of citation statistics.

is the former director Paul Crutzen. The institute has two further members in the top twelve – better than any other institution worldwide; and four other members are recognized as "highly cited."



Annual number of MPIC papers published in the time period 2000-2011 within the source journals covered by the Web of Science (WoS). The number of papers published in these journals has become a standard measure for scientific output (productivity). Note that the publication year 2011 (light blue) is not yet complete (Search Oct. 10, 2011).

PUBLICATION IMPACT OF THE INSTITUTE

8**9**

The most cited geoscientist worldwide

Beside its publications, the MPIC also (co)founded four scientific open access journals which are:

2001: Atmospheric Chemistry and Physics (ACP), U. Pöschl et al.

2004: Biogeosciences (BG), J. Kesselmeier et al.

2008: Atmospheric Measurement Techniques (AMT), T. Wagner et al.

2008: Geoscientific Model Development (GMD), R. Sander et al.



Figure 3, 4: Lise Meitner and Otto Hahn in laboratory in the KWI for Chemistry in 1913 (left). The physicist Josef Mattauch in his laboratory in the 1950ies (right).



Figure 1, 2: The Kaiser Wilhelm Institute for Chemistry in Berlin in 1912 (left). The laboratory of R. Willstätter in 1913 with Richard Willstätter in the center (right).



Figure 1–4: Views of the new institute's buidling. The restored high voltage cascade generator (upper right).



HISTORY OF THE INSTITUTE

Research at the Max Planck Institute for Chemistry has been at the forefront of science throughout its centennial existence. Three of its directors were awarded the Nobel Prize, Richard Willstätter in 1915, Otto Hahn in 1944 and Paul Crutzen in 1995. But it is also a history of change. What began in 1912 with studies on plant pigments in the Kaiser Wilhelm Institute for Chemistry in Berlin was followed by the discovery of nuclear fission by Otto Hahn, Lise Meitner and Fritz Strassmann in 1938.

Towards the end of World War II, scientific work in Berlin was no longer possible as the institute was severely damaged. Tailfingen in today's Baden-Wuerttemberg on the other hand was far from the bombing raids and with its numerous textile factory buildings offered the infrastructure for laboratories under the lead of Otto Hahn. The chemists worked from 1944 to 1949 in the Swabian Alps until the institute moved to its final location on 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 bears the name "Otto Hahn Institute" in honor of its previous director and the first president of the Max Planck Society.

After its restart in Mainz, the range of scientific topics became significantly broader: In the late 1960s Nuclear Physics and mass spectrometry were complemented with the Departments of Air Chemistry, Cosmochemistry and Isotope Cosmology. Samples of the first recovered moon dust were brought to Mainz and studied in the laboratories of the converted military barracks. After the retirement of Hermann Wäffler, the Department of Nuclear Physics was closed in 1978. In the 1980s, the Nobel laureate Paul Crutzen established Atmospheric Chemistry as a research direction.

The research portfolio of the institute was also enhanced by the establishment of the departments for Geochemistry and Biogeochemistry in the years 1980 and 1987 respectively. Subsequent to the successful Mars missions, during which our spectrometers on board the NASA spacecraft were used to study various landing sites, the Cosmochemistry activities were reduced in the mid-2000s. Geochemistry was integrated into the department of Biogeochemistry in 2010. The Particle Chemistry department, founded in 2001, is the youngest of the institute, established jointly with the Institute for Atmospheric Physics at the Johannes Gutenberg University in Mainz.

Nowadays, the research focus of the Max Planck Institute for Chemistry, with nearly 270 staff, is on Earth system science and in particular the chemical processes occurring in the atmosphere and their interactions with oceans, soils and the biosphere. 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.

LOCATION AND BUILDINGS

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. Workshops, cafeterias and lecture halls will be used jointly and thus more efficiently. The new facility with approximately 8,700 square meters floor space houses all departments and service groups. It was designed and developed by Fritsch and Tschaidse Architects in Munich. The institute 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. Inspired by the institute's numerous research topics which range from inner Earth up to the atmosphere,

the building's exterior and the central garden court have different layers.

Two pieces of art complement both the interior and exterior of the new building. The creation "Why How What When Where" by Brigitte Kowanz symbolizes basic research questions. Her art encompasses the four main walls in the central foyers on all floors. In the garden to the west of the main building a high voltage cascade generator has been transformed into a sculpture. It was built and used by the institute in the 1950s to generate high voltages to produce radioactive samples, and is symbolic of the rich research history of the institute.

The overall building costs were 44 million Euros, and the construction time period was 24 months. Whereas for the past 60 years the institute was spread over six separate buildings, the new single building housing the whole institute will promote interdepartmental scientific cooperation.

10 **_ 11**



Figure 1, 2: Poster presentations at the IMPRS days in Heidelberg in 2009.

RESEARCH AND EDUCATION

RESEARCH AND EDUCATION

The institute is not an independent teaching institution. However, it is located on the campus of the University of Mainz, and through joint institutions and research projects and through teaching activities at the University it is part of university life. The Particle Chemistry department is a joint institution of the Max Planck Institute for Chemistry (MPIC) and the Institute for Physics of the Atmosphere of the University of Mainz, and the Satellite Remote Sensing group works in cooperation with the Institute of Environmental Physics of the University of Heidelberg.

GRADUATE SCHOOLS

An important part of the research carried out at the MPIC encompasses PhD dissertation projects. Our doctoral students have the opportunity to widen their horizons under the umbrella of several graduate programs. The International Max Planck Research School (IMPRS) for Atmospheric Chemistry and Physics was established in 2003 on the premises of the MPIC and after successful evaluation prolonged in 2009 for another period of six years. The IMPRS cooperates with scientifically related institutes at the partner Universities of Mainz, Frankfurt and Heidelberg. About 3–5 students are enrolled per year at each partner institute, and are supported by the IMPRS, partner institutes and externally funded projects. In recent years about 75 students were members of the IMPRS, nearly half of them being non-German.

The MPIC is also a partner in the Max Planck Graduate Center. The MPGC was founded in 2009 as a joint venture of the two Max Planck Institutes (Chemistry and Polymer Research) and four divisions of the University of Mainz, the department of Medicine, the department of Physics, Mathematics and Computer Science, the depart-



Figure 3: Poster presentations at the Autumn School in Cyprus in 2010.

International Max Planck Research School for Atmospheric Chemistry and Physics



Figure 4, 5: Visit of the Max Planck Institute for Astronomy in Heidelberg (left) and a course on scientific writing in 2011 (right).

ment of Chemistry, Pharmaceutics and Geosciences, and the department of Biology. Its PhD program focuses on interdisciplinary research topics, building bridges beyond traditional subjects and departments, ranging from Mathematics to Medicine. Like the IMPRS it aims to attract excellent PhD candidates from all over the world. To date nearly 50 PhD students have been admitted. Research under the umbrella of the MPGC includes diverse fields such as "Earth System Science" and "Soft Matter Materials." In the common lecture series the students are introduced to different topics ranging from atmospheric chemistry to the design of bio-molecules for drug delivery in cancer treatment.

The MPIC also cooperates closely with the Geocycles Research Center of the University of Mainz. "Geocycles" focuses on Earth System Sciences and the interplay of Earth processes with human cultures. A major fraction of its PhD students participate in the graduate program of the IMPRS, thus additionally strengthening cooperation. Regardless of their enrolment in the different programs, all doctoral students at the MPIC are active members of the IMPRS for Atmospheric Chemistry and Physics. The two pillars are: structured supervision and advanced education.

SUPERVISION: The students are guided by a PhD advisory committee (PAC), comprising at least 3 scientists with whom the students meet in regular intervals. During the PAC meetings the students present and discuss their scientific work and receive feedback from the senior scientists. Besides the meetings, the students report about their progress at the end of the first and second year. This regular evaluation of scientific progress helps to assure that the PhD project is completed within three (at maximum 3.5) years.

EDUCATION: The IMPRS educational program aims to strengthen the back-ground of the doctoral students in Earth sciences beyond the specialized focus of their research project. In a point based credit system, the students are encour-



12 **_ 13**

aged to attend lecture courses and summer schools offered by the University and the IMPRS, and to present their work at conferences. Furthermore, we offer the students a selection of soft skill courses to improve their presentation, writing and social talents and support students with longer absence times with E-learning options.

The IMPRS promotes the scientific and social exchange among all PhD students at our institute, often also mediating between students and group leaders. Annual events, including the IMPRS days (rotating between partner institutes) bring students closer together. Photo galleries and an extensive intranet portal provide information about who is who and how to get help. The IMPRS thus acts as a hub for exchange, support and team work.

The cooperation of the MPIC with the University's Institute for Physics of the Atmosphere is particularly strong as many students receive formal undergraduate and graduate education in Meteorology there.





MAJOR COLLABORATIONS

EARTH SYSTEM RESEARCH PARTNERSHIP

The study of global change with its many cycles and complex feedback mechanisms cuts across scientific disciplines. Understanding the processes behind global and climate change can only be achieved by looking at the Earth system as a whole. In 2006 therefore the following four institutes joined together to form the Earth System Research Partnership (ESRP):

- Max Planck Institute for Biogeochemistry in Jena
- Max Planck Institute for Chemistry in Mainz
- Max Planck Institute for Meteorology in Hamburg and
- Potsdam Institute for Climate Impact Research, i.e. the part of this institute that focuses on the role of humans in climate change, a subject not covered by the three Max Planck Institutes.

The coordinated research of the four institutes allows a broader and deeper understanding of the relationships between the different processes shaping the Earth system. The partnership investigates the system's organization, its material and energy fluxes, and feedback mechanisms. Focal issues range from geochemical cycles such as the water and the carbon cycle to the global change patterns of socioeconomic factors and induced impacts. Through field studies and laboratory analyses as well as model simulations, the ESRP creates long-term and large-scale data bases necessary for the study of the Earth system.

One of the main projects of ESRP is ENIGMA (Earth System Network of Integrated Modeling and Assessment). Major sub-projects of ENIGMA involve: i) Land use, biosphere and the Earth system; ii) Climate modules for economic optimization; iii) Aerosols and the water cycle; iv) Methane changes since pre-industrial times; v) Links between the nitrogen and carbon cycles; vi) Millennium climate simulation; vii) Atmospheric carbon dioxide in the Holocene. These sub-projects have been defined by participants from the different institutes, and progress is discussed in annual plenary meetings to which ESRP and external experts are invited. ENIGMA provides a spectrum of detailed coupled models of the Earth system and process models that can be coupled to each other on a modular basis. ENIGMA has resulted in several productive collaborations, including joint publications and summer schools for young scientists.

EARTH AND THE ANTHROPOCENE

By promoting top-class research under the Initiative for Excellence, the Federal Government is establishing internationally visible research clusters in Germany. The Max Planck Institute for Chemistry is a main partner in the Excellence Cluster of the University of Mainz. As part of the federally funded qualification initiative for universities, a proposal entitled "Earth and the Anthropocene" for this Excellence Cluster was developed and submitted, which evolved from the state-funded interdisciplinary research center "Geocycles," focusing on Earth System Research. The participating institutions are the University of Mainz, the University of Applied Sciences in Mainz, the Roman-Germanic Central Museum and the Max Planck Institute for Chemistry. Jos Lelieveld was deputy spokesperson for this cluster. The proposal has been admitted into the second round of review, of which the results will be announced in June 2012.

The Earth and the Anthropocene cluster is arranged in four research areas: i) Anthropocene Processes; ii) Paleoanthropocene; iii) The Earth before mankind and iv) Anthropocene Earth System Modeling. Topics covered by the Max Planck Institute for Chemistry are amongst others the exchange processes between land, biosphere and atmosphere and biogenic aerosol interactions. The title of the cluster has been chosen in honor of Paul Crutzen, who coined the term Anthropocene, now recognized as the youngest epoch in the geological timescale.

The cluster aims to quantify developments in the Anthropocene by comparing and contrasting natural element cycles and Earth processes with and without the effects of humans. Central questions include: To what extent does the anthropogenic acceleration of natural processes and cycles affect the functioning of the Earth system? Could tipping points be reached at which

14 **15**

dramatic changes in environmental or climatic conditions will be triggered? These questions will be addressed by investigating and quantifying the exchange rates of volatile compounds within and between the silicate Earth, atmosphere and biosphere, and emphasizing continental regions where shortterm changes and human traces are more pronounced than in the oceanic environment.

The effects of human interference will be studied by comparing processes in the Anthropocene with those in Earth's history, concentrating on the roles of a few key elements, such as carbon, hydrogen, oxygen and nitrogen, and molecules made up by them such as H₂O, CO₂, N₂, NH₃, CH₄, amino acids and nucleic acids. These critical elements control the habitability of the Earth from the climate system, through living environments to the operation of plate tectonics.

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 July 25, 1955 in The Hague. Study of natural sciences Leiden Univ. (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 Univ. (1990), Professor

JOS LELIEVELD

ARE LARGELY INITIATED BY HYDROXYL (OH) RADICALS, PRIMARY FORMATION AND THE RECYCLING OF OH CONTROL THE "SELF-CLEANING" CAPACITY OF THE ATMOSPHERE.

The chemistry of OH in the troposphere chased, but for most applications they is linked to that of ozone (O_3) . The troposphere is the relatively well-mixed lower ~10 km layer which contains about 80% of the atmospheric mass but only 10% of the O₃. Most O₃ is located above in the stratosphere and only a small fraction is transported downward, hence tropospheric O_3 is to a large extent governed by photochemical and transport processes within the troposphere.

The primary formation of OH is controlled by the solar ultraviolet radiation flux (i.e., the small fraction that passes through the stratospheric ozone layer), as well as the local O₃ and water vapor concentrations. Photodissociation of O_3 at ultraviolet wavelengths yields electronically excited O(1D) atoms, and a few percent of the $O(^{1}D)$ react with H₂O to form OH radicals. Tropospheric OH concentrations are therefore whereas field investigations focus on highest in the tropics, where the solar zenith angle is smallest, the ozone layer is thinnest, and the air humidity is highest. For this reason we perform measurements in the tropics, by ship or by aircraft (e.g., over the Amazon) and compare them to measurements at higher latitudes.

ATMOSPHERIC OXIDATION PROCESSES Our research focuses on photo-oxidation mechanisms in which OH and O₃ play a central role. We develop instrumentation to make sensitive measurements of trace gases, including highly reactive radicals that occur in minute amounts. Some instruments can be purmust be modified or we have to build them ourselves. Laser-optical, mass spectrometric and gas chromatographic techniques are used to determine the key reaction intermediates in the oxidation chains of hydrocarbons. For field measurements it is important to measure many compounds comprehensively, so that data analyses and model calculations can be numerically constrained. Currently, the adaptation and certification of instrumentation for the High Altitude – Long range (HALO) aircraft is a major effort.

We perform both laboratory and field measurements, and also use satellite observations (together with the group of Thomas Wagner) to encompass all relevant scales. The lab work focuses on gas-phase and heterogeneous chemistry kinetics, i.e., on the smallest scale, disentangling chemistry effects from those by transport and physical removal processes, such as dry deposition. Collaborations between experimentalists in the field and lab have proven to be highly valuable for advancing instrumentation, calibration techniques, and the analysis of measurements. The discov-

of Atmospheric Physics and Chemistry Univ. 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.

16 **17**

ery of new or poorly known compounds and reactions in the field can be readily investigated under controlled conditions in the laboratory. An example is the chemistry of isoprene, a compound released in vast amounts by tropical forests, in which thus far unnoticed OH recycling has been discovered, which helps in stabilizing the atmospheric oxidation capacity.

We also develop computer models to simulate the interactions of chemical and meteorological processes and the influences of atmospheric composition changes on climate. Our numerical schemes are applied consistently in chemical box, Lagrangian transport, column, regional and general circulation models, both by our group and many others internationally. Since the regional and global models are computationally demanding, we invest in "fast" chemistry schemes that are subjected to benchmark tests against the comprehensive schemes. As an example, version 3 of the Mainz Isoprene Mechafor application in chemistry-transport and climate models, subsequent to tests against a new Master Chemical Mechanism (MCM). Many thus far unknown reaction pathways have been included, partly tested in the laboratory and partly in collaboration with the Theoretical Chemistry group (Luc Vereecken). The models are indispensable tools in the analysis of field measurements.

STABILITY OF THE ATMOSPHERIC OXIDATION CAPACITY

JOS LELIEVELD



Figure 1: Measuring tower of the HUMPPA campaign in the boreal forest in Finland.

Billions of tons of natural and anthropogenic gases are emitted each year, and thus must be removed from the atmosphere. Oxidation reactions, initiated by OH radicals, convert most gases to products that are more easily removed by precipitation and dry deposition at the Earth's surface. This mechanism prevents the build-up of chemical compounds to levels that would cause hothouse – rather than greenhouse – temperatures or be toxic for life.

We perform field measurement campaigns once every 1–2 years in different locations to contrast distinct chemical regimes. For example, we measured polluted air downwind of India over the northern Indian Ocean, compared it with clean air over the southern Indian Ocean, and uncovered the rapidly increasing influence of emerging economies in the tropics. In the Mediterranean region we contrasted air influenced by long-distance transport from Europe, Asia, and North America.

In Spain we investigated how Atlantic air masses are influenced by forest, industry, and urban emissions, and also studied night-time oxidation processes. This was extended by a recent campaign in central Germany (north of Frankfurt), which can also be compared with measurements in a rural environment in southern Germany (Hohenpeissenberg). These ground-based campaigns were complemented with airborne measurements in the free troposphere, crossing Europe from Scandinavia, over Germany, to the Mediterranean.

In South America (Suriname) we contrasted tropical Atlantic air with that influenced by hydrocarbon emissions over the Amazon forest, indicating unexpectedly high OH levels. Next, over the South Atlantic Ocean we encountered the lowest pollution levels ever measured. Although one might expect "textbook" chemistry in this pristine environment, we found important discrepancies that have still not been satisfactorily explained. The tropical forest emissions have been compared with those of the boreal forest in Finland, and large differences have become apparent, pointing to very specific roles of the vegetation.

From the campaigns thus far, though in very different environments, a common picture is emerging. Under most conditions the recycling of OH appears to be quite efficient, and the measured OH concentrations vary less than expected. In the past, chemistry-transport models have underestimated OH recycling and the stability of the atmospheric



oxidation capacity. In urban-industrial environments the OH recycling by nitrogen oxides is important. In remote marine environments the role of ozone as an OH precursor and in recycling is important, leading to local O₃ loss, replenished by transport from regions where its formation is more efficient. Our results indicate that the lowest OH recycling is found over the tropical oceans, regionally affected by ship emissions (see Figure 2). And over forests the oxidation of hydrocarbons is not a strong OH sink, as previously assumed.

Several discrepancies are resolved with our recent MIM3 chemistry model, leading to excellent agreement with OH measurements. A central part of the

mechanism is the photo-oxidation of unsaturated hydro-peroxy-aldehydes, showing that the efficiency of OH recycling is a function of OH itself, suggesting that OH chemistry is generally wellbuffered. With colleagues in the USA (NOAA, Boulder), who have performed long-term global measurements of compounds that are removed by OH (tracers of OH variability), we have shown that the interannual OH variability is only a few percent, whereas previously variations up to 25% were derived, suggesting that the atmospheric oxidation capacity is much less stable than it thus appears to be. A key remaining question is how this will evolve in the future. Is there a tipping point at which this apparent stability will be surpassed?

MIM3: OH RECYCLING PROBABILITY (%)



Figure 2: EMAC model calculated annual mean OH recycling probability near the Earth's surface, indicating that OH buffering is efficient over most continents though much less over the tropical oceans.

"Urbanization and industrialization in the Anthropocene have caused an exponential increase of air pollution on a global scale. How does the atmosphere cope with this?"

18 _ **19**

SELECTED PUBLICATIONS

Martinez, M., Harder, H., Kubistin, D., Rudolf, M., Bozem, H., Eerdekens, G., Fischer, H., Gurk, C., Klüpfel, T., Königstedt, R., Parchatka, U., Schiller, C. L., Stickler, A., Williams, J., Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: Airborne measurements. Atmos. Chem. Phys., 10, 3759–3773 (2010).

Montzka, S., Krol, M., Dlugokencky, E., Hall, B., Jöckel, P., Lelieveld, J.: Small inter-annual variability of global atmospheric hydroxyl. Science 331, 67–69 (2011).

Hosaynali Beygi, Z., Fischer, H., Harder, H. D., Martinez, M., Sander, R., Williams, J., Brookes, D. M., Monks, P. S., Lelieveld, J.: Oxidation photochemistry in the Southern Atlantic boundary layer: Unexpected deviations of photochemical steady state. Atmos. Chem. Phys. 11, 8497–8513 (2011).

Crowley, J. N., Thieser, J., Tang, M., Schuster, G., Bozem, H., Hosaynali Beygi, Z., Fischer, H., Diesch, J., Drewnick, F., Borrmann, S., Song, W., Yassaa, N., Williams, J., Pöhler, D., Platt, U., Lelieveld, J.: Variable lifetimes and loss mechanisms for NO_3 and N_2O_5 during the DOMINO campaign: Contrasts between marine, urban and continental air. Atmos. Chem. Phys. Discuss. 11, 17825–17877 (2011).

Taraborrelli, D., Lawrence, M. G., Crowley, J. N., Dillon, T. J., Gromov, S., Groß, C. B. M., Vereecken, L., Lelieveld, J.: Hydroxyl radical buffered by isoprene oxidation over tropical forests. Nature Geosci. (submitted) (2011).

GLOBAL ATMOSPHERIC MEASUREMENTS BY A FLYING OBSERVATORY

CARL A. M. BRENNINKMEIJER



Figure 1: CARIBIC instrument platform, a modified air freight container with 20 automated in-flight experiments. Dimensions: 3.1 meters wide, 1.6 tons weight.

Our group develops, maintains, and operates the CARIBIC system in support of research at ten European partner institutions. CARIBIC is the only passenger aircraft-based atmospheric chemistry observatory worldwide. It provides detailed, large-scale, regular, and long-term observations of parts of the atmosphere that are otherwise difficult to access. Flight destinations include airports in South Africa, North and South America, and South and East Asia. The collected data support many research projects that advance the understanding of transport and chemistry in the atmosphere and how they change in time. About 50% of the flights take place at the interface between the troposphere and stratosphere, the tropopause region.

d CARIBIC uses a 1.6-ton measurement upurtner laboratory with 20 different instruments, measuring more than 100 dif-

ments, measuring more than 100 different species – which is deployed each month to perform four intercontinental flights (more than one million miles covered by 2011) aboard a Lufthansa Airbus A340-600. In this aircraft we have installed the necessary techni-



Figure 2: Distribution of methane in the troposphere along the CARIBIC flight path. Similar maps are produced for carbon dioxide, nitrous oxide, carbon monoxide, ozone, ethane, nitrogen oxides, and many other gases and aerosols.



cal provisions in close collaboration with Lufthansa Technik, including a multiprobe air inlet system. Results are available through a user-friendly data base. For publications based on this system (~80) we refer the reader to www. caribic-atmospheric.com.

Recently we have accomplished a major upgrade of the instrumentation, including its re-certification according to the increasingly strict air safety regulations. We have implemented instrument upgrades, improved the sensitivity of the DOAS (Differential Optical Absorption Spectroscopy) remote sensing system, and extended the air sampling capacity from 28 to 116 air samples. From these air samples we measure a host of hydrocarbons and greenhouse gases. Another important accomplishment was the construction of a new inlet. This complex sampling system, permanently installed on the aircraft, includes three DOAS telescopes, temperature sensors, a video camera, and inlets for gases, aerosols, and cloud particles.

The enhanced scientific payload was first deployed during three special missions in the wake of the eruption of Eyjafjallajökull April–May 2010 that disrupted air traffic in Europe. The CARIBIC missions over England and Scandinavia comprehensively measured the volcano plume (without passengers, only pilots and scientists). Analyses of the hydrocarbon data revealed a high abundance of chlorine radicals in the volcanic plume. The publication was highlighted by the journal Science and the American Geophysical Union. The new DOAS data have enabled the first comparison between aircraft and satellite observations of sulfur dioxide. A detailed study showed good agreement between the GOME-2 instrument aboard the MetOp-A satellite and the CARIBIC measurements.

A major question concerning the global carbon cycle is how much CO₂ is taken up by the vegetation. Using CARIBIC data from flights to Chennai in India, we estimated the source and sink fluxes of CO₂ over southern Asia, and also of the greenhouse gases CH_4 and N_2O . A follow-up study, using a three-dimensional atmospheric transport and ecosystem system model, showed that India is currently a net sink of carbon, mostly as a result of strong CO₂ uptake during the summer monsoon. The continued regular measurements of CO₂ and the other greenhouse gases will show how these fluxes will change in time.

The CARIBIC observatory will be continually upgraded without disrupting its monthly sequence of observations. A new goal is to measure SO_2 directly with high sensitivity (in addition to the DOAS), as it is the main precursor of particle formation by its reaction with OH, forming sulfuric acid which has a very low volatility.

A growing number of institutions in Europe, Japan, the USA, and China use the CARIBIC data in modeling studies and for the validation of satellite observations. It is planned that CARIBIC will participate in the European infrastructure for systematic observations by passenger aircraft, IAGOS. "The unique airborne laboratory "CARIBIC" contributes to observing, monitoring, and understanding changes in the composition of the Earth's atmosphere."

20 **_ 21**

SELECTED PUBLICATIONS

Baker, A. K., Rauthe-Schöch, A, Schuck, T. J., Brenninkmeijer, C. A. M., van Velthoven, P. J., Wisher, A., Oram, D. E.: Investigation of chlorine radical chemistry in the Eyjafjallajökull volcanic plume using observed depletions in non-methane hydrocarbons. Geophys. Res. Lett., 38, L13801, doi:10.1029/2011GL047571 (2011).

Patra, P., Niwa, Y., Schuck, T. J., Brenninkmeijer, C. A. M., Machida, T., Matsueda, H, Sawa, Y.: Carbon balance of South Asia constrained by passenger aircraft CO₂ measurements. Atmos. Chem. Phys., 11, 4163–4175, doi:10.5194/acp-11-4163 (2011).

Rauthe-Schöch, A., Weigelt, A., Hermann, M., Martinsson, B. G., Baker, A. K., Heue, K.-P, Brenninkmeijer, C. A. M., Zahn, A., Scharffe, D., Eckhardt, S., Stohl, A., van Velthoven, P. J. F.: CARIBIC aircraft measurements of Eyjafjallajökull volcanic plumes in April/ May 2010. Atmos. Chem. Phys. Discuss., 11, 16693–16744 (2011).

Heue, K.-P., Brenninkmeijer, C. A. M., Baker, A. K., Rauthe-Schöch, A., Walter, D., Wagner, T., Hörmann, C., Sihler, H., Dix, B., Frieß, U., Platt, U., Martinsson, B. G., van Velthoven, P. F. J., Hermann, M., Zahn, A., Ebinghaus, R.: SO₂ and BrO observation in the plume of the Eyjafjallajökull volcano 2010: CARIBIC and GOME-2 retrievals. Atmos. Chem. Phys., 11, 2973-2989, doi:10.5194/acp-11-2973 (2011).

Schuck, T. J., Brenninkmeijer, C. A. M., Baker, A. K., Šlemr, F., Velthoven, P. F. J. v., Zahn, A.: Greenhouse gas relationships in the Indian summer monsoon plume measured by the CARIBIC passenger aircraft. Atmos. Chem. Phys., 10, 3695-3984, doi: 10.5194/acp-10-3965 (2010).

PHOTOCHEMISTRY AND KINETICS IN THE LABORATORY AND IN THE FIELD

JOHN N. CROWLEY



Figure 1: Measuring facilities of the station on the Kleiner Feldberg, a rural, mountain site in central Germany, north of Frankfurt.

The photochemistry and kinetics group investigates atmospheric chemistry both in the laboratory and in the field. Using optical and mass-spectrometric methods we investigate the photochemistry, kinetics, and mechanisms of atmospheric reactions. In our field work we employ highly sensitive laser-cavity methods and chemical ionization mass spectrometry to investigate the coupling between reactive nitrogen oxides and their organic and inorganic reservoir species, and their role in radical propagation. John Crowley is a member of the IUPAC committee evaluating kinetic and photochemical data for the atmospheric chemistry community.

Our gas-phase research has examined reactions of both short-lived radicals and long-lived traces gases. Our interest in radical recycling stems from its role in maintaining the oxidation capacity of the atmosphere. Though traditionally regarded as radical *termination* reactions, we have quantified radical *generation* (recycling) in reactions of several organic peroxy radicals (RO_2) with HO_2 . We find that the OH radical is formed in very high yields (~70–80%) when the peroxy radical contains a carbonyl group (e.g., CH₃C(O)O₂ or HOCH₂C(O)O₂).

In contrast to radical species with lifetimes of fractions of seconds, greenhouse gases can be transported throughout the atmosphere. We have provided a comprehensive description of the reaction of NF₃ with OH, O(¹D), and O₃ and also derived the photolysis quantum yield and cross sections. By combining experimental and theoretical studies (see report of Luc Vereecken) we derived a chemical lifetime of about 500 years.

Our research on heterogeneous chemistry has focused on two very different particle types: mineral dust and ice. The interaction of NO_3 radicals with authentic Saharan dust was found to be efficient with an uptake coefficient of about 0.02, similar to that of N_2O_5 . The uptake of trace gases to growing ice crystals ("trapping") can influence for example chemical processes in the presence of cirrus and convective clouds. So far, trapping has been observed for HCl only. Insights into the physics of the trapping process were provided by the dependence on the ice growth rate, the HCl concentration, and the temperature.

One focus of our field work is the role of radical-induced, night-time oxidation processes. Night-time oxidation via the NO₃ radical can supplement or, under some conditions, even exceed photochemically driven daytime oxidation. We have developed a two-channel, off-axis cavity-ring-down system to



measure NO₃ and N₂O₅, which took part in an instrument intercomparison at an environmental chamber. Recently the measurements have been extended to include NO₂. We have measured NO₃ and other nocturnal nitrogen oxides (NO₂, N₂O₅) at a variety of sites including a rural mountain site (Kleiner Feldberg in Germany), boreal forest (Finland), and urban / industrial (Spain). Very high NO₃ reactivity was observed in the boreal and urban environment,

indicating rapid processing by biogenic and anthropogenic hydrocarbons, respectively. At all sites, the NO₃ radical provided an important contribution to oxidation of certain classes of organics and the removal of NO*x*, whereas the loss of N₂O₅ to particles was of limited importance. At the Kleiner Feldberg, north of Frankfurt, we measured for the first time significant concentrations (up to several hundred ppt) of nitryl chlorine (ClNO₂). The abundant presence of reactive chlorine is thought to be the result of heterogeneous reactions of N_2O_5 on chlorine containing particles, though further research is needed to confirm and quantify this.

Organic radicals play a central role in atmospheric oxidation, their fate depending strongly on the levels of NO*x*. We have explored the chemistry of carbonyl peroxy radicals derived from biogenic and anthropogenic hydrocarbons in the boreal forest by measuring a number of peroxy-nitrates (RC(O)OONO₂) and peroxy-acids (RC(O)OOH) using both chemical ionization mass spectrometry and thermal dissociation cavity-ringdown spectroscopy. Peroxy-nitrate mixing ratios were generally low in this largely pristine environment (100-400 ppt) with occasionally similar concentrations of the peroxy-acids, formation of which was favored by high temperatures and/or low NOx.

Figure 2: NO₃, N₂O₅, and NO₃ measured at the Kleiner Feldberg.

"A detailed understanding of gas-phase and heterogeneous processes is basic to studies of the chemistry of the atmosphere."

22 **_ 23**

SELECTED PUBLICATIONS

Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A. M., Rossi, M. J., Troe, J., Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V – heterogeneous reactions on solid substrates. Atmos. Chem. Phys., 10, 9059–9223 (2010).

Crowley, J. N., Schuster, G., Pouvesle, N., Parchatka, U., Fischer, H., Bonn, B., Bingemer, H., Lelieveld, J.: Nocturnal nitrogen oxides at a rural mountain site in south-western Germany. Atmos. Chem. Phys., 10, 2795–2812 (2010).

Dillon, T. J., Horowitz, A., Crowley, J. N.: Cross-sections and quantum yields for the atmospheric photolysis of the potent greenhouse gas nitrogen trifluoride. Atmos. Environ., 44, 1186–1191 (2010).

Pouvesle, N., Kippenberger, M., Schuster, G., and Crowley, J.N.: The interaction of H_2O_2 with ice surfaces between 203 and 233 K. Phys. Chem. Chem. Phys, 12, 15544–15550 (2010).

Tang, M.J., Thieser, J., Schuster, G., and Crowley, J.N.: Uptake of NO_3 and N_2O_5 to Saharan dust, ambient urban aerosol and soot: a relative rate study. Atmos. Chem. Phys., 10, 2965–2974 (2010).

CHEMICAL PROCESSES RELATED TO OZONE **PRODUCTION IN REMOTE AREAS**

HORST FISCHER

Figure 1: The next measuring campaign is planned on board the High Altitude Long Range (HALO) aircraft.

The optical spectroscopy group develops and deploys instrumentation to measure atmospheric trace gases using optical detection methods. The main target molecules are NO, NO₂, O₃, CO, HCHO, H₂O₂, and CH₄. These are detected by mid-infrared absorption, fluorescence and chemiluminescence spectroscopy. The instruments are deployed on the ground, on ships and aircraft, and therefore need to be compact, robust, and highly sensitive. The focal aspects of our research are the photochemical formation and control mechanisms of ozone in the background troposphere, i.e., in air that is not directly anthropogenically polluted. This involves studies of the photochemical steady state of the NO/NO₂/O₃ system and experimental identification of ozone formation and destruction tendencies. Further, we are particularly interested in the formation of ozone in the outflow

region of deep convective clouds that efficiently transport trace gases from the boundary layer to the tropopause region at 8–15 km altitude.

Ozone in the atmosphere is an important oxidant, OH precursor, and a greenhouse gas. A recent study by our group combined data from several airborne measurement campaigns (e.g., over Suriname, South America, and several missions across Europe). In a number of case studies detailed chemistrytransport ozone budgets of the free troposphere were composed both for background conditions and those direct ly affected by deep convection. In situ measurements of O₃, NO, OH, HO₂, and actinic radiation were used to derive large-scale ozone tendencies from the calculated net ozone production rate (NOPR) for the free troposphere.

The experimental results were compared to simulations with a global chemistry-transport model, showing consistent tendencies of ozone production in the boundary layer and in the upper troposphere, both at low and high latitudes. In contrast to the upper troposphere, the tropical middle troposphere was characterized by a strong ozone destruction tendency. In the mid-latitudes during summer photochemical activity can be quite high, though a distinct ozone tendency was absent. Comparing these results with a chemistry-transport model indicates general agreement of the chemistry and transport tendencies to either produce or destroy ozone in most parts of the measurement regions.

Several case studies showed that convection can substantially enhance the NOPR in the upper troposphere. Furthermore, deep convection is a highly

3 4 5 6 7

NO, (ppt,)

efficient mechanism for vertical trace gas transport from the Earth's surface to the upper troposphere (UT). Surprisingly, this also includes rather soluble species like formaldehyde (HCHO) and hydrogen peroxide (H_2O_2) . We found that in particular H₂O₂ is released from freezing cloud particles, thus explaining the strong difference between observed and modeled H_2O_2 concentrations in the upper troposphere over Europe.

JNO. (s

To investigate the photochemistry in the marine boundary layer under the clean background conditions of the Southern Atlantic Ocean, ship measurements of NO, NO₂, O₃, JNO₂, J(O¹D), HO₂, OH, and RO_x were evaluated for consistency with photochemical steady-state (PSS) conditions. The calculations indicate substantial deviations from PSS ($\Phi > 1$). The deviations observed under low NO_x conditions (5-25 pptv) demonstrate

a remarkable upward tendency in the Leighton ratio (used to characterize PSS) with increasing NO_x mixing ratio and JNO₂ intensity.

It is a paradigm in atmospheric chemistry that OH largely controls the oxidation efficiency of the atmosphere. However, evidence is growing that for unpolluted low-NO_x (NO+NO₂) conditions the atmospheric oxidant budget is poorly understood. Nevertheless, for the very cleanest conditions, typical for the remote marine boundary layer, good model agreement with measured OH and HO₂ radicals has been interpreted as an accurate understanding of baseline photochemistry. Our study shows that such agreement may be deceptive and that a yet unidentified oxidant is needed to explain the photochemical conditions observed over the Atlantic Ocean.

"The atmospheric transport of trace gases that influence chemical ozone production and destruction supports the self-cleaning mechanism of the atmosphere."

24 **25**

SELECTED PUBLICATIONS

Schiller, C. L., Bozem, H., Gurk, C., Parchatka, U., Königstedt, R., Harris, G. W., Lelieveld, J., Fischer, H.: TRISTAR: Application of a Quantum Cascade TDLAS for sensitive trace gas measurements of CO, CH_4 , N_2O and HCHO. Appl. Phys. B, 92, 419–430 (2008).

Gurk, C., Fischer, H., Hoor, P., Lelieveld, J., Wernli, H.: Airborne in-situ measurements of *vertical, seasonal and latitudinal distributions* of carbon dioxide over Europe. Atmos. Phys. Chem., 8, 6395-6403 (2008).

Hoor, P., Borken-Kleefeld, J., Caro, D., Dessens, O., Endresen, O., Gauss, M., Grewe, V., Hauglustaine, D., Isaksen, I. S. A., Jöckel, P., Lelieveld, J., Meijer, E., Olivie, D., Prather, M., Schnadt-Poberaj, C., Staehelin, J., Tang, Q., van Aardenne, I., van Velthoven, P., Sausen, R.: The impact of traffic emissions on atmospheric ozone and OH: results from QUANTI-FY. Atmos. Chem. Phys. 9, 3113-3136 (2009).

Klippel, T., Fischer, H., Bozem, H., Lawrence, M. G., Butler, T., Jöckel, P., Tost, H., Martinez, M., Harder, H., Regelin, E., Sander, R., Schiller, C. L., Stickler, A., Lelieveld, J.: Distribution of hydrogen peroxide, methyl hydroperoxide and formaldehyde over central Europe during the HOOVER project. Atmos. Chem. Phys., 11, 4391-4410 (2011).

Hosaynali Beygi, Z., Fischer, H., Harder, H. D., Martinez, M., Sander, R., Williams, I., Brookes, D. M., Monks, P. S., Lelieveld, J.: Oxidation photochemistry in the Southern At*lantic boundary layer: Unexpected deviations* of photochemical steady state. Atmos. Chem. Phys., 11, 8497-8513 (2011).

MODEL STUDIES OF THE CHEMISTRY AND PHYSICS OF THE ATMOSPHERE

MARK LAWRENCE AND HOLGER TOST

Figure 1: Smog is a typical phenomen in megacities such as New York

Two groups (led by Mark Lawrence and Holger Tost) have been applying models to the study of atmospheric chemistry during this evaluation period. The models used by the groups range from highly complex global and regional models to simpler process models, including:

- EMAC (ECHAM/MESSy Atmospheric Chemistry model), a global chemistry-climate model with a comprehensive set of state-of-the-art parameterizations;
- MATCH-MPIC (Model of Atmospheric Transport and Chemistry –

50 100 150 200 250 300 400 500

A Total Column (10⁻⁹ kg/m²)

Max Planck Institute for Chemistry version), an older chemistry-transport model which we use for chemical weather forecasts and analyses;

- WRF-Chem (Weather Research and Forecast – Chemistry community model), a regional model which we use for process studies, for example, of clouds and chemistry;
- MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere), an EMAC submodel which we employ as a photochemical "box" model to develop and examine photochemical oxidation mechanisms.

The current main projects of the groups include:

- studies on the chemistry in and the effect of pollutants from highly populated regions ("megacities," see below);
- development and testing of an improved representation of aerosol chemistry, thermodynamics and microphysics for use in EMAC;
- development and testing of improved mechanisms for isoprene oxidation and its impact on OH (see also the report of the Group on Theoretical Chemistry, Luc Vereecken);

Figure 2: Regional megacity pollution potentials, showing the annual mean sum of all simulated major population center tracers with a 10-day lifetime for (a) the total column (10^{-9} kg/m^2) , (b) the model surface layer $(10^{-12} \text{ kg/m}^3)$, and (c) the column above 5 km (10^{-9} kg/m^2) .

- determination of emissions characteristics for various gases and aerosols;
- the general characteristics of tracer transport away from various sources;
- the impact of deep convection and lightning on atmospheric chemistry;
- providing chemical weather forecasts and analyses; and
- global model sensitivity simulations and focused box model studies in support of the department's field campaigns.

Of the various activities in the groups, one which has gotten particular attention over the last few years is the global air pollution from megacities, major emitters of pollutant gases and aerosols which we have been studying as part of the EU project "MEGAPOLI" (http:// megapoli.dmi.dk), co-coordinated by M. Lawrence. We have examined the general potential of pollutants emitted from 36 megacities and "major population centers" worldwide to influence downstream regions (see Figure 2). Two main findings are: vertical transport plays a surprisingly strong role, both for pollution buildup around the megacities, and for the amounts of pollution affecting near-surface regions over 1000 km downstream; and the long-range transport of aerosols is substantial, with about 50% of small aerosol particles (r < 1 μ m) being deposited over 1000 km away.

We have also analyzed the detailed impacts of megacity emissions on O₃, finding differences between classes of VOCs: some rapidly produce O₃, while for others there is a delay of about a day. Further detailed model studies of the chemistry of individual megacities have been carried out in "sandwich" Ph.D. programs with students from China and South Africa, and with a Max Planck partner group in India.

The group led by Holger Tost has been involved in developing a comprehensive aerosol microphysics and gas aerosol partitioning submodel (Global Modalaerosol eXtension, GMXe) for applications in atmospheric chemistry and climate models. It was used to simulate global fields of the aerosol hygroscopicity to describe the influence of chemical composition on the cloud condensation nucleus (CCN) activity of aerosol particles. At the top of the planetary boundary layer the aerosol hygroscopicity can deviate substantially from that at the surface (up to 30%) especially in marine and coastal regions. Thus, surface observations of CCN may not be representative for the altitudes where cloud formation mostly occurs.

An important achievement has been that EMAC-GMXe can be consistently applied throughout the lower and middle atmosphere. For example, we applied it to simulate the background stratospheric sulfur cycle, i.e., during volcanically quiescent periods. The model results indicate that upward transport of carbonyl sulfide (COS) from the troposphere largely controls the sulfur budget and the aerosol optical depth of the background stratosphere. This differs from previous studies, which indicated that short-lived sulfur gases are also important. "The study of atmospheric chemistry, transport, and chemistryclimate interactions in the troposphere and stratosphere requires a hierarchy of numerical models."

26 **_ 27**

SELECTED PUBLICATIONS

Beirle, S., Boersma, K. F., Platt, U., Lawrence, M. G., Wagner, T.: Megacity emissions and lifetimes of nitrogen oxides probed from space. Science, 333, 1737–1739 (2011).

Butler, T. M., Lawrence, M. G., Taraborrelli, D., Lelieveld, J.: Multi-day ozone production potential of volatile organic compounds calculated with a tagging approach. Atmos. Environ., 45, 4082–4090 (2011).

Butler, T. M., Lawrence, M. G.: The influence of megacities on global atmospheric chemistry: A modelling study. Env. Chem., 6, 219–225 (2009).

Lawrence, M. G., Butler, T. M., Steinkamp, J., Gurjar, B. R., Lelieveld, J.: Regional pollution potentials of megacities and other major population centers. Atmos. Chem. Phys., 7, 3969–3987 (2007).

Pringle, K.J., Tost, H., Pozzer, A., Pöschl, U., Lelieveld, J.: Global distribution of the effective hygroscopicity parameter for CCN activation. Atmos. Chem. Phys. 10, 5241–5255 (2010).

ORGANIC REACTIVE SPECIES: UNDERSTANDING AND MEASUREMENTS

JONATHAN WILLIAMS

Figure 1: The site of the Boreal forest HUMPPA-COPEC campaign 2010.

Our group investigates gas-phase reactive organic compounds, primarily through field measurements. We are involved in the development of new instrumentation for airborne, ship-borne, and ground-based field measurements. The analysis of the data leads to a better understanding of the sources, sinks, and the oxidation chemistry of organic compounds, and ultimately to global budget estimations. Our measurement capability includes organo-nitriles, carbonyls, organo-halides, isoprene, organo-sulfur compounds, aromatic species, and total OH reactivity.

We have specialized in measurements with PTR-MS (Proton Transfer Mass Spectrometers) and GC-MS (Gas Chromatography - Mass Spectrometry). Members of the group have performed measurements of organic species across

the globe including: tropical, temperate and boreal forests, the Indian, Atlantic and Southern Oceans, urban environments, and the stratosphere.

In summer 2010 an intensive field measurement campaign, HUMPPA (Hyytiälä United Measurement of Photochemistry and Particles), was organized jointly by our department and the University of Helsinki. The measurements took place in Hyytiälä, Finland in July-August 2010. In summer emission fluxes of Volatile Organic Compounds (VOCs), OH-initiated photochemistry and particle growth rates reach their seasonal maximum. We measured enantiomeric mono- and sesquiterpenes both in emission cuvettes and ambient air. The novel use of chiral compounds allows the identification of different tree chemotypes. OH reactivity measurements were conducted both

within and above the forest canopy. Fast GC-MS measurements of alkanes and PTR-MS measurements of various organic gases were also completed.

In the past years we have developed a new technique to determine total OH reactivity, and helped several external groups to duplicate our method. Furthermore, we have demonstrated that our method, which was originally developed using PTR-MS, can also be applied with GC-PID (Photo-ionization detector) making it much more widely applicable. This technique has been deployed in laboratory chambers, forest environments, and downwind of Paris, indicating an array of characteristic OH reactivities, varying from near-zero to 100 s⁻¹, information which has helped constrain OH chemistry in measurement analyses and models.

The role of organics at the air-sea interface has been investigated both in the Heidelberg wind tunnel (Aeolotron) and in "future ocean" mesocosm experiments performed in the North Sea. The wind tunnel is designed to determine transfer coefficients of organic species covering a wide range of solubilities and boiling points. The results for acetone from one such experiment are shown in Figure 2. From the mesocosm experiments we have examined the relative emissions of DMS and monoterpenes for different ocean water acidities.

This is a natural follow-up of the first reported oceanic monoterpene emissions which was made by our group in 2008. By pooling data with external groups we have contributed to a better understanding of the global methanol and acetaldehyde budgets, and the role of ocean isoprene emissions.

Over the past three years our instrumental capability has improved significantly. A GC-MS system, typically slow but specific, has been adapted to measure key species within just a few minutes, so that it may be used on an aircraft. In parallel the PTR-MS systems, typically fast but unspecific, have strongly improved in mass resolution through the acquisition of a PTR-MS-ToF (Time-of-Flight), and therefore the species identification capability has increased tremendously.

We expect that in the following three years the PTR-MS-ToF instrument and the fast GC-MS will be flown on aircraft. In addition, ground and shipbased campaigns will provide opportunities to test new instrumentation and to better characterize VOCs over globally relevant ecosystems.

Figure 2: PTR-MS-ToF measurements of acetone as a function of windspeed from within the Aeolotron wind-wave facility at Heidelberg University.

"Sources, sinks, and the chemistry of Volatile Organic Compounds are central in the composition of the atmosphere."

28 **29**

SELECTED PUBLICATIONS

Warneck, P., Williams, J.: "The Atmospheric Chemist's Companion," Springer, 1st Ed. (2012), ISBN-10: 9400722745.

Williams, J., Crowley, J., Fischer, H., Harder, H., Martinez, M., Petäjä, T., Rinne, J., Bäck, J., Boy, M., Dal Maso, M., Hakala, J., Kajos, M., Keronen, P., Rantala, P., Aalto, J., Aaltonen, H., Paatero, J., Vesala, T., Hakola, H., Levula, J., Pohja, T., Herrmann, F., Auld, J., Mesarchaki, E., Song, W., Yassaa, N., Nölscher, A., Johnson, A. M., Custer, T., Sinha, V., Thieser, J., Pouvesle, N., Taraborrelli, D., Tang, M. J., Bozem, H., Hosaynali-Beygi, Z., Axinte, R., Oswald, R., Novelli, A., Kubistin, D., Hens, K., Javed, U., Trawny, K., Breitenberger, C., Hidalgo, P. J., Ebben, C. J., Geiger, F. M., Corrigan, A. L., Russell, L. M., Ouwersloot, H., Vilà-Guerau de Arellano, J., Ganzeveld, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C. J., Bertelmann, M., Köllner, F., Hoffmann, T., Valverde, J., González, D., Riekkola, M.-L., Kulmala, M., *Lelieveld*, *I.: The summertime Boreal forest* field measurement intensive (HUMPPA-COPEC-2010): An overview of meteorological and chemical influences. Atmos. Chem. Phys., 11, 10599-10618 (2011).

Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T. M., Kajos, M. K., Patokoski, J., Hellen, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., Kulmala, M.: OH reactivity measurements within a boreal forest: Evidence for unknown reactive emissions. Environ. Sci. Technol. 44 (17), 6614-6620 (2010).

Williams, J., Crutzen, P. J.: Nitrous oxide from aquaculture. Nat. Geosci. 3, 143 (2010), doi:10.1038/ngeo804.

Yassaa, N., Custer, T., Song, W., Pech, F., Kesselmeier, J., Williams, J.: Quantitative and *enantioselective analysis of monoterpenes* from plant chambers and in ambient air using SPME. Atmos. Meas. Tech., 3, 1615–1627 (2010), doi:10.5194/amt-3-1615-2010.

RADICAL MEASUREMENTS

HARTWIG HARDER

Hydroxyl (OH) is a highly reactive radical and, despite its importance, occurs in very low mixing ratios of less than a part per trillion. Therefore it is intrinsically difficult to measure. The development of instruments and their continual improvement is a key activity in our group, relying on the Laser-Induced Fluorescence (LIF) technique to measure OH, HO₂, and most recently also NO₂. These instruments are deployed on aircraft, ships and at ground-based stations, depending on whether the free troposphere or stratosphere, the marine or continental boundary layer are to be investigated.

To investigate sources, sinks, and associated concentrations of these reactive species we analyze and interpret our measurement data by detailed comparisons with model calculations. Discrepancies between measurement data and model predictions often hint at flaws in our understanding of the processes occurring in the atmosphere. For example, a box model constrained by aircraft measurements in the upper troposphere over Europe can describe the measured OH concentrations rather well, whereas our global EMAC model, using the same chemical scheme underestimates it (Figure 1). It appears that

the underestimation of OH arises when H_2O_2 is underestimated by the EMAC model. While H₂O₂ is a photolytic source of OH in the upper troposphere it is soluble and can thus interact with aerosol and cloud droplets and be released in the upper troposphere by the evaporation of ice in the outflow of convection. These results show that improvement of the model to simulate OH in the upper troposphere requires improvement of the representation of transport processes and heterogeneous chemical processes that affect H_2O_2 .

Our aircraft measurements over the Amazon forest during the campaign in Suriname, as well as measurements by other groups in Borneo, China and other locations, have shown that atmospheric models typically underestimate OH and HO₂ in air affected by biogenic VOC emissions. This issue is high on our research agenda, and simultaneously we address possible interferences within our instruments and air inlets to prevent misinterpretations, which cannot be entirely excluded considering the difficulties of measuring highly

Figure 1: OH measurements versus model results. A constrained box model accurately computes OH (left) whereas the global EMAC model shows a systematic bias, being a function of the H_2O_2 mixing ratio.

reactive radical species. Therefore, we participated in international instrument intercomparisons and measurement campaigns, i.e., in southern Spain, at the boreal site Hyytiälä (Finland), and most recently on the Kleiner Feldberg north of Frankfurt.

An important instrumental advancement has been to reliably detect interferences through methodical, intermittent removal of atmospheric OH from the measured air volume prior to injection into our instrument. This method has been applied at all three sites, revealing the presence of a variable interference signal due to the generation of nonatmospheric OH within the instrument. After correcting for the interference signal, model calculations still tend to underestimate OH concentrations, for example in southern Spain. Using this new technique our instrument was intercompared with a chemical ionization mass spectrometer (CIMS) in Finland,

indicating good agreement (Figure 2).

Interestingly, both techniques independently point to a significant OH presence during nighttime, which must be nonphotolytic. This mechanism may - or may not - be related to the process producing OH within our instrument, likely involving the decomposition of Criegee intermediates (radicals arising from the ozonolysis of certain unsaturated hydrocarbons). The Criegee radicals could also contribute to the oxidation of SO₂ into H₂SO₄, which was observed simultaneously during the night.

In the presence of VOC and NOx, OH, HO₂ and organic peroxy radicals (RO₂) are strongly coupled by cycling reactions. RO₂ measurements are therefore important for understanding OH and HO₂ concentrations, and we are currently developing an additional instrument to measure RO₂ radicals.

Figure 2: Comparison of OH measurements by our LIF technique and by CIMS. The black line indicates the measured ozone photodissociation rate (JO1D).

"The challenging measurement of radical species is central to our understanding and capability to model atmospheric photochemistry."

30 31

SELECTED PUBLICATIONS

Schlosser, E., Brauers, T., Dorn, H.-P., Fuchs, H., Häseler, R., Hofzumahaus, A., Holland, F., Wahner, A., Kanaya, Y., Kajii, Y., Miyamoto, K., Nishida, S., Watanabe, K., Yoshino, A., Kubistin, D., Martinez, M., Rudolf, M., Harder, H., Berresheim, H., Elste, T., Plass-Dülmer, C., Stange, G., Schurath, U.: Formal blind intercomparison of OH measurements: Results from the international campaign HOxComp. Atmos. Chem. Phys., 9, 7923-7948 (2009).

Martinez, M., Harder, H., Kubistin, D., Rudolf, M., Bozem, H., Eerdekens, G., Fischer, H., Klüpfel, T., Gurk, C., Königstedt, R., Parchatka, U., Schiller, C. L., Stickler, A., Williams, J., Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: Airborne measurements. Atmos. Chem. Phys., 10, 3759–3773 (2010).

Kubistin, D., Harder, H., Martinez, M., Rudolf, M., Sander, R., Bozem, H., Eerdekens, G., Fischer, H., Gurk, C., Klüpfel, T., Königstedt, R., Parchatka, U., Schiller, C., Stickler, A., Taraborrelli, D., Williams, J., Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rain forest: Comparison of measurements with the Box Model MECCA. Atmos. Chem. Phys., 10, 9705-9728 (2010).

Fuchs, H., Brauers, T., Dorn, H.-P., Harder, H., Häseler, R., Hofzumahaus, A., Holland, F., Kanaya, Y., Kajii, Y., Kubistin, D., Lou, S., Martinez, M., Miyamoto, K., Nishida, S., Rudolf, M., Schlosser, E., Wahner, A., Yoshino, A., Schurath, U.: Technical Note: Formal blind intercomparison of HO₂ measurements in the atmosphere simulation chamber SAPHIR during the HOxComp campaign. Atmos. Chem. Phys., 10, 12233-12250 (2010).

Mao, J, Ren, X., Chen, S., Brune, W. H., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglück, B., Flynn, J., Leuchner, M.: Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies. Atmospheric Environment, 44, 4107-4115 (2010).

BIOGEO-CHEMISTRY

BIOGEOCHEMISTRY

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

MEINRAT O. ANDREAE

Biogeochemistry is the scientific discipline that studies the interactions of the biosphere with the Earth's chemical environment. It is an essential part of the evolving field of Earth System Science, which looks at the Earth as an integral system, in which the biota interact with the atmosphere, the hydrosphere, and the solid earth. Our department investigates a number of key aspects of global biogeochemistry: the role of the terrestrial biota as sources and sinks of climatically important trace gases and aerosols, the effect of vegetation fires on ecology, climate and air quality, and the role of aerosols in the climate system.

Current projects include the study of the exchange of volatile organic compounds (VOC) by plants in tropical and temperate ecosystems. One of the main objectives of this research is to understand the role of VOC exchange in the carbon budget. For some substances, the vegetation acts as a source of reactive compounds to the atmosphere, whereas other substances can be emitted or taken up by the plants, depending on their atmospheric concentrations. Once in the atmosphere, the VOCs undergo complex chemical oxidation chains and thereby play a central role in the atmospheric self-cleansing mechanisms. Oxidation of VOC also leads to the formation of lowvolatility substances, which condense to form organic aerosol particles.

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 to 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. The conversion of rainforest and savanna into agricultural lands also has a strong influence on the exchange of trace gases, particularly for nitrogen-containing species. We are investigating the fluxes of trace gases such as NO, NO₂ and HONO from temperate and semiarid sites, in combination with laboratory studies and remote sensing.

We operate a station in Manaus, where we are conducting integrated studies on the biogeochemistry and ecology of the Central Amazon, in collaboration with the Brazilian National Institute for Amazon Research. Here, we are planning the construction of a 300-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 (Zotino Tall Tower Observatory, ZOTTO).

Vegetation fires are an important determinant in the ecology of many

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

32 **_ 33**

terrestrial systems. We study 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.

In the paleobiogeochemistry group, we are investigating changing biogeochemical cycles and their interaction with the climate system, e.g. by measuring the isotopic compositions of elements like uranium, thorium, neodymium, cadmium, and lead in airborne dust, seawater, sediments, and stalagmites. We are exploring the use of new isotopic systems as potential tracers of nutrient cycles in the oceans. The transatlantic transport of dust from Africa to the Amazon and the Caribbean is examined using isotopes in dust samples. In collaboration with Mainz University, we are investigating the use of novel paleo-archives, e.g., bivalve shells, ostracods, and speleothems, to reveal changes in climates and biogeochemical processes in the past.

The Department hosts three additional groups: The Cosmochemistry Group uses noble gas isotopes to explore the history of the cosmos as well as exposure ages and ice sheet behavior in Antarctica. The Mantle Geochemistry Group investigates magma formation in the Earth's mantle and the effects of volcanism in Large Igneous Provinces on the Earth environment. The High Pressure Group studies elements and compounds under ultrahigh pressures, discovering new phases with unusual physical and chemical properties.

SEARCHING FOR THE WORLD BEFORE THE *ANTHROPOCENE*

MEINRAT O. ANDREAE

Figure 1: The 80-m measurement tower in the Amazon forest.

The world we live in bears everywhere the mark of human activities, from polluted skies and industrialized continents to overfished oceans. This is captured in the term Anthropocene, the geologic era shaped by human influence. Global Change is then the transformation of the "pristine" world, where little or no human perturbations were present, into the world of the Anthropocene. It is quite obvious that we can fully understand Global Change only if we also know how the Earth System functioned before the advent of humankind, or at least before the industrial age.

Because of the pervasiveness of Global Change, this is not an easy task. Records of ancient environmental conditions are sparse, and in most cases allow multiple interpretations. They also tend to record state variables rather than the processes that define the system. In the Biogeochemistry Department, we investigate traditional and novel archives of pa-

leoenvironments, as described in other sections of this report. But we also make use of 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 biosphereatmosphere interactions, and particularly the exchange of trace gases and aerosols between the forest biota and the atmosphere. Obviously, we would not dare to call either location pristine in the true sense. Aerosol particles, for example, have an atmospheric lifetime

of a week or so, which allows them to circle the globe. Some trace gases even live much longer. But there are periods in both systems, when airmasses have not made contact with large sources of human emissions for a considerable length of time, such as during some events of inflow of Arctic air in the boreal region in summer, or during the wet season of the Amazon. Our measurements show that 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 prehuman times (Figure 2).

We have conducted several measurement campaigns in the Amazon forest in the Manaus region, and maintain continuous sampling and in situ

Figure 2: Aerosol light absorption at the ZOTTO Tower, showing the presence of soot from pollution in winter and nearly pristine periods in summer. Sharp peaks in spring are from vegetation fires.

measurements there. The results show that the forest's emissions dominate the abundance and composition of the trace gases in the region during the wet season. The plants emit trace gases, such as isoprene and terpenes, whose oxidation products we find in the aerosol particles which go on to serve as cloud condensation nuclei. But our most recent work also suggests that the forest biota also release small particles with a sugar-like composition by a still unknown mechanism, and that these particles serve as substrates for the condensation of the material from terpenoid oxidation. Of the particles larger than a micron, most seem to be fungal spores or similar

material. A surprising observation was how few of aerosol particles are in the near-pristine atmosphere, in spite of the abundant rainforest biota. Interestingly, the boreal forest, with its very different biological composition and ecosystem processes, produces a particle concen-

tration very similar to that over the Amazon, suggesting the presence of similar regulating mechanisms.

In collaboration with the MPI for Biogeochemistry in Jena, we are operating a Tall Tower Observatory at Zotino (ZOTTO) in central Siberia, where air is sampled from a height of 300 m to make observations that are representative for a large region. Here, we are providing a baseline for the observation of present and future changes in atmospheric composition and processes. At present, we are working on setting up a similar facility with a 320-m tall tower in the Amazon forest some 150 km upwind of Manaus, Brazil. This is a daunting task given the logistical obstacles of working in that region. In preparation, we have already set up a pair of 80-m towers with meteorological and chemical sensors where we are obtaining the first continuous records (Figure 1).

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

34 **35**

SELECTED PUBLICATIONS

Andreae, M. O.: Correlation between cloud condensation nuclei concentration and aerosol optical thickness in remote and polluted regions. Atmos. Chem. Phys., 9, 543-556 (2009).

Heintzenberg, J., Birmili, W., Otto, R., Andreae, M. O., Mayer, J.-C., Chi, X., Panov, A.: Aerosol particle number size distributions and *particulate light absorption at the ZOTTO* tall tower (Siberia), 2006–2009. Atmos. Chem. Phys., 11, 8703-8719 (2011).

Pöschl, U., Martin, S. T., Sinha, B., et al.: Rainforest aerosols as biogenic nuclei of clouds and precipitation in the Amazon. Science, 329, 1513-1516 (2010).

Kuhn, U., Ganzeveld, L., Thielmann, A., Dindorf, T., Welling, M., Sciare, J., Roberts, G., Meixner, F. X., Kesselmeier, J., Lelieveld, J., Ciccioli, P., Lloyd, J., Trentmann, J., Artaxo, P., Andreae, M. O.: Impact of Manaus City on the Amazon Green Ocean atmosphere: Ozone production, precursor sensitivity and aerosol load. Atmos. Chem. Phys., 10, 9251–9282 (2010).

Gunthe, S. S., King, S. M., Rose, D., Chen, Q., Roldin, P., Farmer, D. K., Jimenez, J. L., Artaxo, P., Andreae, M. O., Martin, S. T., Pöschl, U.: Cloud condensation nuclei in pristine tropical rainforest air of Amazonia: size-resolved measurements and modeling of atmospheric aerosol composition and CCN activity. Atmos. Chem. Phys., 9, 7551-7575 (2009).

ECOPHYSIOLOGY AND TRACE GAS EXCHANGE OF THE AMAZONIAN RAINFOREST

JÜRGEN KESSELMEIER

Figure 1: Inundated (flooded) forest at the Uatuma River 150 km northeast of Manaus. Large areas of the Amazonian rainforest are flooded periodically with inundation periods lasting for several months.

Approximately 20% of the area of the Amazon basin is covered by wetlands with permanent or seasonal soil water saturation. These wetlands vary considerably in relation to climate, hydrology, geochemistry, plant species composition and diversity, as well as biomass accumulation and productivity. They represent ecosystems most affected by climate change and inappropriate use of their resources. We developed a classification of Amazonian wetlands by determining key parameters for the definition of wetland types, in order to provide information for wetland science, environmental protection, and sustainable development policy. We showed that Amazonian floodplains consist of the most species-rich floodplain forest worldwide. The degree of endemism amounts to at least 10% of all flood-tolerant tree species evidencing that the wetlands have been part of the Amazon landscape since the existence of modern neotropical flora, and that wetland conditions are important drivers of the whole Amazonian biodiversity. Time series of climate and hydrology in the Amazon basin are too short to produce solid future climate scenarios. Our dendroclimatic studies have the potential to reconstruct the regional climate (precipitation, hydrology) and its association with global climate (sea surface temperatures of the Equatorial Pacific and Tropical Atlantic) to increase the knowledge on natural variability for periods before man-made global warming. Tree ring analyses contribute to a fast assessment estimating the productivity of tropical forests in terms of carbon sequestration in the wood biomass. Growth modeling of commercial tree species allows a species and site-specific definition of management criteria such as minimum logging diameters and cutting cycle to increase the sustainability of timber resource management. Our studies are of high relevance to public policies that contribute to a sustainable development of the largest tropical forest in the world.

The heterogeneity and high biodiversity of the Amazonian rainforest challenge our understanding of biosphere-atmosphere exchange especially as the environment is changing. Therefore, we

intensified our process-related studies of the exchange of volatile organic compounds (VOC) by investigating young tree individuals at the Instituto Nacional de Pesquisas da Amazônia (INPA), Manaus and contributing to ecosystemwide studies in cooperation with other groups. Organic acid measurements in close relation to our older data sets demonstrate that such oxygenated VOC species are exchanged bidirectionally, showing emission as well as uptake. This exchange is best described by a compensation point, represented by the ambient trace gas concentration at which the exchange is zero (production = consumption). Resuming our leaf level measurements in close relation to studies of ambient trace gas ratios, the role of such a compensation point could be demonstrated for the first time for a whole tropical ecosystem based on studies in the natural Amazonian forest and within Biosphere II, Arizona. From our European studies we learned that young leaves are suitable to classify the tree species in terms of their general emission pattern. Therefore, we screened young potted Amazonian

trees and demonstrated the release of isoprene, monoterpenes, methanol, and acetone to be the dominant VOC species emitted (Figure 2). Lightdependent monoterpene emission was found to be comparable to European tree species, though not reaching the Mediterranean ecosystem emission levels. Sesquiterpenes were not detected in these studies, but seem to be of

importance for the chemistry within the forest air. Contributing to a recent study comparing measurements within the natural Amazonian forest and within an artificial tropical rainforest ecosystem in Biosphere II, Arizona, it could be concluded that sesquiterpenes accumulate during the night, but that 50% of total emissions undergo within-canopy ozonolysis under day time conditions.

Figure 2: Assimilation and emission graph. CO₂ assimilation (top) and standardized isoprenoid emissions (5-min day time averages) of two young Amazonian tree species originating from different floodplain areas given on a leaf area or dry weight basis in $\mu g g^{-1} h^{-1} \pm SD$. In most cases highly significant (*** = P-value < 0.0001) differences between the igapó and várzea species were found. Measurements were performed under semicontrolled environmental conditions near the INPA laboratories in Manaus. Emissions under natural conditions in course of the flooding events with duration of several months have not been investigated so far (Bracho-Nunez et al., in preparation).

"The Amazonian rainforest is the world's largest tropical forest system and as such plays a dominant role in biosphere-atmosphere exchange with all its climatic effects. This forest is under pressure, and basic research is needed to contribute to political decisions concerning protection and sustainable use."

36 **37**

SELECTED PUBLICATIONS

Jardine, K., Yañez Serrano, A., Arneth, A., Abrell, L., Jardine, A., Artaxo, P., Alves, E., Kesselmeier, J., Taylor, T., Saleska, S., Huxman, *T.: Ecosystem-scale compensation points of* formic and acetic acid in the central Amazon. Biogeosci. Discuss., 8, 9283–9309 (2011), doi:10.5194/bgd-8-9283-2011.

Kesselmeier, J., Guenther, A., Hoffmann, T., Piedade, M. T. F., Warnke, J.: Natural volatile organic compound emissions from plants and their roles in oxidant balance and particle formation, in: M. Keller et al. (Eds.): "Amazonia and Global Change", Geophys. Monogr. Ser., Vol. 186, doi:10.1029/2008GM000717, AGU, Washington, D.C., 183-206 (2009).

Schöngart, J.: Growth-Oriented Logging (GOL): A new concept towards sustainable forest management in Central Amazonian varzea floodplains. For. Ecol. Manage. 256, 46-58 (2008).

Schöngart, J., Wittmann, F. Worbes, M.: Biomass and net primary productivity of central Amazonian floodplain forests, in: Junk et al. (Eds.): "Amazonian floodplain forests, Ecophysiology, Biodiversity and Sustainable Management", Ecological Studies Vol. 210, Springer Verlag, Berlin, 347-388 (2010).

Wittmann, F., Schoengart, J., Montero, J. C., Motzer, T., Junk, W. J., Piedade, M. T. F., Queiroz, H. L., Worbes, M.: Tree species composition and diversity gradients in whitewater forests across the Amazon Basin. J. Biogeography 33, 1334–1347 (2006).

VEGETATION FIRE EMISSIONS, HUMAN HEALTH, AND HUMAN SECURITY

JOHANN GEORG GOLDAMMER

Figure 1: Severe smoke pollution episodes have been documented in the Russian Federation since the 1990s. This photograph shows a mid-day situation in downtown Khabarovsk, Russian Federation in March 2008, typically resulting from spring time fires in the Far East of Russia and China.

Changes of fire regimes and an increasing vulnerability of humans to direct and secondary consequences of wildland fire are observed in many regions globally. Both increasing and decreasing intensity of land use are associated with set fires and often uncontrollable wildfire episodes. This was revealed by the fire emergencies in Greece, Russia, Canada, and the U.S.A. between 2007 and 2011. Wildfires burning at the interface between wildlands, the fringes of suburbs, metropolitan agglomerations, and rural settlements are increasingly impacting large populations, notably by extreme air pollution affecting human health and resulting in premature mortality. Other critical issues include wildfires burning on terrain contaminated by hazardous chemicals (e.g., by mercury) and radioactivity, which have been largely ignored in the past. Wildfires burning houses, infrastructures, storehouses, landfills, and agricultural

areas with deposits of pesticides and fertilizers generate substantial amounts of hazardous pollutants such as dioxins. Other threats are related to the heritages of armed conflicts, for example unexploded ordnance (UXO), depleted uranium ammunition, and landmines are posing additional threats. Wildfires occurring in such contaminated terrain are resulting in secondary damages, such as chemical and radioactive air pollution, and explosion of UXO and landmines.

RECENT THREATS CALLING FOR ACTION

The episode of drought, wildfires, and smoke pollution in Western Russia in July-August 2010 revealed the high vul nerability of modern society to vegetation fire smoke. Burning of desiccated natural and drained peatlands caused severe near-ground smoke pollution in rural and metropolitan areas. Statistics of the government of Russia revealed that in July and August 2010 about 55,800 more people died as compared to 2009. These additional deaths are likely to be premature and attributed to the combined effects of the heat wave and fire smoke pollution.

The Global Fire Monitoring Center (GFMC) / Fire Ecology Research Group of the Biogeochemistry Department, based in Freiburg, launched a scientific and political initiative in 2008 to address the challenges of fire occurring on terrain contaminated by radioactivity and unexploded weapons, and options for fire management. One of the newly developed methods of using prescribed fire in managing high-conservation value habitats of active and former military areas and war theater sites involves the use of armored equipment, remote ignition and monitoring systems (unmanned aerial systems).

Figure 2: Estimated total dose (Sv) (with and without ingestion), as a function of distance from the center of the CEZ, that could be received by children (1 year old) and adults during the year following a catastrophic wildfire.

RADIOACTIVE FIRE EMISSIONS

The territories most affected by radioactive pollution were contaminated by the release of radionuclides during the failure of reactor four of the Chernobyl Nuclear Power Plant in 1986 and cover a total area 20×10^6 ha with the main contaminator being 137Cs, but including also ⁹⁰Sr and ²³⁹Pu. The Chernobyl Wildfire Project, consisting of scientists from the Ukraine, USA, and Germany, developed a model to assess the potential implications of a catastrophic wildfire in the Ukrainian portion of the Chernobyl Exclusion Zone (CEZ) on populations living and working near the CEZ. The complete model consists of a source model, a transport model, and an exposure model. As a worst case

scenario, it is assumed that a fire would consume the biomass of pine forests and former agricultural lands and release any associated radionuclides into the atmosphere. The transport model assumes that the wind would blow primarily towards Kiev throughout the fire event.

child (1 year old) external exposures and doses via five exposure pathways (Firgure 2). Excluding the food ingestion pathways, calculated doses to populations at distances 30 km or greater from the release point are less than the critical thresholds that would require evacuations. However, Ukrainian law would require limiting consumption of certain foodstuffs to avoid exposure through ingestion.

"We are aiming to better understand, prevent, and manage the health and security consequences of fires burning in vegetation modified by cultural activities or by heritages of civilization."

38 **39**

The exposure model estimates adult and

SELECTED PUBLICATIONS

Goldammer, J. G., Statheropoulos, M., Andreae, M. O.: Impacts of vegetation fire emissions on the environment, human health and security – A global perspective, in: A. Bytnerowicz, M. Arbaugh, A. Riebau, C. Andersen (Eds.): *"Wildland fires and air pollution"*, *3–36*, Elsevier B.V., Developments in Environmental Science, Vol. 8, doi:10.1016/S1474-8177(08)00001-6. ISBN 978-0-08-055609-03; ISSN 1474-8177 (2009).

Goldammer, J. G.: Preliminary Assessment of the Fire Situation in Western Russia. Analysis of 15 August 2010, presented at the State Duma, Moscow, 23 September 2010. Int. Forest Fire News 40, 2-23 (2010).

Goldammer, J. G.: Wildland fires and human security: Challenges for fire management in the 21st century, in: Proceedings of the International Forest Fire Symposium Commemorating the International Year of Forests 2011, Sol Beach, Gangwon-do, Republic of Korea, 7-8 June 2011, p. 36-49. Korea Forest Research Institute, Seoul, Korea, 461 p. (2011).

Hohl, A., Niccolai, A., Oliver, C., Zibtsev, S., Goldammer, J. G., Petrenko, M., Gulidov, V.: The human health effects of radioactive smoke from a catastrophic wildfire in the Chernobyl Exclusion Zone: A worst case scenario. Earth Bioresources Life Quality (2011, in press).

Goldammer, J. G., Brunn, E., Held, A., Meyer, F., Pahl, K., Restas, A., Schulz, J., Stuber, H.-C.: Kontrolliertes Brennen zur Pflege von Zwergstrauchheiden (Calluna vulgaris) auf munitionsbelasteten Flächen: Problemstellung, bisherige Erfahrungen und geplantes Vorgehen im Pilotvorhaben im Naturschutzgebiet "Heidehof-Golmberg" (Landkreis Teltow-Fläming). Naturschutz und Biologische Vielfalt (2011, in press).

MULTISCALE TRACE GAS FLUX MEASUREMENT METH-ODOLOGIES FOR SEMIARID, ARID, AND HYPERARID **ECOSYSTEMS**

FRANZ X. MEIXNER

Figure 1: Chinese map showing the Taklamakan desert of Xinjiang (left). Fully automated incubation system for simultaneous fumigation of six soil samples under prescribed conditions of soil moisture, soil temperature and NO concentration (right).

Atmospheric CO, CH₄, and VOCs are oxidized by the hydroxyl and other radicals through various catalytic cycles, where nitrogen oxides ($NO_x = NO +$ NO₂) are key catalysts. Their concentrations decisively determine whether tropospheric O₃ is generated (usually in polluted regions) or destroyed (in remote parts of the globe). Adverse effects of O_3 on human health, plant productivity, and global warming has attracted scientific attention to globally increasing NO_X emissions. While fossil-fuel combustion in power stations and vehicles is still the best documented global NO_x source, knowledge of soil biogenic NO emissions is indeed steadily emerging, but is not available for natural and managed semiarid, arid, and hyperarid regions.

NO fluxes from soils are controlled by abiotic and many microbiological processes which themselves depend on N-availability and environmental conditions. In arid and hyperarid soils, nitrification is considered to be the dominant process. Because of its microbial nature, the most important (macroscopic) factors are soil moisture, soil diffusion, and soil temperature. Once emitted to

the atmosphere, NO reacts quite rapidly with O₃ to form NO₂, which may photolyze back to NO. Hence, NO_x fluxes may be highly variable with respect to time and space. This immediately poses the question of appropriate scales (and scale interaction), as soon as spatiotemporal averaging (integration) and/ or up-scaling of NO (NO_x) emissions from soils is applied. Therefore, we have developed a suite of methodologies for measurements of NO, NO₂, and O₃ fluxes on different spatial and temporal scales, particularly for arid and hyperarid ecosystems.

In our laboratory measurements small (100 g) soil samples are incubated and fumigated by variable NO concentrations to parameterize biogenic soil NO emissions in terms of soil moisture, soil temperature, N-fertilization, and ambient NO concentrations. For that, two fully automated incubation systems have been developed, which allow simultaneous treatment of 12 soil samples (Figure 1). This laboratory method enables fast scanning of biogenic NO soil emissions from the variety of subecosystems of drylands, for example desert, scrubland grassland, natural oasis, irrigated and

fertilized oasis. Knowing corresponding soil moisture, temperature and texture from meteorological monitoring (e.g., WMO data), NO emissions are up-scaled from laboratory-derived parameterizations to plot, ecosystem, oasis, and even regional scales.

For verification of our laboratory results, as well as for estimation (and parameterization) of NO_x fluxes in the atmospheric boundary layer, we perform in situ flux measurements of NO, NO₂, O₃, CO₂, H₂O, and energy by dynamic chamber, aerodynamic gradient, eddy covariance, and tethered balloon/kite techniques. These field techniques cover spatial scales from plot to oasis. Most recently, we have also applied Multi-Axis-Differential Optical Absorption Spectroscopy (MAX-DOAS) to measure NO₂ and H₂O column densities. Here, scattered sun light under various (mostly slant) elevation angles is observed, which makes MAX-DOAS measurements very sensitive to surface-near trace gas concentrations. Under conditions of desert oases, NO₂ and H₂O column densities can be assumed to be identical to the vertically integrated NO₂ and H₂O concentrations of the (internal) boundary layer caused by the oasis itself. Given the vertical boundary layer distribution of wind speed up- and downwind of the oasis, the so-called Integrated Horizontal Flux Technique can be applied to infer areaintegrated NO_X fluxes on the oasis scale. Preliminary results from a very recent field experiment at Milan oasis (June 2011, Xinjiang, NW China) are shown in Figure 2. These results confirm our laboratory results, that, because of efficient fertilization and irrigation, particularly cotton fields (greenish plots in Figure 2) emit substantial amounts of NO (5-10-fold more than mid-European wheat fields (10–30 ng m⁻²s⁻¹).

Given, that 80% of the Chinese cotton production originates from the 3000km long belt of oases surrounding the Taklamakan desert of Xinjiang (Figure 1), soil biogenic NO emission may exceed anthropogenic NO_X sources in NW China. Evapotranspiration from these (irrigated) cotton fields (also measured by our suite of flux methods) increase atmospheric H₂O concentrations considerably, at least on local scale. This, together with enhanced NO_X and VOC concentrations, will have interesting effects on local/regional atmospheric chemistry, particularly considering the strong and still increasing land use change (desert land to managed oases) in Xinjiang.

Figure 2: Diel variation of MAX-DOAS slant NO₂ column density (in 10¹⁴ molec cm⁻²) at the "natural forest (NF)" and the "Jujube field (JU)" site, upwind (NF) and downwind (JU) of Milan oasis, SE Xinjang, P.R. China, under different conditions of main wind direction.

"About 40% of planet Earth's land surface consists of semiarid, arid, and hyperarid land (drylands). While particularly biogenic emissions of nitric oxide (NO) from drylands may form more than half of the NO source to global soil, their quantification is entirely lacking."

40 **41**

SELECTED PUBLICATIONS

Foken, T., Meixner, F. X., Falge, E., Zetzsch, C., Serafimovich, A., Bargsten, A., Behrendt, T., Biermann, T., Breuninger, C., Dix, S., Gerken, T., Hunner, M., Lehmann-Pape, L., Hens, K., Jocher, G., Kesselmeier., J., Lüers, J., Mayer, J.-C., Moravek, A., Plake, D., Riederer, M., Rütz, F., Scheibe, M., Schier, S., Siebicke, L., Sörgel, M., Staudt, K., Trebs, I., Tsokankunku, A., Welling, M., Wolff, V., Zhu, Z.: ExchanGE processes in mountainous Regions (EGER) - Overview of design, methods, and first results. Atmos. Chem. Phys. Discuss., 11, 26245-26345 (2011).

Mamtimin, B., Meixner, F. X.: Air pollution and meteorological processes in the growing dryland city of Urumqi (Xinjiang, China). Sci. Total Environ., 409, 1277-1290 (2011).

Bargsten, A., Falge, E., Pritsch, K., Huwe, B., Meixner, F. X.: Laboratory measurements of nitric oxide release from forest soil with a thick organic layer under different understory types. Biogeosciences, 7, 1425-1471 (2010).

Pape, L., Ammann, C., Nyfeler-Brunner, A., Spirig, C., Hens, K., Meixner, F. X.: An auto*mated dynamic chamber system for surface* exchange measurement of non-reactive and reactive trace gases of grassland ecosystems. Biogeosciences, 6, 405–429 (2009).

Nyanganyura, D., Makarau, A., Mathuthu, *M.*, *Meixner*, *F. X.*: *A five-day back trajectory* climatology for Rukomechi Research Station (northern Zimbabwe) and the impact of large-scale flows on concentrations of coarse and fine size particulate mass. South Afr. J. Science, 104, 43-52 (2008).

THE ROLE OF BIOGENIC AEROSOLS AND MULTIPHASE CHEMISTRY IN THE EARTH SYSTEM AND IN PUBLIC HEALTH

ULRICH PÖSCHL

Figure 1: Birch pollen under a fluorescence microscope: mapping the microstructure and chemical composition of airborne allergens (left). Overlay of fluorescence and bright field microscope image (right).

Biogenic aerosols are ubiquitous in the atmosphere, influencing the biosphere, climate, and public health. They play an important role in the spread of biological organisms and ecosystems, and they can cause or enhance human, animal, and plant diseases. Moreover, aerosol particles serve as nuclei for water droplets and ice crystals initiating the formation of clouds and precipitation. The abundance, sources, and multiphase chemical interactions of biogenic aerosols are, however, still poorly understood and quantified.

Primary biological aerosols (PBA) include bacteria, fungal spores, and pollen emitted directly from the biosphere to the atmosphere, while secondary organic aerosols (SOA) are formed in the atmosphere by oxidation and condensation of volatile organic compounds (VOC) released from plants and microorganisms. Over vegetated continental

regions, biogenic particles constitute the biological reproduction in the ecosysnatural background aerosol and are thus key elements of the unperturbed climate system. One of the few continental regions where atmospheric aerosol properties and effects are not dominated by anthropogenic sources is the Amazon. In the wet season, when ambient conditions approach those of the pristine preindustrial era, we found that the fine submicron particles accounting for most cloud condensation nuclei (CCN) are predominantly composed of SOA, while supermicron particles relevant as ice nuclei (IN) consist mostly of PBA. The Amazon Basin can be pictured as a large biogeochemical reactor in which plant and microbial emissions in combination with high water vapor, solar radiation, and photo-oxidant levels produce PBA and SOA particles. The biogenic aerosol particles serve as nuclei for clouds and precipitation sustaining the hydrological cycle and

tem. The feedback mechanisms involved are likely important for stabilizing the Amazonian rainforest ecosystem, and they may also be generally relevant for the evolution of ecosystems and climate on global scales and in the Earth's history. To test and quantify this hypothesis we continue further mechanistic studies and long-term observations of aerosolcloud-precipitation interactions under pristine conditions in tropical, temperate, and boreal forest regions.

In laboratory and field experiments we found that organic aerosols can form a variety of solid or semisolid amorphous phases (glasses, rubbers, gels, etc.) depending on ambient temperature and relative humidity. The different amorphous phases provoke a rethinking of atmospheric aerosol processes, because organic aerosols were traditionally assumed to be in a liquid state. The phase

state, however, can strongly influence the particles' ability to act as CCN or IN, the partitioning of semivolatile compounds, and the rate of chemical reactions.

Multiphase chemical reactions are highly relevant for aerosol health effects, because they can change the particles' surface properties and bulk composition. We discovered that the reaction of ozone with aerosol particles leads to the formation of long-lived reactive oxygen intermediates (ROI). These intermediates are of central importance in the chemical transformation and adverse health effects of toxic and allergenic air particulate matter like

soot, polycyclic aromatic hydrocarbons, and proteins. For example, ROI are involved in the nitration of proteins by polluted air, which can strongly increase the allergenic potential of proteins. It may explain why air pollution leads to an enhancement of allergic diseases in industrialized countries as indicated by epidemiological studies. In collaboration with life scientists we continue to explore the role of reactive oxygen and nitrogen species and multiphase chemical reactions in the coupling of environmental and physiological processes from the self-cleaning of the atmosphere and secondary organic aerosol formation to oxidative stress, biological aging, inflammation, and disease.

"We aim at understanding the properties, interactions, and effects of biogenic aerosols and multiphase processes in the Earth system and public health."

42 **43**

SELECTED PUBLICATIONS

Pöschl, U.: Atmospheric aerosols: composition, transformation, climate and health effects. Angew. Chem. Int. Ed. 44, 7520-7540 (2005).

Pöschl, U., Martin, S. T., Sinha, B., Chen, Q., Gunthe, S. S., Huffman, J. A., Borrmann, S., Farmer, D. K., Garland, R. M., Helas, G., Jimenez, J. L., King, S. M., Manzi, A., Mikhailov, E., Pauliquevis, T., Petters, M. D., Prenni, A. J., Roldin, P., Rose, D., Schneider, J., Su, H., Zorn, S. R., Artaxo, P., Andreae, M. O.: Rainforest aerosols as biogenic nuclei of clouds and precipitation in the Amazon. Science 429, 1513-1516 (2010).

Shiraiwa, M., Sosedova, Y., Rouvière, A., Yang, H., Zhang, Y. Y., Abbatt, J. P. D., Ammann, M., Pöschl, U.: The role of long-lived reactive oxygen intermediates in the reaction of ozone with aerosol particles. Nature Chem. 3, 291-295 (2011).

Shiraiwa, M., Ammann, M., Koop, T., Pöschl, U.: Gas uptake and chemical aging of semisolid organic aerosol particles. Proc. Nat. Acad. Sci. 108, 11003-11008 (2011).

Su, H., Cheng, Y., Oswald, R., Behrendt, T., Trebs, I., Meixner, F. X., Andreae, M. O., Cheng, P., Zhang, Y., Pöschl, U.: Soil nitrite as a source of atmospheric HONO and OH radicals. Science 333, 1616-1618 (2011).

Figure 2: Aerosol and water cycle over pristine tropical rainforest: primary biological and secondary organic aerosols from forest emissions serve as nuclei for water droplets and ice crystals in clouds and precipitation.

GEOROC AND GEOREM DATABASES

BÄRBEL SARBAS

The open-access geochemical database GEOROC (http://georoc.mpch-mainz. gwdg.de) contains published analyses of volcanic rock samples from ten different geological settings. It contains analyses of whole rocks, minerals as well as melt inclusions. While at the beginning, GEOROC was confined mainly to young oceanic basalts, in the last couple of years it was extended to samples from numerous continental occurrences ranging in geological age from Recent to Archean. The data are collected from more than 10,000 peer-reviewed publications. The GEOROC webpage allows queries based on geological, geographical, chemical, petrographical as well as bibliographical criteria.

The GEOROC database is cross-linked with GeoReM, a database for reference materials used in geological and environmental research which is also maintained at the Max Planck Institute for Chemistry. GEOROC is used by scientists from about 100 different countries. The total number of users per month varies between 2,000 and 3,000. Applications of the database are found mainly in hard-rock geochemical but also in biogeochemical and atmospheric research. GEOROC is among the Earth sciences databases recommended by Nature journals.

Currently, a map application that allows the illustration of geochemical trends as a function of latitude and longitude as well as the link of the data in GEOROC to the original publications is being prepared. In the long term a mechanism has to be prepared that allows authors to supply their data directly into the database.

Figure 1: Screenshot of the GEOROC database.

Figure 2: Reference glasses of different providers used in microanalysis. The GeoReM database contains all published analytical data of these glasses and approximately 2,500 other reference materials.

GEOREM DATABASE

Reference materials are essential to quite different fields of geochemical and environmental research. They are used as samples for calibration, method validation, quality control, quality assurance and to establish metrological traceability. In paleoclimate research, important reference materials are corals, mussels, synthetic carbonates, silicates and phosphates, lake sediments, seawater and others. Because the number of reference materials and their analytical data have significantly increased in the last decades, the GeoReM database was developed, implemented and continually updated by members of the Paleoclimate Research Group. Analytical geochemists can easily have access on the internet (www.georem. mpch-mainz.gwdg.de) to information about those materials that are of particular importance to their research. Currently, GeoReM contains ca. 2,500 reference materials and almost 27,000 analyses from more than 5,600 scientific

publications. In an average month, this site is visited more than 3,200 times, and this tool is now being consulted by researchers from over 70 countries.

The database also contains data for microanalytical reference materials, which have gained a wide interest because of the increasing use of in-situ microanalytical techniques, such as laser ablation (LA) – ICP – mass spectrometry (MS). Using LA-ICP-MS, it is possible to get highly resolved data sets for paleoclimate research in a variety of geological and biogenic samples, such as speleothems, ostracods, and mussels. The Max Planck Institute has also contributed to create new microanalytical reference materials, the eight MPI-DING glasses. These materials have been certified in cooperation with 60 international laboratories using 16 different analytical techniques. They are the best characterized reference materials for microanalytical element and isotopic analysis, and are used worldwide in 331 laboratories.

"Considering the constantly increasing amount of published geochemical analytical data, GEOROC has become an essential tool for geoscientists."

44 **_ 45**

SELECTED PUBLICATIONS

Sarbas, B.: The GEOROC database as part of a growing geoinformatics network, U. S. Geological Survey Scientific Investigations Report 2008-5172, 42-43 (2008).

Jochum, K.P., Nohl, U, Herwig, K., Lammel, E., Stoll, B., Hofmann, A.W.: GeoReM: A new geochemical database for reference materials and isotopic standards, Geostandards and Geoanalytical Research, 29, 333-338 (2005).

Jochum, K.P., Nohl, U.: Reference materials in geochemistry and environmental rersearch and the GeoReM database, Chemical Geology, 253, 50-53 (2008).

Jochum, K.P., Stoll, B.: Reference materials for elemental and isotopic analyses by LA-(MC)-ICPMS: successes and outstanding needs, In: Laser ablation ICP-MS in the Earth sciences: Current practices and outstanding issues (P. Sylvester, ed.). Mineral. Assoc. Can. Short Course Series, 40, 147-168 (2008).

Jochum, K.P., Wang, X.-H.: Geochemical and environmental reference materials and the GeoReM database, 地球化学与环境分析标 准物质及其GeoReM数据库 (in Chinese), Rock and Mineral Analysis (China), 28, 311-315 (2009).

OSTRACOD SHELLS IN LAKE SEDIMENTS FROM TIBET AS PALEOENVIRONMENTAL ARCHIVES OF PAST CLIMATE

KLAUS PETER JOCHUM

Figure 1: Lake Nom Co in the Central Tibetan Plateau is a source for ostracods.

A promising new application in paleoclimate research is the investigation of ostracod shells found in lake sediments. Ostracods are millimeter size crustaceans with a shell consisting of calcite and chitin (Figure 2), and exist in the fossil record all the way back to the Cambrian. Their shells can be used as archives of information about past environmental conditions, such as climate, vegetation, landscape evolution, and human activity. We are especially interested in the investigation of ostracod shells from lake Nam Co, the Central Tibetan Plateau, for studying regional and supraregional climatic events. These investigations are being done in co-operation with groups of the Max Planck Institute for Biogeochemistry in Jena and the Universities of Mainz, Braunschweig, and Jena.

Our laboratory offers the possibility to perform precise trace element and Pb,

U, and Th isotope ratio measurements of single ostracod shells at high spatial resolution using inductively coupled plasma (ICP) mass spectrometers coupled with laser ablation (LA) systems.

High sensitivity and precision is important since the mass of the shell (several µg) and the concentrations of some trace elements are low. An extreme example is the Th-230 isotope, which is important for the Th-U dating method, where an ostracod shell contains only 10⁻¹⁷g ²³⁰Th or 30,000 atoms.

In our study, we focused on two sediment cores drilled in lake Nam Co. The sections correspond to age intervals from 250 a to 6,750 a (core 1) and 17,600 a (core 2) BP, respectively. About

Figure 2: Ca. 0.6-mm-long ostracod shell from Tibet and U/Th mapping determined by LA-ICP-MS using a spot size of 12 µm.

100 shells of ostracods, belonging to three taxa, were selected and analyzed for trace element abundances and Pb and U isotope ratios by LA-ICP-MS. Whereas the CaO content for ostracods is uniform (about 56.1% m/m), MgO, Sr, Ba, and Pb show significant variations. For example, the shells show high Sr content (about 10,000 μ g/g) within the age interval of 250 to 1,000 a BP, low Sr (about 1500 μ g/g) from 2,400 to 10,000 a BP, and highly variable and pronounced peak values between 10,000 and 17,600 a BP (Figure 3). In addition, our results from core 1 show identical U and Pb isotope ratios for ostracods from the same core depth indicating that they reflect the isotope composition of the lake water. Influence of vital effects may, hence, be negligible or stable. The ²⁰⁸Pb/²⁰⁶Pb isotope ratios and the

²³⁴U/²³⁸U activity ratio are correlated, and also show significant variability with age. These results are in agreement with geochemical and mineralogical investigations of the sediments and suggest that some trace element abundances (e.g., Sr), and Pb and U isotope ratios reflect past climate variability: reduced precipitation and runoff, low lake water volume and maximum salinity since ca. 1,000 a BP, a large contribution of monsoonal precipitation and melt water input between ca. 2,400 and 10,000 a BP, and a high variability of precipitation between 10,000 and 17,600 a BP. The lowest U and Pb isotope ratios determined in core 1 are observed in a 6,000-a old ostracod shell, where a high intensity of monsoonal precipitation, associated with elevated lake levels in Tibet, is recorded.

Figure 3: LA-ICP-MS data for Sr concentrations, (234U/238U) activity and 208Pb/206Pb isotope ratios determined in single ostracod shells of lake Nam Co, Tibet.

"Ostracod shells found in lake sediments are useful archives of information about past environmental conditions."

46 **47**

SELECTED PUBLICATIONS

Müller, W. E. G., Jochum, K. P., Stoll, B., Wang, *X. H.: Formation of giant spicule from quartz* glass by the deep sea sponge Monorhaphis. Chem. Mater. 20, 4703-4711 (2008).

Mertz-Kraus, R., Brachert, T. C., Jochum, K. P., Reuter, M., Stoll, B.: LA-ICP-MS analyses on coral growth increments reveal heavy winter rain in the Eastern Mediterranean at 9 Ma. Palaeogeogr., Palaeoclimatol., Palaeoecol. 273, 25-40 (2009).

Jochum, K.P., Stoll, B., Friedrich, J.M., Amini, M., Becker, S., Dücking, M., Ebel, D.S., Enzweiler, J., Hu, M., Kuzmin, D., Mertz-Kraus, R., Müller, W.E.G., Regnery, J., Sobolev, A., Wang X., Zhan, X.: Laser ablation-inductively coupled plasma-mass spectrometry and its application in geochemistry, cosmochemistry and environmental research, Rock and Mineral Analysis, 28, 53-68 (2009).

Mertz-Kraus, R., Jochum, K. P., Sharp, W. D., Stoll, B., Weis, U., Andreae, M. O.: In situ ²³⁰Th-²³²Th-²³⁴U-²³⁸U analysis of silicate glasses and carbonates using laser ablation single-collector sector-field ICP-MS. JAAS, 25, 1895–1904 (2010).

Sobolev, A. V., Hofmann, A. W., Jochum, K. P., Kuzmin, D. V., Stoll, B: A young source for the Hawaiian plume. Nature 476, 434-437 (2011).

Wang, X., Gan, L., Jochum, K.P., Schröder, H.C., Müller, W.E.G.: The largest bio-silica structure on Earth: The giant basal spicule from the deep-sea glass sponge Monorhaphis chuni, Evidence-Based Complementary and Alternative Medicine, Vol. 2011, doi:10.155/2011/540987 (2011).

STABLE ISOTOPES IN THE MODERN OCEANS

STEPHEN GALER

Figure 1: Hydrocasting using the NIOZ ultraclean Titan frame aboard RRS James Cook on GEOTRACES leg 3 in the Western Atlantic (left), a seasonal phytoplankton bloom in the Southern Atlantic ocean (middle), and Acantharia species under the microscope (right).

The research of the Isotope Biogeochemistry Group spans a wide range of Earth Science disciplines. Our two main tools are 1) radiogenic isotope systems, which are used to trace provenance, and 2) natural mass-dependent stable isotope fractionation, where we are leaders in double-spike analytical methodology; measurements are performed by thermal ionization mass spectrometry.

Our recent focus has been on understanding the biogeochemistry of key

nutrient trace metals in the world's oceans and how they impact on ocean ecosystems and the carbon cycle. The approach is to develop new geochemical proxies that 1) provide information on the distribution of trace nutrients and mechanisms regulating their utilization, 2) complement existing information from other nutrients, and 3) serve as potential tracers of past changes in the global carbon cycle. Below we highlight two novel case studies on the oceanic distribution of stable isotopes of two nutrient elements.

The Southern Ocean is a high nutrient, low chlorophyll (HNLC) region, meaning that available macronutrients (C, N, P, Si) are capable of supporting a huge plankton crop, but biological productivity is limited by the availability of micronutrients, such as Fe, Zn, and Cd. These transition metals are embedded in vital enzymes, such as carbonic anhydrase, involved in photosynthetic fixation of carbon dioxide, and their biological availability impacts directly on the efficiency of the "biological carbon pump."

Figure 2: Schematic cartoon showing the location of Antarctic fronts, ocean circulation, and water mass distribution in the Southern Ocean (left) *Cd* isotope fractionation factors (α) following Rayleigh model ($\varepsilon^{112/110}$ Cd, deviation in parts per 10⁴; right).

The isotope fractionation of cadmium was examined in a suite of seawater samples from the Southern Ocean, including a surface transect as well as depth profiles, collected under the auspices of the GEOTRACES consortium (www.geotraces.org). Our results show that Cd becomes isotopically "heavy" in surface waters due to the incorporation of "light" Cd into phytoplankton. Further, the vertical consumption/regeneration cycle of cadmium follows simple first-order Rayleigh kinetics, with the principal control being the vigor of biological productivity in surface waters. Also striking is evidence for a biogeochemical Cd isotope "divide" located at 56°S, corresponding exactly to the front marking the southerly boundary of the Antarctic Circumpolar Current with the Weddell Gyre. The divide also marks a jump in the Rayleigh isotope fractionation factor, which appears to relate to the mechanism of biological Cd uptake, since phytoplankton communities differ across the front (Figure 2). Thus, cadmium isotopes are able to delimit biogeochemical provinces in the ocean and trace surface productivity and thus, importantly, the CO₂ drawdown. Additional insights will come from studies in other key nutrient-limited regions of the oceans, which will provide a basis

Early work on dissolved Sr in GEOSECS ocean profiles from the Atlantic and Pacific showed Sr/salt variations with depth, providing evidence for depletion of dissolved Sr in surface waters. This depletion was attributed to uptake

for exploiting Cd isotopes as proxies for

past nutrient distribution and produc-

tivity in paleoarchives.

of Sr from surface waters by acantharians, whose skeleton is made of celestite (SrSO₄), which subsequently dissolves at depth, thus exerting a control on strontium cycling in the water column. We have explored the potential of stable Sr isotopes as a tracer of such nutrient-like behavior in seawater, by analyzing a full North to South transect in the Atlantic Ocean (Figure 3). The $^{88}\text{Sr}/^{86}\text{Sr}$ ratios, expressed as $\delta^{88/86}\text{Sr}$ (deviations in per mil), show little variation in the deep waters. In contrast, surface waters show subtle variations along the transect. The Southern Ocean compositions tend to be isotopically slightly lighter, overall, than those of the Atlantic further north. Our data suggest that constancy of $\delta^{88/86}$ Sr in seawater cannot be assumed a priori. Mapping the ocean $\delta^{88/86}$ Sr distribution appears to be an important task, and may help elucidate the internal biological cycling of strontium in the water column.

Figure 3: Distribution of $\delta^{88/86}$ Sr in seawater along a North–South transect in the Atlantic Ocean from three cruises.

"It is crucial to understand the biogeochemical cycling of key nutrient trace metals in the world's oceans and how this impacts on marine ecosystems and the global carbon cycle."

48 **49**

SELECTED PUBLICATIONS

Abouchami, W., Galer, S.J.G., Middag, R., de Baar, H., Laan, P., Alderkamp, A., Feldmann, H., Andreae, M.O.: Modulation of the Southern Ocean Cd isotope signature by ocean circulation and primary productivity. Earth Planet. Sci. Lett. 305, 83-91 (2011).

Heuser, A., Tütken, T., Gussone, N., Galer, S.J.G.: Calcium isotopes in fossil bones and teeth - diagenetic versus biogenic origin. Geochim. Cosmoch. Acta, 75, 3419-3433 (2011).

Knipper, C., Maurer, A-F., Peters, D., Meyer, C., Brauns, M., Galer, S.J.G., von Freeden, U., Schöne, B.R., Alt, K.W.: Mobility in Thuringia or mobile Thuringians: a strontium isotope study from early medieval central Germany. In: J. Burger, E. Kaiser W. Schier, eds., Population Dynamics in Pre- and Early History. TOPOI, Berlin Studies of the Ancient World (April 2012).

Moore, I., White, W.M., Paul, P., Duncan, R.A., Abouchami W., Galer, S.J.G.: Evolution of shield-building and rejuvenescent volcanism of Mauritius. J. Volc. Geotherm. Res., 207, 47-66 (2011).

Schmitt, A.D., Galer, S.J.G., Abouchami W.: Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. Earth Planet. Sci. Lett., 277, 262-272 (2009).

Skonieczny, C., Bory, A., Bout-Roumazeilles, V., Abouchami, W., Galer, S.J.G., Crosta, X., Stuut, J.-B., Meyer, I., Chiapello, I., Podvin, T., Chatenet, B., Diallo, A., Ndiaye T.: The 7-13 March 2006 major Saharan outbreak: multiproxy characterization of mineral dust deposited on the West African margin. J. Geophys. Res. 116, D18210, doi:10.1029/2011JD016173 (2011).

COSMOGENIC NOBLE GAS ISOTOPES IN EARTH AND SPACE SCIENCES

ULRICH OTT

Figure 1: Meteorite samples wrapped in nickel foil waiting for gas extraction by heating them up to 2000°C, followed by mass spectrometric analysis.

This is because noble gases are rare. The rare neon isotope ²¹Ne, in particular, is efficiently produced by spallation reactions on the abundant elements Mg, Al, and Si and is a useful indicator for the length of "cosmic ray exposure" (CRE). Cosmic ray spallation is taking place throughout the Galaxy – from the interstellar medium on the largest scale down to our Solar System and the terrestrial environment. This process also works on all time scales – from before the formation of the Solar System and throughout its history.

BEFORE THE BEGINNING

Primitive meteorites contain solids that predate the Solar System: stardust grains formed from the winds emanating from low-mass stars or from the ejecta of exploding supernovae. Showing in their isotopic makeup the effects of element synthesis in their parent stars, the nonradiogenic composition of elements commonly used for age dating via long-lived radionuclides is ill determined. This – plus the limited number of atoms in µm-sized grains - makes the traditional approach to date them challenging if not impossible.

An alternative is the determination of a presolar CRE age, which in the case of silicon carbide grains from Red Giant stars can be done by measuring cosmogenic ²¹Ne produced on the silicon of these grains. An important consideration is the loss of Ne due to nuclear recoil. The recoil range – as we have determined in previous work – is about 2.5 µm, and we have applied the appropriate corrections to grains analyzed in collaboration at ETH Zürich (Ott et al., 2009). Resulting presolar CRE ages are surprisingly short, typically less than 100 Ma (Figure 2).

IN THE SOLAR SYSTEM

The traditional application of cosmogenic noble gases is determining CRE ages of meteorites, which then provides information about dynamics in the Solar System at the present time. In some cases, peaks in the age distribution point to major impact events in the asteroid region (e.g., ~45% of all H chondrites belong to the ~7 Ma peak). Similarly, the several tens of meteorites derived from Mars were most likely ejected in not more than ~8 separate events (cf. Mohapatra et al., 2009). In work recently completed, we have ana-

lyzed noble gases in a large L chondrite breccia contributing to a study of solar wind implantation and regolith dynamics of the parent asteroid (Welten et al., 2009). Currently we pursue similar studies on howardite meteorites that are presumably derived from asteroid 4 Vesta. The results will help in understanding observations by the Dawn spacecraft which is currently orbiting and observing Vesta.

Further studies involving cosmogenic noble gas isotopes deal with possible preirradiation of chondrules in the Solar Nebula and with micrometeorites found in Antarctica. Results from the latter study may put constraints on possible sources as well as their possible importance as suppliers of volatiles to Earth.

ON EARTH

While Earth's atmosphere and magnetic field are potent shields against cosmic rays, sensitive methods still allow the identification of cosmic-ray produced nuclides on Earth, in particular near the magnetic poles and at high altitudes. While most commonly radionuclides such as ¹⁰Be, ²⁶Al, or ³⁶Cl have been used, neon isotopes have a role to play

Figure 2: SEM images of two representative stardust silicon carbide grains from Red Giant stars analyzed for cosmogenic neon.

when exposure ages are long so that the radionuclides are getting saturated (Figure 3). Care has to be taken, however, to minimize and/or correct for competing reactions such as ${}^{18}O(\alpha,n){}^{21}Ne$ initiated by α -particles from U/Th decay as well as for trapped crustal neon.

We have participated in a joint radionuclide-noble gas study of quartz samples from Queen Maud Land (East Antarc-

tica). Several samples show extremely long surface exposures ages (>8 Ma) and correspondingly low inferred erosion rates (<5 cm/Ma), which in turn requires extremely cold and hyperarid climate conditions. The data do not support the notion of a temporary large scale retreat of the East Antarctic ice sheet during a suspected warming episode in the Pliocene (Altmaier et al., 2009).

"Abundances of noble gas isotopes in solids are easily affected by cosmic ray-induced reactions, allowing their use as sensitive tracers and time markers."

50 **51**

SELECTED PUBLICATIONS

Altmaier, M., Herpers, U., Delisle, G., Merchel, S., Ott, U.: Glaciation history of Queen Maud Land (Antarctica) reconstructed from in-situ produced cosmogenic ¹⁰Be, ²⁶Al and ²¹Ne. Polar Science 4, 42–61 (2010).

Mohapatra, R. K., Schwenzer, S. P., Herrmann, S., Murty, S. V. S., Ott, U., Gilmour, J. D.: Noble gases and nitrogen in Martian meteorites Dar al Gani 476, Sayh al Uhaymir 005 and Lewis Cliff 88516: EFA and extra neon. Geochim. et Cosmochim. Acta 73, 1505-1522 (2009).

Ott, U., Heck, P. R., Gyngard, F., Wieler, R., Wrobel, F., Amari, S., Zinner, E.: He and Ne *ages of large presolar silicon carbide grains:* Solving the recoil problem. Publ. Astron. Soc. Aust. 26, 297-302 (2009).

Welten, K., Caffee, M. W., Franke, L., Jull, A. J. T., LeClerc, M. D., Metzler, K., Ott, U.: The L3-6 chondritic regolith breccia Northwest Africa (NWA) 869: (II) Noble gases and cosmogenic radionuclides. Meteor. Planet. Sci. 46, 970-988 (2011).

Figure 3: Minimum surface ages for quartz samples from Queen Maud Land. For long ages, ${}^{26}Al$ ($T_{\frac{1}{2}} = 0.7 \text{ Ma}$) and ${}^{10}Be$ (T = 1.4*Ma*) are in saturation so that ages based on stable ²¹Ne are more realistic.

MANTLE GEOCHEMISTRY

ALEXANDER V. SOBOLEV

Figure 1: Sibirian flood basalts flows at Putorana plateau, Taymyr Penninsula, Russia.

The timescale of crustal recycling is important to our understanding of mantle circulation rates. Correlations of uranogenic lead isotopes in lavas from ocean islands such as Hawaii or Iceland, when interpreted as model isochrons, have yielded source differentiation ages between 1 and 2.5 billion years (e.g., Gast, 1981). However, if such correlations are produced by mixing of unrelated mantle components they will have no direct age significance. Re-Os decay model ages take into account the mixing of sources with different histories (Sobolev et al., 2008), but they depend on the assumed initial Re/Os ratio of the subducted crust, which is poorly constrained because of the high mobility of rhenium during subduction. Recently (Sobolev et al., 2011a) we reported the first data on ⁸⁷Sr/⁸⁶Sr ratios for 138 melt inclusions in olivine phenocrysts from lavas of Mauna Loa shield volcano, Hawaii, indicating enormous mantle source heterogeneity. We show that highly radiogenic strontium in severely rubidium-depleted melt inclusions matches the isotopic composition of 200–650-Myr old seawater (Figure 2). We infer that such seawater must have contaminated the Mauna Loa source rock, before subduction, imparting a unique "time stamp" on this source. Small amounts of seawater-derived strontium in plume sources may be common but can be identified clearly only in ultradepleted melts originating from generally highly (incompatible-element) depleted source components. The presence of 200–650-Myr old oceanic crust in the source of Hawaiian lavas implies a timescale of general mantle circulation with an average rate of about 2 cm yr⁻¹, much faster than previously thought.

Large igneous provinces (LIPs) are known for their rapid production of enormous volumes of magma (up to several million cubic kilometers in less than a million years), for marked thinning of the lithosphere, often ending with a continental break-up, and for their links to global environmental catastrophes, for example mass-extinction

Figure 2: Isotope composition of the most radiogenic Hawaiian melt inclusions over the time evolution of Sr isotopic composition of seawater (Sobolev et al., 2011a). The blue field represents the acceptable age range for the recycled seawater component. events. Despite the importance of LIPs, controversy surrounds even the basic idea that they form through melting in the heads of thermal mantle plumes. The Permo-Triassic Siberian Traps - the type example and the largest continental LIP – is located on thick cratonic lithosphere, and was synchronous with the largest known end-Permian massextinction event. However, there is no evidence of premagmatic uplift or of a large lithospheric stretching, as predicted above a plume head. Moreover, estimates of magmatic CO₂ degassing from the Siberian Traps are considered insufficient to trigger climatic crises, leading to the hypothesis that the release of thermogenic gases from the sediment pile caused the mass extinc-

tion. Recently, we presented petrological evidence for a large amount (15 wt%) of dense recycled oceanic crust in the head of the plume and developed a thermomechanical model that predicts no premagmatic uplift and requires no lithospheric extension (Sobolev et al., 2011b). The model (Figure 3) implies extensive plume melting and heterogeneous erosion of the thick cratonic lithosphere over the course of a few hundred thousand years. The model suggests that massive degassing of CO₂ and HCl, mostly from the recycled crust in the plume head, could alone trigger a mass extinction and predicts it happening before the main volcanic phase, in agreement with stratigraphic and geochronological data for the Siberian Traps and other LIPs.

"Recycling of oceanic crust through subduction, mantle upwelling and remelting is a key mechanism to explain mantle composition, geodynamics, and magmatism."

52 **_ 53**

SELECTED PUBLICATIONS

Sobolev, A. V., Hofmann, A. W., Jochum, K.-P. et al.: A young source for the Hawaiian plume. Nature 476, 434–437 (2011a).

Sobolev, S. V., Sobolev, A. V., Kuzmin, D. V. et al.: Linking mantle plumes, large igneous provinces and environmental catastrophes. Nature 477, 312–316 (2011b).

Sobolev, A. V., Hofmann, A. W., Brügmann, G. et al.: A quantitative link between recycling and osmium isotopes. Science 321, 536 (2008).

Sobolev, A. V., Hofmann, A. W., Kuzmin, D. V. et al.: The amount of recycled crust in sources of mantle-derived melts. Science 316, 412–417 (2007).

Sobolev, A. V., Hofmann, A. W., Sobolev, S. V., Nikogosian, I. K.: An olivine-free mantle source of Hawaiian shield basalts. Nature 434, 590–597 (2005).

Figure 3: Numerical model for interaction of thermo-chemical plume containing 15 wt% of recycled crust with an excess temperature of 250°C (Sobolev et al., 2011b). a – Premagmatic uplift; b,c – temperature distributions at model times of 0.15 and 0.50 Myr.

The solid line marks the boundary of the depleted lithosphere, and the dashed half-circle denotes the initial shape of the starting plume.

HIGH PRESSURE CHEMISTRY AND PHYSICS

MIKHAIL I. EREMETS

Figure 1: Multimegabar pressures in a diamond anvil cell. Photographs of a pair of diamond anvils with a transparent gasket in between, taken in transmission mode. The diamond darkens at these pressures.

The production of metallic hydrogen is our main current goal. We received an Advanced Grant from the European Research Council in 2010 in the amount of €1.9 million to support this research.

Molecular hydrogen is expected to display metallic properties at pressures of ~4 Mbars (400 GPa). This metal is predicted to be superconducting with a very high critical temperature T_c of 200-400 K, and it may acquire a new quantum state as a metallic superfluid and a superconducting superfluid. However, in previous experiments which were performed at low temperatures, <100 K, and up to 300 GPa, hydrogen remained in the molecular insulating state.

We found that molecular hydrogen transforms to the conductive and metallic state at high pressures at room temperature (Eremets and Troyan 2011). At P>200 GPa the Raman frequency of the molecular vibron strongly decreased

and spectral width increased evidencing strong interaction between molecules. Deuterium behaved similarly. Above 220 GPa hydrogen became opaque and electrically conductive. At 260–270 GPa hydrogen transformed to metal as the conductance of hydrogen sharply increased and little changed upon further pressurizing up to 300 GPa (corresponding to a 13-fold compression of solid hydrogen), or cooling down to at least 30 K; the sample also reflected light well. The metallic phase transformed back into molecular hydrogen at 295 K and ~200 GPa. This significant hysteresis indicates that the transformation of molecular hydrogen to metal is accompanied by a first-order structural transition presumably into a monoatomic liquid state. We also determined the melting curve of hydrogen (Eremets and Trojan 2009) and found that the melting temperature decreases at pressures above ~150 GPa indicating that metallic hydrogen might be in the

liquid state at zero temperature similar

to helium where quantum effects also are high.

On the way to metallic hydrogen we overcame a lot of experimental difficulties. To study hydrogen multimegabar pressures are required. We reached record static pressures of 440 GPa and were able to study a number of substances at ultrahigh pressures. We measured the density of iron up to 370 GPa (a pressure exceeding that found in the center of the Earth). Recently, we found at megabar pressures new pressure-induced superconductors: silane (Eremets, Trojan et al. 2008) and FeSe (Medvedev, McQueen et al. 2009).

An example of amazing transformations under high pressure is transparent sodium (Ma, Eremets et al. 2009). Intuitively, under pressure metals should exhibit a more pronounced free-electron-like behavior because interatomic distances decrease and hence the widths of the valence and conduction bands increase.

But at very high densities core electrons can overlap and force their outer electrons into the interstitials between the atoms where electron density strongly localizes. This is responsible for the collapse of the metallic state. Sodium thus transforms to the elemental ionic solid where sodium atoms play the role of cations while the localized electrons behave as anions.

Our group works on the following problems of solid-state physics and chemistry: metallic hydrogen, hightemperature superconductivity in hydrogen-rich materials, polymeric nitrogen, and related materials. We use high-pressure diamond anvil cells (DAC) and perform various optical, Xray diffraction and electrical measurements in a wide temperature range from millikelvin to several kilokelvin.

Figure 2: Sodium clamped in a metallic rhenium gasket in between diamond anvils. Photographs are taken through the diamond anvil under combined transmitted and reflected illumination. Sodium, a white metal at pressures below 1.1 Mbar (1 Mbar = 1 million atmospheres), turns black at 1.3 Mbar and becomes transparent at 2 Mbar.

Figure 3: Opaque and reflecting hydrogen at high pressures (left). Phase diagram of hydrogen (right). Red square indicates transformation to metallic hydrogen.

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

54 55

199 GPa

SELECTED PUBLICATIONS

Eremets M. I. and Troyan I. A.: Conductive dense hydrogen. Nature Materials DOI: 10.1038/NMAT3175 (2011).

Ma Y., Eremets M., A. R. Oganov, Yu Xie, I. Trojan, S. Medvedev, A. O. Lyakhov, M. Valle, V. Prakapenka: Transparent Dense Sodium. Nature 458, 182-185 (2009).

Eremets M. I., Trojan I.A. S. A. Medvedev, J. S. Tse, Y. Yao.: Superconductivity in Hydrogen Dominant Materials: Silane. Science 319, 1506-1509 (2008).

Medvedev S., McQueenT.M. I. A. Troyan, T. Palasyuk, M. I. Eremets, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, *C. Felser: Electronic and magnetic phase* diagram of β -Fe_{1.01}Se with superconductivity at 36.7 K under pressure. Nature Materials 8, 630 - 633 (2009).

Eremets M. I. and Trojan I.A.: Evidence of *maximum in the melting curve of hydrogen at* megabar pressures. Letters JETP 89, 198-203 (2009).

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.

STEPHAN BORRMANN

STRUCTURE AND RECENT DEVELOP-

MENTS: In 2001 the Particle Chemistry Department was established as a shared structure between the Johannes Gutenberg University of Mainz (JGUM) and the Max Planck Institute for Chemistry (MPIC). Its director, Stephan Borrmann is a full professor at the JGUM (professor in the Institute for Physics of the Atmosphere, IPA) and has a formal part-time ("Direktor im Nebenamt") position at the MPIC. Currently the department consists of the Instrumental Aerosol Analytics Group (Frank Drewnick), the Aerosol and Cloud Chemistry Group (Johannes Schneider), the Atmospheric Hydrometeors Group (Subir Mitra and Miklós Szakáll), the Aerosol and Cloud Physics Group (Ralf Weigel), and the Nano- and Microparticle Research Group (NAMIP; blades. previously the Cosmochemistry Department; Peter Hoppe) which joined the department in 2005. The cosmic and Wind Tunnel (MAVERT), the Mobile meteoric dust analyses of NAMIP were continued, but the available techniques and methods have also increasingly been applied to atmospheric aerosol samples. Associated with the department is the Helmholtz Society Junior Research Group AEROTROP ("Impact of Aircraft Emissions on the heteROgeneous Chemistry of the TROPopause region;" Junior Professor Christiane Voigt), which was jointly established in lower stratosphere. 2008 between JGUM, MPIC and DLR (with full funding from the Helmholtz Society) and which was successfully evaluated by the Helmholtz Society in October 2011.

Born on January 18, 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 Planck Institute for Chemistry (since for Atmospheric Research (NCAR) in

RESEARCH FOCUS: The scientific activities of the department are dedicated to fundamental processes concerning atmospheric aerosols, clouds, large hydrometeors, heterogeneous chemistry, pollution, impact of air traffic emission, and cosmic particulate matter. However, considerable industry- and applicationrelated research is also performed. In the past this research was focused on vehicle and aircraft exhausts (with the automotive industry), on inhalable pharmaceutical sprays, and instrument developments (e.g., dangerous substance detection for airport protection). Currently there are contracts concerning emissions from waste incineration, steel and coal manufacturing plants, and for prevention of riming and iceaccretion on wind energy turbine

Large facilities: As large facilities our department uses the Mainz Vertical Laboratory for Atmospheric research (MoLa), and the NanoSIMS laboratory of NAMIP. For field research five stateof-the-art aerosol mass spectrometers are available (including two certified for implementation on three different European research aircraft), as well as eight instruments for aircraft-borne experiments on cloud and aerosol microphysics in the upper troposphere/

TEACHING AND EDUCATION: In the reporting period from 2009 to 2011 the group leader of AEROTROP, Christiane Voigt, was formally appointed Junior Professor at the JGUM. Also Johannes Schneider completed

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 2001).

56 **57**

his formal "Habilitation" (Postdoctoral Lecturer Qualification) procedure. Both were and are heavily engaged in the teaching at IPA. The successful completion of their qualification procedures can be regarded as examples for the implementation of the "Hochschulpakt" of the Max Planck Society. Current formally accredited "Habilitation" candidates are Miklós Szákall and Frank Drewnick. Following the European "Bologna-Process" the teaching at IPA/ JGUM had to be completely redesigned during the reporting period for the transition from the previous "Diplom Meteorologie" curriculum to the new "Bachelor/Master in Meteorology" scheme. The corresponding labor-intensive external evaluations of the new curricula were successfully completed. From 2009 to 2011 nine Ph.D. and six diploma theses have been completed at the department, and a further 16 Ph.D. and six diploma theses are in progress. Since 2001, altogether 38 Ph.D. and 29 diploma theses were – or presently are - conducted within the department. Of these graduate students 45% are female.

FUNDING: Without significant financial contributions from external funds the research for these many theses would not have been possible. Roughly $\in 4.7$ million of external funds have been raised since 2001 through 28 research or technology development contracts.

PUBLICATIONS: For the period between January 2009 and October 2011 the number of peer-reviewed papers published by the department was 37.

WIND TUNNEL INVESTIGATIONS OF COLLECTION KERNELS DURING RIMING AND GRAUPEL FORMATION

SUBIR MITRA AND MIKLÓS SZAKÁLL

Figure 1: 3-D tomogram of a graupel (\approx 800 μ m diameter) from our laboratory for porosity and density analyses. For tomography monochromatic X-rays from the Swiss Light Source synchrotron facility at PSI (Villingen, Switzerland) were used (Enzmann et al., 2011).

The Mainz vertical wind tunnel allows free levitation of various hydrometeor types such as droplets, ice particles and crystals, snowflakes, graupels (as in Figure 1), and hailstones from tens of micrometers to centimeter sizes (Diehl et al., 2011). Experiments on individual free-floating hydrometeors are performed under controlled air conditions (e.g., Szakáll et al., 2009): The ranges are for temperatures from -30 to $+30^{\circ}$ C, for (humidity) dew points from -40°C to saturation, and for flow speeds from 10 cm s⁻¹ up to 40 m s⁻¹. The turbulence level in the tunnel is below 0.5% at all speeds. The wind tunnel design is of the so-called Z-type consisting of a horizontal air conditioning part, a vertical experimental part, and a horizontal part for flow control.

In tropospheric mixed-phase clouds, where ice particles and supercooled droplets are present simultaneously, precipitation is mostly initiated via the ice phase (e.g., Diehl and Wurzler, 2010). Here the ice particles grow to precipitation sizes at the expense of liquid drops either by diffusion of water vapor or by riming. Riming – i.e., the growth of glaciated hydrometeors by the deposition and subsequent freezing of supercooled liquid droplets - leads to the formation of graupel and hail. To estimate graupel formation and precipitation rates for numerical simulation in cloud models detailed knowledge of the collection kernels for the involved ice particles and liquid droplets is essential. The kernel by definition is the collection efficiency multiplied by the volume swept by the collector per unit time. Experiments on the riming of graupels

were performed in the wind tunnel in a temperature range from -8 to -12°C and with liquid water contents lying between 0.9 and 1.6 g m⁻³, which are values typically found in mixed-phase clouds. Individual ice particles with initial diameters of 700 µm were freely suspended in the wind tunnel while a mist of supercooled droplets with mean volume radius of 15 µm was injected upstream from a number of sprayers. After sufficient time for growth the rimed graupels were extracted (contact free) from the wind tunnel and the mass increase was determined. From the mass increase and the liquid water content the collection kernel of the graupels could be derived.

Together with earlier experiments performed with average droplet diameters of 12 and 20 µm, the graupel collection kernels were compared to theo-

retically determined kernels for liquid drop collectors (Figure 2). The kernel indicates a power law dependence on the collector momentum (mass times fall velocity) but is independent from ambient temperature, liquid water content, and growth time. Similar to earlier parameterizations of liquid drop collection kernels for warm clouds, new parameterizations of graupel collection kernels were obtained from the wind tunnel measurements for mixed-phase clouds (von Blohn et al., 2009). The comparison shows that the values of graupel collection kernels are enhanced with respect to those obtained for liquid collector drops. Also this enhancement increases with the size of the collected droplets. A general reason for the enhanced ice-phase collection kernel

during collisional growth lies in the fact that riming graupels move irregularly so that they sweep out a larger volume than liquid collector drops. The increase of this enhancement is affected by surface protrusions on the graupel surface which produce local flow deviations around the graupel such that more droplets are captured. Because of the growing inertia this effect increases with collected droplet size. An enhancement factor was obtained from the measurements to modify collection kernels in cloud models describing the riming process. In summary, crucial parameterizations for the collection kernels were extracted from these laboratory experiments for the direct numerical simulation of microphysical processes in mixed-phase clouds.

Figure 2: Collection kernel of small graupels as a function of collector momentum. Blue and black symbols: 6 and 10 µm droplets (Pflaum and Pruppacher, 1979); red symbols: 15 µm droplets (v. Blohn et al., 2009); lines: regression curves from experimental data.

"Adequately designed laboratory experiments are the basis of process understanding and provide the essential parameterizations for numerical simulation."

58 **59**

10-1

SELECTED PUBLICATIONS

Diehl, K., Wurzler, S.: Air parcel model simulations of a convective cloud: Bacteria acting as immersion ice nuclei. Atmos. Environ., 44, 4622-4628 (2010).

Diehl, K., Szakáll, M., Mitra, S. K., Pruppacher, H. R., Borrmann, S.: The Mainz vertical wind tunnel facility – A review of 25 years of laboratory experiments on cloud physics and chemistry, in: J. D. Pereira (Ed.): "Wind Tunnels: Aerodynamics, Models and Experiments", NOVA Publishers Inc., ISBN 978-1-61209-204-1 (2011).

Enzmann F., Miedaner M. M., Kersten M., von Blohn N., Diehl K., Borrmann S., Stampanoni M., Ammann M., Huthwelker T.: 3-D imaging and quantification of graupel porosity by synchrotron-based micro-tomography. Atmos. Meas. Tech. 4, 2225-2234 (2011).

Szakáll, M., Diehl, K., Mitra, S. K., Borrmann, S.: A wind tunnel study on the shape, oscillation and internal circulation of large raindrops with sizes between 2.5 and 7.5 mm. J. Atmos. Sci., 66, 755-765 (2009).

von Blohn, N., Diehl, K., Mitra, S. K., Borrmann, S.: Wind tunnel investigations on the growth rates and regimes, and the collection kernels during riming. J. Atmos. Sci., 66, 2359-2366 (2009).

DEVELOPMENT AND FIELD DEPLOYMENT OF A MOBILE LABORATORY FOR STUDIES OF URBAN POLLUTION AND EMISSION SOURCES

FRANK DREWNICK

Figure 1: Stationary MoLa operation outside the Paris metropolitan area (left) and in southern Spain (center) during the winter MEGAPOLI and the DOMINO field campaigns. The compact instrumentation setup and parts of the sample flow system are shown in the right panel.

In 2008 for the first time in the history of mankind more than 50% of the world population was living in cities and rapidly growing urban environments. Today 20 cities worldwide are called "megacities" having populations of more than 10 million. These cities are major sources of atmospheric pollution often with severe impact on human health conditions. Even in developed countries megacities and their surroundings suffer from poor air quality due to the enormous density of industrial, residential, and transportrelated emissions. In order to investigate the spatial distribution, transport and transformation processes, and local impact of particulate and gaseous urban emissions sophisticated, flexible research platforms are needed that allow sensitive in-situ measurements of pollutants with high temporal resolu-

tion. Since 2007 we have developed a ground-based mobile aerosol research laboratory (MoLa, Figure 1) for on-line measurement of a broad range of aerosol properties as well as concentrations of various trace gases. State-of-the-art aerosol instruments have been adopted for highly time-resolved measurements of particle number and mass concentrations, size distributions, and chemical composition (Drewnick et al., 2005; 2009) covering the submicron size fraction. A central data acquisition system was designed for efficient data collection and processing and to provide a direct real-time overview of ambient aerosol and gas parameters (Figure 2). The vehicle is equipped with electrical power generators and an exhaust removal system for completely autonomous operation in the field. The inlet system was optimized for minimum

sampling artifacts (von der Weiden et al., 2009) with well-known efficiency and loss characteristics. MoLa is designed for both stationary operation and measurement while driving which provides the opportunity of "scanning" over extended areas for more realistic comparison with satellite data or model results than from (station) point measurements.

The European megacity Paris is well suited for investigation of the transport and transformation of its emissions (Jimenez et al., 2009) due to the relatively flat, uniform terrain with low levels of industrial activities in this part of France. In 2009 and 2010 the MEGAPOLI summer and winter field campaigns were conducted here. Besides the operation of an in-house developed laser ablation particle mass

Figure 2: The MoLa data acquisition panel provides a real-time, direct overview of the current measurements of gaseous and particulate components.

spectrometer on a French research aircraft (Brands et al., 2011) our group performed measurements of aerosols and trace gases from a fixed station within the city. In addition MoLa was used to probe ambient air in the greater surroundings of the metropolitan area, performing both, stationary as well as mobile measurements at distances of up to 150 km from downtown Paris. Surprisingly, a relatively low influence of Paris' emissions on local air quality was observed already close to the city. Longrange transport of polluted continental air masses as well as local sources - e.g., residential wood burning during the winter months - typically dominated local air quality over the impact of transported emissions from Paris.

MoLa was also adopted for in situ characterization of particulate and gaseous

emissions from various "individual" anthropogenic sources like integrated steel plants, large waste incineration facilities, or sea-going ships. Especially for the investigation of such smallscale sources our approach of a flexible setup which allows measurements with different instrument configurations at different locations or even whilst driving proved to be efficient and highly advantageous. Thus, further improvement of the mobile measurement platform is envisaged. For example we intend to integrate a laser ablation particle mass spectrometer (Kamphus et al., 2008) in addition to the available flash vaporization, electron impact ionization mass spectrometer (Drewnick et al., 2005; 2009) together with advanced facilities for particle sampling.

"The investigation of transport and transformation processes of urban air pollutants demands modern research platforms with high temporal resolution and spatial flexibility."

60 **_ 61**

SELECTED PUBLICATIONS

Brands, M., Kamphus, M., Böttger, T., Schneider, J., Drewnick, F., Voigt, C., Borrmann, S.: Development of an aircraft-based laser ablation aerosol mass spectrometer (ALABAMA) and first deployment during MEGAPOLI in urban pollution plumes over Paris. Aerosol Sci. Technol., 45, 46–64, doi: 10.1080/02786826.2010.517813 (2011).

Jimenez, J. L., M. R. Canagaratna, N. M. Donahue, A. S. H. Prevot, Q. Zhang, J. H. Kroll, P. F. DeCarlo, J. D. Allan, H. Coe, N. L. Ng, A. C. Aiken, K. D. Docherty, I. M. Ulbrich, A. Grieshop, A. L. Robinson, J. Duplissy, J. D. Smith, K. R. Wilson, V. Lanz, Y. L. Sun, A. Laaksonen, T. Raatikainen J. Rautiainen, P. Vaattovaara, M. Ehn, M. Kulmala, J. Tomlinson, D. R. Collins, M. C. Cubison, E. Dunlea, J. A. Huffman, T. B. Onasch, M. R. Alfarra, P. Williams, K. Bower, Y. Kondo, N. Takegawa, J. Schneider, F. Drewnick, S. Borrmann, S. Weimer, K. Demerjian, D. Salcedo, L. Cottrel, R. Griffin, A. Middlebrook, R. Bahreini, A. Takami, T. Miyoshi, S. Hatakeyama, A. Shimono, J. Y. Sun, Y. M. Zhang, K. Dzepina, J. R. Kimmel, D. Sueper, J. T. Jayne, S. C. Herndon, A. M. Trimborn, L. R. Williams, E. C. Wood, C. E. Kolb, U. Baltensperger, D. R. Worsnop, Evolution of organic aerosols in the atmosphere: A New Framework connecting measurements to models, Science, 326, 1525-1529 (2009).

von der Weiden, S.-L., Drewnick, F., Borrmann, S.: Particle Loss Calculator – a new software tool for the assessment of the performance of aerosol inlet systems. Atmos. Meas. Tech., 2, 1099–1141 (2009).

Drewnick, F., Hings, S. S., Alfarra, M. R., Prévôt, A. S. H., Borrmann S.: Aerosol quantification with the aerodyne aerosol mass spectrometer: detection limits and ionizer background effects. Atmos. Meas. Tech., 2, 33–46 (2009).

Drewnick, F., Hings, S.S., DeCarlo, P., Jayne, J.T., Gonin, M., Fuhrer, K., Weimer, S., Jimenez, J.L., Demerjian, K.L., Borrmann, S., Worsnop, D.R.: A new Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS) – Instrument Description and First Field Deployment. Aerosol Science & Technology 39, 637-658 (2005).

AIRCRAFT-BASED AEROSOL COMPOSITION MEASUREMENTS IN THE MIDDLE AND LOWER TROPOSPHERE

JOHANNES SCHNEIDER

Figure 1: The French research aircraft ATR42, on the runway of Kangerlussuaq airport (Greenland), July 2008.

Tropospheric aerosol particles influence the atmospheric radiation budget (1.) directly by scattering sunlight back to space, and (2.) indirectly by acting as ice nuclei (IN) or as cloud condensation nuclei (CCN) for cirrus and liquidphase cloud formation. Anthropogenic aerosol enhances the number of cloud droplets, but on average these droplets are smaller because the amount of water vapor available for condensation remains limited. Such clouds with smaller and more droplets scatter light more efficiently, appear brighter, and tend to take more time until they develop precipitation. This commonly is referred to as first and second indirect aerosol effects.

In 2008 and 2009 our "Aerosol and Cloud Chemistry" research group took part in two field campaigns where we operated two different aerosol mass spectrometers to obtain real-time, in situ measurements of the (submicron) particle chemical composition. For the

POLARCAT (Polar Study using Aircraft, Remote Sensing, Surface Measurements and Models, of Climate, Chemistry, Aerosols, and Transport, July 2008) campaign the French research aircraft ATR42 (Figure 1) was operated out of Kangerlussuaq (Greenland). During POLARCAT pollution of the Arctic atmosphere was sampled which resulted from long-range transport of biomass burning plumes and fossil fuel combustion events. We deployed a modified C-ToF-AMS (Compact Time-of-Flight Aerosol Mass Spectrometer; Schmale et al., 2010) during eight research flights at altitudes up to 7.6 km. About 50 Arctic pollution plumes were encountered (Schmale et al., 2011, Quennehen at al., 2011) and classified according to their sources by means of a dispersion model. The chemical signatures of the analyzed particles enabled us to differentiate between combustion of biomass and fossil fuel. Both sources are regarded as anthropogenic although some natural wildfires in Canada or Siberia may have

contributed also. As shown in Figure 3, the resulting classification of the plumes ranges from pure biomass burning on the left to Asian fossil fuel burning towards the right. The sulfate fraction of the pure biomass-derived aerosol is rather low, while the Asian fossil fueldominated plumes contain about 50% sulfate and 50% organics. Such data allow detailed modeling of the particulate chemical composition for pollution plumes including a prediction of the particles' hygroscopic properties and their cloud nucleation ability.

In 2009 a newly developed, different instrument, the ALABAMA (Aircraft-Based Laser Ablation Aerosol Mass Spectrometer; Figure 2) was operated also on board the French ATR42 during the MEGAPOLI (Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation) summer campaign over Paris. The ALABAMA is a further develop-

Figure 2.: The ALABAMA instrument (Brands et al., 2011) in the British research aircraft BAe 146.

ment of a ground-based laser ablation aerosol mass spectrometer (SPLAT, Kamphus et al., 2008). It is designed for the chemical analysis of single aerosol particles in the submicrometer-size range (Brands et al., 2011) allowing

Figure 3: Fraction of particulate sulfate/organics associated with the type of pollution plume (BB: biomass burning, FF: fossil fuel. Boxes: 25th and 75th percentiles, horizontal line: median, uncertainty bars: 10th and 90th percentiles, black and white stars: mean value) (Schmale et al., 2011).

"Knowing the sources, properties, and pathways of tropospheric aerosol particles is crucial to quantify the anthropogenic contribution to the direct and indirect radiative effects."

62 _ **63**

- unlike the C-ToF-AMS - the detection of metals, soot, mineral dust, and other nonvolatile components. Initially ALABAMA was developed at the MPIC between 2007 and 2009 for the new German research aircraft HALO, and the MEGAPOLI flights were its first successful aircraft-based application. The analysis of the recorded data has shown that the instrument is able to detect differences in particle composition with respect to the air mass origin. We could distinguish between air masses mainly influenced by the Paris megacity and pollution due to long-range transport (Brands et al., 2011). Worldwide there are currently four aircraft-based laser ablation aerosol mass spectrometers and ALABAMA is the only one available in Europe. The C-ToF-AMS and ALABAMA instruments constitute a unique set of complementary systems for aircraft-borne in situ, real-time, direct-reading aerosol chemical analyses.

SELECTED PUBLICATIONS

Brands, M., Kamphus, M., Böttger, T., Schneider, J., Drewnick, F., Roth, A., Curtius, J., Voigt, C., Borbon, A., Beekmann, M., Bourdon, A., Perrin, T., and Borrmann, S.: Characterization of a newly developed aircraft-based laser ablation aerosol mass spectrometer (ALABAMA) and first field deployment in urban pollution plumes over Paris during MEGAPOLI 2009. Aerosol Sci. Technol., 45, 46–64 (2011).

Kamphus, M., Ettner-Mahl, M., Brands, M., Curtius, J., Drewnick, F., Borrmann, S.: Comparison of two aerodynamic lenses as an inlet for a single particle laser ablation mass spectrometer. J. Aerosol Sci., 42, 970–980 (2008).

Quennehen, B., Schwarzenboeck, A., Schmale, J., Schneider, J., Sodemann, H., Stohl, A., Ancellet, G., Crumeyrolle, S., Law, K. S.: Physical and chemical properties of pollution aerosol particles transported from North America to Greenland as measured during the POLAR-CAT summer campaign. Atmos. Chem. Phys., 11, 10947–10963 (2011).

Schmale, J., Schneider, J., Jurkat, T., Voigt, C., Kalesse, H., Rautenhaus, M., Lichtenstern, M., Schlager, H., Ancellet, G., Arnold, F., Gerding, M., Mattis, I., Wendisch, M., Borrmann, S.: Aerosol layers from the 2008 eruptions of Mt. Okmok and Mt. Kasatochi: In-situ UT/ LS measurements of sulfate and organics over Europe. J. Geophys. Res., 115, D00L07 (2010).

Schmale, J., Schneider, J., Ancellet, G., Quennehen, B., Stohl, A., Sodemann, H., Burkhart, J., Hamburger, T., Arnold, S. R., Schwarzenboeck, A., Borrmann, S., Law, K. S.: Source identification and airborne chemical characterisation of aerosol pollution from long-range transport over Greenland during POLARCAT summer campaign 2008. Atmos. Chem. Phys., 11, 10097–10123 (2011).

IMPACT OF AIRCRAFT EMISSIONS ON THE TROPOPAUSE REGION - AEROTROP

CHRISTIANE VOIGT

Figure 1: Contrails from a A319 and a A340 aircraft. Photos taken from the cockpit of the Falcon during the CONCERT campaign on 19 November 2008 (Voigt et al., 2011).

The minimization of its climate impact is amongst the biggest challenges for the aviation industry, especially since the passenger transport volume has doubled within the past 14 years and its growth is expected to continue. While the climate impact from aircraft CO₂ emissions is well understood, the radiative forcing from aircraft-induced cloud modifications is only poorly quantified, in part caused by uncertainties in the contrail particle size distribution, optical depth and coverage. Even less is known of the climate impact from ozone perturbations caused by aircraft NOx emissions taking into account reactions on particles. Actually, these uncertainties prevent the development

of measures for the dedicated reduction of the climate impact from aviation.

It is therefore the aim of the Helmholtz University Junior Research Group AER-OTROP (Impact of Aircraft Emissions on the heteROgeneous chemistry of the TROPopause region) to reliably detect aircraft emissions, contrails and contrail cirrus and to better quantify aircraft NOx effects on ozone. The results will provide a scientific base for the discussion of minimization strategies of the climate impact from aviation.

The Helmholtz University Junior Research Group AEROTROP (with its seven members) is a co-operation between the DLR-Institute for Physics of the Atmosphere, the Johannes Gutenberg University and the MPI-Particle Chemistry Department.

We use the chemical ionization mass spectrometry CIMS to detect reactive nitrogen (NOy) and sulfur containing species (e.g. HNO₃, HONO, SO₂) as well as halogen compounds (e.g. HCl and HBr) in the atmosphere. In addition, we operate three different hygrometers, including a novel water vapor mass spectrometer, in the laboratory and on aircraft. Besides ground based activities, we perform aircraft measurements and evaluate observations in the upper troposphere / lower

stratosphere region for example within the EU projects SCOUT-O3 (Australia) and AMMA (Burkina Faso). Certainly, the organization of the aircraft missions CONCERT2008 and CONCERT2011 (CONtrail and Cirrus ExpeRimenT) by AEROTROP with the DLR research aircraft Falcon constitutes a major research highlight during the reporting period (Voigt et al., 2010).

During the CONCERT2008 campaign we detected numerous contrails, cirrus clouds, and a volcanic aerosol layer (Jurkat et al., 2010, Schmale et al., 2010) in the mid latitude tropopause region at altitudes between 8 and 12 km. The contrails were produced by a suite of commercial airliners with weights between 47 and 508 t, among them the largest passenger aircraft Airbus A380. We derived an OH induced sulfur con-

Figure 2: Normalized probability distributions of the optical depth and the ice water content (IWC) of contrails (Voigt et al., 2011).

method. In addition, we evaluated an extensive data set of microphysical contrail properties and derived reliable probability density functions of the contrail optical depth and the ice water content (Figure 2), which are likely representative for young contrails from the present-day commercial aircraft fleet at observation conditions (Voigt et al., 2011). Based on these in-situ measurements we estimated a year-2005 radiative forcing from linear contrails of 15.9 mWm⁻² (range 11.1 to 47.7 mWm⁻²), which is more than half of the radiative forcing from aircraft CO₂ emissions alone (28 mWm⁻², Lee et al., 2009).

In future, we will investigate the climate impact from contrail cirrus based on observations during CONCERT2011. Furthermore, we will address the heterogeneous processing of NOy and halogen species on particles and its effect on ozone. For this purpose the mass spectrometers will be optimized for ground based measurements in the Amazonian rainforest and for operation on the high-altitude long-range research aircraft HALO.

"At present, large uncertainties prevent the development of dedicated measures to reduce the climate impact from aviation."

64 **65**

version efficiency of 2.2% +/-0.5% from our mass spectrometer measurements (Jurkat et al., 2011) in combination with NOy data, roughly confirming previous estimates using a new independent

SELECTED PUBLICATIONS

Voigt, C., Schumann, U., Jurkat, T., Schäuble, D., Schlager, H., Petzold, A., Gayet, J.-F., Krämer, M., Schneider, J., Borrmann, S., Schmale, J., Jessberger, P., Hamburger, T., Lichtenstern, M., Scheibe, M., Gourbeyre, C., Meyer, C., Kübbeler, M., Frey, W., Kalesse, H., Butler, T., Lawrence, M. G., Holzäpfel, F., Arnold, F., Wendisch, M., Döpelheuer, A., Gottschaldt, K., Baumann, R., Zöger, M., Sölch, I., Rautenhaus, M., Dörnbrack, A.: In-situ observations of young contrails -*Overview and selected case studies from the* CONCERT campaign. Atmos. Chem. Phys., 10, 9039–9056, www.atmos-chem-phys. net/10/9039/2010, doi:10.5194/acp-10-9039-2010 (2010).

Voigt, C., Schumann, U., Jessberger, P., Jurkat, T., Petzold, A., Gavet, I.-F., Krämer, M., Thornberry, T., Fahey, D.: Extinction and optical depth of contrails. Geophys. Res. Lett., 38, L11806, doi:10.1029/2011GL047189 (2011). Highlighted by AGU.

Jurkat, T., Voigt, C., Arnold, F., Schlager, H., Aufmhoff, H., Schmale, J., Schneider, J., Lichtenstern, M., Dörnbrack, A.: Airborne stratospheric ITCIMS-measurements of SO₂, HCl, and HNO₃ in the aged plume of volcano Kasatochi. J. Geophys. Res., 115, D00L17, doi:10.1029/2010JD013890 (2010).

Schmale, J., Schneider, J., Jurkat, T., Voigt, C., Kalesse, H., Rautenhaus, M., Lichtenstern, M., Schlager, H., Ancellet, G., Arnold, F., Gerding, F., Mattis, I., Wendisch, M., Borrmann, S.: Aerosol layers from the 2008 eruptions of Mount Okmok and Mount Kasatochi: In situ upper troposphere and lower stratosphere measurements of sulfate and organics over Europe. J. Geophys. Res., 115, D00L07, doi:10.1029/2009JD013628 (2010).

Jurkat, T., Voigt, C., Arnold, F., Schlager, H., Kleffmann, J., Aufmhoff, H., Schäuble, D., Schäfer, M., Schumann, U.: Measurements of HONO, NO, NOy and SO₂ in aircraft exhaust plumes at cruise, Geophys. Res. Lett., 38, L10807, doi:10.1029/2011GL046884 (2011).

IN SITU STUDIES OF AEROSOLS AND POLAR STRATOSPHERIC CLOUDS IN THE ARCTIC UPPER TROPOSPHERE/LOWER STRATOSPHERE

RALF WEIGEL

Figure 1: The instrumented Russian high-altitude research aircraft M-55 Geophysica during take off.

In both hemispheres a Polar Winter Vortex (PWV) forms in the stratosphere as a low-pressure system above the Arctic and the Antarctic. Inside the PWV large-scale air mass subsidence causes downward transport of aerosols and trace gases from the mid/ upper stratosphere and sometimes the lower mesosphere. At altitudes between 15 and 25 km the Polar Stratospheric Clouds (PSC) heterogeneously nucleate on these aerosol particles particularly in times of volcanic quiescence when the production of stratospheric Junge-layer aerosols from SO₂ and OCS is slowed down. The PSCs provide sufficient particulate surface area for heterogeneous chemical reactions which ultimately cause ozone depletion. Most models assume *pure* binary H_2SO_4/H_2O solution

droplets (resulting from homogeneous gas-to-particle conversion processes) as cloud condensation nuclei for PSC formation. However, our measurements show that up to 70% of the submicron particles contain nonvolatile materials, which clearly implies that such model assumptions are overly simplistic. Thus, our current understanding of the PSC formation processes and possibly the efficiency of some heterogeneous reactions need to be reassessed.

For detailed studies of the PWV aerosol and PSCs the EUPLEX and RECON-CILE field campaigns were performed in the years 2003 and 2010 from Kiruna (Northern Sweden) deploying the Russian high-altitude research aircraft M-55 Geophysica (Figure 1). For our

fully automated in-situ measurements at altitudes up to 21 km a set of four independent, continuous flow condensation particle counters (i.e., the in-house developed COndensation PArticle counting System COPAS; Weigel et al., 2009; Weigel et al., 2011a) was adopted as well as optical cloud particle instrumentation (Frey et al., 2011). COPAS counts aerosols covering the diameter range from 6 nm to approximately 1 μm while the optical instruments (based on light scattering and imaging techniques) measure cloud particle size distributions between 2 µm and 1500 μm. In addition, during RECONCILE stratospheric aerosol particles were collected by means of a specially designed, miniaturized impactor for a posteriori chemical composition measurements

using Scanning Electron Microscopy and Energy Dispersive X-ray analyses. During EUPLEX air originating from the upper stratosphere and lower mesosphere was probed (Curtius et al., 2005) with increasing number densities of submicron refractory (nonvolatile) particles as a function of altitude inside the PWV. In the absence of composition measurements it was concluded that nonvolatile metal particles of meteoric origin had been transported downward. In 2010 a similar increase of the (refractory) particle number concentration was found. However, a significant fraction of these particles consisted of typical fly ash with anthropogenic signatures. Occasionally metals (e.g., Mn, Pb) and combinations of elements were detected that are not typical for micrometeorites, and - quite unexpectedly – particles containing silicates, carbon, calcium sulfate, and soot also

were sampled (Figure 2; Weigel et al., 2011b). The origin and microphysical processes of such particles are unknown and extended experimental efforts are focused on this for the planned 2012 and 2014 Geophysica campaigns.

PSCs of synoptic scale (i.e., not lee wave clouds) were frequently encountered during RECONCILE and in situ data could be recorded for more than ten flight hours. Images of very large cloud particles (so-called "NAT-rocks") could be captured as shadow casts for the first time providing visual proof of their existence. The "NAT-rock" particles are larger than 20 µm and cause significant dehydration and denitrification inside the PWV which are key processes underlying ozone destruction. In essence the results from the RECONCILE campaign cast a new light on the key questions of PSC formation and processing efficiency.

Figure 2: Scanning electron microscope images of refractory aerosol sampled at 20 km altitude during RECONCILE 2010 inside the Arctic polar winter vortex.

"High altitude aerosols and clouds are key elements of atmospheric chemistry and climate especially in the polar regions."

66 **67**

SELECTED PUBLICATIONS

Curtius, J., Weigel, R., Vössing, H.-J., Wernli, H., Werner, A., Volk, C.-M., Konopka, P., Krebsbach, M., Schiller, C., Roiger, A., Schlager, H., Dreiling, V., Borrmann, S.: Observation of meteoritic material and implication for aerosol nucleation in the winter arctic lower stratosphere derived from in situ measurements. Atmos. Chem. Phys., 5, 3053–3069 (2005).

Frey, W., Borrmann, S., Kunkel, D., Weigel, R., de Reus, M., Schlager, H., Roiger, A., Voigt, C., Hoor, P., Curtius, J., Krämer, M., Schiller, C., Volk, C. M., Homan, C. D., Fierli, F., Di Donfrancesco, G., Ulanovsky, A., Ravegnani, F., Sitnikov, N. M., Viciani, S., D'Amato, F., Shur, G. N., Belyaev, G. V. Law, K. S., Cairo, F .: In situ measurements of tropical cloud properties in the West African monsoon: upper tropospheric ice clouds, mesoscale convective system outflow, and subvisual cirrus. Atmos. Chem. Phys., 11, 5569-5590 (2011).

Weigel, R., Hermann, M., Curtius, J., Voigt, C., Walter, S., Böttger, T., Lepukhov, B., Belyaev, G., Borrmann, S.: Experimental characterization of the COndensation PArticle counting System for high altitude aircraft-borne application. Atmos. Meas. Tech., 2, 243-258 (2009).

Weigel, R., Borrmann, S., Kazil, J., Minikin, A., Stohl, A., Wilson, J. C., Reeves, J. M., Kunkel, D., de Reus, M., Frey, W., Lovejoy, E. R., Volk, C. M., Viciani, S., D'Amato, F., Schiller, C., Peter, T., Schlager, H., Cairo, F., Law, K. S., Shur, G. N., Belyaev, G. V., Curtius, J.: In situ observations of new particle formation in the tropical upper troposphere: The role of clouds and the nucleation mechanism. Atmos. Chem. Phys., 11, 9983-10010 (2011a).

Weigel, R., Ebert, M., Molleker, S., Frey, W., Günther, G., Volk, C. M., Schlager, H., Cairo, F., Di Donfrancesco, G., Borrmann, S.: The abundance, shape and chemical composition of non-volatile particles in the Arctic winter *Stratosphere and their potential activation* by Polar Stratospheric Cloud elements. Oral presentation EGU2011-7192, European Geoscience Union General Assembly, Vienna (2011b).

SOURCES OF SUBMICRON AEROSOL IN THE TROPICAL UPPER TROPOSPHERE

STEPHAN BORRMANN

Figure 1: Cumulus congestus cloud with pileus.

Extending from the southern to the northern hemispheric subtropical jets the Tropical Transition Layer (TTL) forms the interface between the troposphere and the stratosphere. As the TTL vertically ranges from potential temperatures of 355 K to 425 K (roughly corresponding to geometrical altitudes between 14 and 18 km) the thermal tropopause is located inside, as are the levels of zero net radiative heating and neutral buoyancy for clouds (Law et al., 2010). Below the TTL deep convection rapidly overturns the air while above and within the TTL slow upwelling is driven by radiation. A maximum of the mixing ratios was found for submicron particles at TTL altitudes over Hawaii by Brock et al. (1995) and our measurements over Brazil, West Africa, and tropical Australia (adopting the Russian M-55 high-altitude research aircraft "Geophysica") confirmed its existence as a circum-equatorial belt (Figure 2). The

measured vertical profiles of the particle mixing ratios n are remarkably similar for these tropical locations and also for Costa Rica (Borrmann et al., 2010). The data do not exhibit any trends between 1987 and 2006. Initially the particles of this tropical layer were believed to consist of homogeneously nucleated binary sulfuric acid-water solution droplets until we demonstrated by in situ measurements that half of these particles are nonvolatile at temperatures where H₂SO₄/H₂O evaporates, and thus at least the particle cores contain other materials. The exact chemical composition of this submicron aerosol is unknown, as are sources, sinks, and relevant microphysical mechanisms (Borrmann et al., 2010). In the upper troposphere new particle formation (NPF) of binary solution droplets does occur from gas-to-particle-conversion in "burst-like events" under favorable thermodynamic conditions. Surpris-

ingly these NPF-events seem to happen most frequently in a very narrow altitude range at the bottom of the TTL. This follows from our measurements of particles with sizes between 5 nm and 15 nm (N_{NM} in Figure 3) on "Geophysica" (Weigel et al., 2011) in Brazil, West Africa, and Australia. Further analyses by Frey et al., 2011, showed that NPF can proceed at TTL levels even inside the glaciated anvils of large tropical Mesoscale Convective cloud Systems (MCS) despite the fact that in the presence of many large ice particles any condensable vapors and freshly nucleated nanoparticles should be scavenged quickly. Such "quenching" of NPF indeed can be identified in the aircraft data, albeit only under specific cloud conditions. Quantitatively the mechanisms underlying in-cloud NPF are not well described yet. Thus, new particle formation by homogeneous nucleation in clear air and inside clouds at the TTL bottom can be a source for the tropical particle layer although this still does not explain the large fraction of nonvolatile components. Detailed trajectory analyses by Law et al., 2010, however indicate that a significant fraction of the air residing in the West African TTL originates from the boundary layer of the Indian subcontinent and Asia. Within the TTL they also identified air from biomass burning events in

Figure 2: The particle layer at the TTL bottom from our in situ measurements in Brazil, West Africa, and Northern Australia. The horizontal bars are the 25 and 75% percentiles.

– <mark>Brazil (2005)</mark> – Australia (2005)

- Tropical Profile

540

520

otential temperature in K

340

320

300

Tropical Profile

- Burkina Faso (2006)

Brock et al. (1995), data from 1987-1994:

1000

particle mixing ratio n in mg⁻¹

Tropical transition lave

10000

"Characterization of persistent aerosol layers requires identification of their sources, sinks, and long-term trends, as well as a description of the mechanisms maintaining their equilibrium."

68 **69**

Central Africa. This may be indicative of an anthropogenic contribution to the particle reservoir in the tropical TTL. To what extent the particles from this tropical belt are transported aloft and serve as nuclei for the formation and maintenance of the global stratospheric "Junge aerosol layer" is another open question, which even connects to the formation of Polar Stratospheric Clouds over the winter hemispheric poles and to polar ozone destruction.

•••••••• aircraft: M55 Geophysica

SELECTED PUBLICATIONS

Brock, C., Hamill, P., Wilson, J., Jonsson, H., *Chan, K.: Particle formation in the upper* tropical troposphere – A source of nuclei for the stratospheric aerosol. Science, 270, 1650–1653 (1995).

Borrmann, S., Kunkel, D., Weigel, R., Minikin, A., Deshler, T., Wilson, J. C., Curtius, J., Volk, C. M., Homan, C. D., Ulanovsky, A., Ravegnani, F., Viciani, S., Shur, G. N., Belyaev, G. V., Law, K. S., Cairo, F.: Aerosols in the tropical and subtropical UT/LS: In-situ measurements of ultrafine particle abundance and volatility. Atmos. Chem. Phys. 10, 5573-5592 (2010).

Frey, W., Borrmann, S., Kunkel, D., Weigel, R., de Reus, M., Schlager, H., Roiger, A., Voigt, C., Hoor, P., Curtius, J., Krämer, M., Schiller, C., Volk, C. M., Homan, C. D., Fierli, F., Di Donfrancesco, G., Ulanovsky, A., Ravegnani, F., Sitnikov, N. M., Viciani, S., D'Amato, F., Shur, G. N., Belyaev, G. V. Law, K. S., Cairo, F.: In-situ measurements of tropical cloud properties in the West African monsoon: upper tropospheric ice clouds, mesoscale convective system outflow, and subvisual cirrus. Atmos. Chem. Phys., 11, 5569–5590 (2011).

Law, K. S., Fierli, F., Cairo, F., Schlager, H., Borrmann, S., Streibel, M., Real, E., Kunkel, D., Schiller, C., Ravegnani, F., Ulanovsky, A., d'Amato, F., Viciani, S., Volk, C. M.: Air mass origins influencing TTL chemical composition over West Africa during the 2006 summer monsoon. Atmos. Chem. Phys., 10, 10753-10770 (2010).

Weigel, R., Borrmann, S., Kazil, J., Minikin, A., Stohl, A., Wilson, J. C., Reeves, J. M., Kunkel, D., de Reus, M., Frey, W., Lovejoy, E. R., Volk, C. M., Viciani, S., D'Amato, F., Schiller, C., Peter, T., Schlager, H., Cairo, F., Law, K. S., Shur, G. N., Belyaev, G. V., Curtius, J.: In-situ observations of new particle formation in the tropical upper troposphere: The role of clouds and the nucleation mechanism. Atmos. Chem. Phys., 11, 9983-10010 (2011).

STARDUST IN THE LABORATORY

PETER HOPPE

Figure 1: Presolar SiC grain separated from the Murchison CM2 meteorite (left). The Stardust spacecraft on its way to comet Wild 2 (right).

Dust plays an important role in the Universe. It is found in a variety of environments, for example around evolved stars and in interstellar clouds. Of particular importance is carbonaceous, silicate, and oxide dust that forms efficiently around red giant stars and, to a lesser extent, also in the ejecta of supernova explosions. Although most of the solid matter that went into the making of our Solar System was destroyed during Solar System formation, a small fraction survived and is found in primitive Solar System materials. Among this are so-called presolar grains which have been identified in primitive meteorites, interplanetary dust particles (IDPs), and samples from NASA's Stardust mission to comet 81P/ Wild 2 on the basis of large isotope anomalies, the fingerprints of nucleosynthetic and mixing processes in their parent stars. We have been studying a variety of presolar materials with different nano- and microanalytical analysis techniques, in particular secondary ion mass spectrometry (NanoSIMS) and electron microscopy (SEM, TEM, Auger spectroscopy). These studies allowed us (1.) to obtain new insights into stellar nucleosynthesis, evolution, chemistry, and dust formation, and (2.) to identify some of the building blocks from which our Solar System formed.

1. THE STELLAR 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 presolar grains it is possible to obtain detailed insights into these processes and to track stellar evolution. We have used the technique of ion imaging, specifically developed for the Nano-SIMS ion probe at our institute, to study thousands of individual, submicrometer-sized presolar SiC grains chemically separated from meteorites (Figure 1, left). In this way dozens of rare supernova grains were identified by specific isotopic fingerprints and subsequently analyzed in more detail. Our data suggest that complex chemical processes occur in the Si- and S-rich zone of supernovae and that molecule formation must precede macroscopic mixing and dust formation in supernova ejecta (Hoppe et al., 2010). Furthermore, our measurements gave a first observational hint that boron is partly produced by neutrino reactions in supernovae, as predicted by stellar models, and not only by spallation reactions in the interstellar medium induced by Galactic cosmic rays (Fujiya et al., 2011). Studies by Auger spectroscopy and TEM (after lift-out by FIB) of selected presolar silicate and oxide grains identified in situ in meteoritic thin sections by NanoSIMS ion imaging showed that silicate dust often forms under nonequilibrium conditions in the winds of red giant stars and that refractory oxides sometimes serve as condensation nuclei for silicates and even for other oxides (Vollmer et al., 2009).

2. THE SOLAR SYSTEM PERSPECTIVE

To investigate the distribution and survival of presolar matter in the solar nebula we have studied its abundance and nature in primitive meteorites, IDPs, and cometary matter. Among the analyzed materials are about 200 impact residues in small (mostly subµm) craters on Al foils from NASA's Stardust mission to comet Wild 2 (Figure 1, right) which were measured for O-isotopic composition. One of these residues (Figure 2) exhibits the isotopic fingerprints of a supernova silicate grain. This result suggests that the presolar grain abundance may be 1–2 orders of magnitude higher than previous measurements suggested, which gave abundances lower than in primitive meteorites (McKeegan et al., 2006), in agreement with expectations for comets that are assumed to represent the most primitive matter in our Solar System. Studies of IDPs associated with comet 26P/Grigg-Skjellerup revealed the most primitive assembly of interstellar matter found to date, including an unusually high abundance of presolar grains and very isotopically anomalous and disordered organic matter of likely interstellar origin (Busemann et al., 2009).

Figure 2: SEM picture and NanoSIMS ion images of an impact crater on an Al foil target from NASA's Stardust mission to comet Wild 2. The impactor is likely a silicate grain from a supernova which was preserved in comet Wild 2.

"Bringing stars to the laboratory – Presolar dust grains as tracers for stellar nucleosynthesis and evolution, and for the origin of our Solar System."

70 **_ 71**

SELECTED PUBLICATIONS

Busemann H., Nguyen A. N., Cody G. D., Hoppe P., Kilcoyne A. L. D., Stroud R. M., Zega T. J., Nittler L. R.: Ultra-primitive interplanetary dust particles from the comet 26P/ Grigg-Skjellerup dust stream collection. Earth Planet. Sci. Lett. 288, 44–57 (2009).

Fujiya W., Hoppe P., Ott U.: Hints for neutrino-process boron in presolar silicon carbide grains from supernovae. Astrophys. J. 730, L7 (2011).

Hoppe P., Leitner J., Gröner E., Marhas K. K., Meyer B. S., Amari S.: NanoSIMS studies of small presolar SiC grains: New insights into supernova nucleosynthesis, chemistry, and dust formation. Astrophys. J. 719, 1370–1384 (2010).

McKeegan K. D. et al.: Isotopic compositions of cometary matter returned by Stardust. Science 314, 1724–1728 (2006).

Vollmer C., Hoppe P., Stadermann F. J., Floss C., Brenker F. E.: NanoSIMS analysis and Auger electron spectroscopy of silicate and oxide stardust from the carbonaceous chondrite Acfer 094. Geochim. Cosmochim. Acta 73, 7127–7149 (2009).

INDEPENDENT RESEARCH GROUPS AND JUNIOR RESEARCH GROUPS

INDEPENDENT RESEARCH GROUPS AND JUNIOR RESEARCH GROUPS

Satellite data, theory and practice of the exchange of chemical compounds in biosphere and atmosphere

Independent Research Group Satellite Junior research group ORCAS Remote Sensing

Junior research group Reactive Nitrogen Species

Independent Research Group Theoretical Atmospheric Chemistry

Currently the institute hosts the following four additional research groups:

THE SATELLITE REMOTE SENSING

GROUP (*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 REACTIVE NITROGEN GROUP

(Ivonne Trebs) is a Minerva program research group in the special program for the advancement of outstanding female scientists at the Max Planck Society which investigates the cycling of established to apply quantum chemical

THE ORCAS RESEARCH GROUP *(Frank Keppler)* is funded through a European Young Investigator Award (EURYI) and investigates the production of climate relevant volatile organic compounds and their life cycles. Emphasis is on the trace gases methane and the halomethanes and their contributions to the greenhouse effect and ozone

destruction.

THE THEORETICAL CHEMISTRY GROUP

(Luc Vereecken), a new group in the Max Planck Graduate Center, has been 72 73

nitrogen compounds at the surface atmosphere interface of forest ecosystems.

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.

SATELLITE REMOTE SENSING

THOMAS WAGNER INDEPENDENT RESEARCH GROUP

Figure 1: Mean NO₂ troposheric columns from SCIMACHY during 2003–2006.

The research activities of the Satellite Remote Sensing Group focus on the exploitation of the spectral information from a new generation of satellite instruments (GOME on ERS-2, SCIAMACHY on ENVISAT, OMI on AURA, and GOME-2 on METOP). In addition trace gases, clouds, aerosols, and surface properties are studied in our group.

A particular advantage of satellite observations is that they provide information about atmospheric constituents on many scales, principally from local to global, and allow the identification and quantification of various natural and anthropogenic emission sources (see case study below). We also compare the satellite results with those from chemistry-transport and climate models to advance our knowledge of the atmosphere from an Earth system perspective.

As an example of our activities we describe a new method for the simultaneous determination of NOx emissions and lifetimes with a focus on megacities and other strong "point" sources, which has been recently published in *Science*. An essential element of our approach is that the mean NO₂ distribution is calculated separately for different wind directions. We used the OMI data of tropospheric NO2 columns, i.e., vertically integrated concentrations, from "cloud-free" (cloud fraction below 30%) measurements at ~2 p.m. local time for 2005–2009 (v1.02 from the TEMIS data base). Wind data (below 500 m) are taken from the European Center for Medium-range Weather Forecasts (EC-MWF). To demonstrate our approach, we focus on Riyadh, the capital of Saudi Arabia, with a population of about 5 million (city) to 7 million (greater area) inhabitants. Riyadh is particularly suited because it is rather isolated and is a strong "point source" surrounded by deserts. Also, Riyadh is only rarely covered by clouds, allowing undisturbed satellite observations down to the ground.

Figure 2 (left) displays mean NO₂ tropospheric columns for the Middle East region for calm conditions (wind speeds w <2 m/s). On the right, zooms for Riyadh and the surrounding area are shown, where NO₂ tropospheric columns have been differentiated according to wind direction sectors (SE, S, SW, etc.). The resulting spatial patterns clearly illustrate the outflow of NO₂ from Riyadh, consistent with ECMWF winds.

Assuming a pseudo first-order loss of NO_2 , the mean NOx lifetime and total

NOx emissions can be determined from the observed downwind decay. Since the satellite is only sensitive to NO₂, the determined emissions are scaled by a factor of 1.32, according to typical [NO]/[NO₂] ratios of 0.32 under urban conditions at noon. Our method for determining NOx lifetimes and emissions is generally applicable for any strong, localized source. Figure 3 compares the resulting NOx emissions to the EDGAR (V4.1) emission inventory for the year 2005 for a set of (mega)cities and one other strong point source, the Four Corners power plants. In addition, the derived mean lifetimes are color-coded in the scatterplot.

Despite the large uncertainties of approximately 50%, both for our results and the EDGAR emissions, the derived emissions are generally in good agreement with the EDGAR inventory. For Riyadh, however, the satellite data-derived emissions are higher by a factor of 3. This indicates that the EDGAR NOx emissions are likely too low for Riyadh, though the reason for this is not yet clear; however, from a trend analysis of the satellite observations we can exclude that this discrepancy is only due to emission changes since the EDGAR reference year of 2005. The simultaneously derived daytime lifetimes are in the range of 2.3-6.4 hours (with typical uncertainties

of 40–60%), in good agreement with prior measurements. Because of the global coverage of satellite observations, our method can be applied to various major "point sources" such as megacities around the world. With the ongoing time series of current and especially future (geostationary) satellite instruments with better spatial resolution, our method can serve as an independent tool to validate NOx emission inventories of megacities, and might also be applied to other trace gases in the future as retrievals continue to improve.

Figure 2, left: Mean NO₂ tropospheric columns from OMI during 2005–2009 for calm (w < 2 m/s) conditions. Right: NO₂ distribution around Riyadh (white cross) for different wind conditions, i.e., calm (center) and eight main wind direction sectors indicated by the arrows.

Figure 3: Scatterplot of the NOx emissions determined from satellite observations for different megacities and power plant complexes versus the EDGAR emissions. Resulting NOx lifetimes are color-coded.

"Satellite observations provide a global view on atmospheric trace constitutents."

74 **_ 75**

SELECTED PUBLICATIONS

Wagner, T., Beirle, S., Deutschmann, T., Penning de Vries, M.: A sensitivity analysis of Ring effect to aerosol properties and comparison to satellite observations. Atmos. Meas. Tech., 3, 1723–1751 (2010), doi:10.5194/amt-3-1723-2010.

Beirle, S., Kühl, S., Puķīte, J., Wagner, T.: Retrieval of tropospheric column densities of NO₂ from combined SCIAMACHY nadir/ limb measurements. Atmos. Meas. Tech., 3, 283–299 (2010), doi:10.5194/amt-3-283-2010.

Puķīte, J., Kühl, S., Deutschmann, T., Dörner, S., Jöckel, P., Platt, U., Wagner, T.: The effect of horizontal gradients and spatial measurement resolution on the retrieval of global vertical NO₂ distributions from SCIAMACHY measurements in limb only mode. Atmos. Meas. Tech., 3, 1155–1174 (2010), doi:10.5194/amt-3-1155-2010.

Steffen Beirle, K. Boersma, F., Platt, U., Lawrence, M. G., Wagner, T.: Megacity emissions and lifetimes of nitrogen oxides probes from space. Science, 333, 1737–1739 (2011).

Liu, C., Beirle, S., Butler, T., Liu, J., Hoor, P., Jöckel, P., Pozzer, A., Frankenberg, C., Lawrence, M. G., Lelieveld, J., Platt, U., Wagner, T.: Application of SCIAMACHY and MOPITT CO total column measurements to evaluate model results over biomass burning regions and Eastern China. Atmos. Chem. Phys., 11, 6083–6114 (2011), doi:10.5194/acp-11-6083-2011.

SURFACE-ATMOSPHERE EXCHANGE OF REACTIVE NITROGEN COMPOUNDS

IVONNE TREBS JUNIOR RESEARCH GROUP

Figure 1: Experimental setup to measure surface-atmosphere exchange fluxes of Nr compounds at a nutrient-poor steppe-like grassland ecosystem in Rhine Hessen (Germany).

Our studies focus on the characterization of surface-atmosphere exchange fluxes of reactive nitrogen compounds (Nr). These include nitrogen monoxide (NO), nitrogen dioxide (NO₂), ammonia (NH₃), nitric acid (HNO₃), nitrous acid (HONO), and peroxyacetyl nitrate (PAN). Nr compounds are deposited to vegetation and soil; conversely, particularly NO and NH₃ are simultaneously produced by microbial and/or physicochemical processes and are subsequently released to the atmosphere. The main goal of our research is the experimental investigation and quantification of the emission and removal processes of Nr compounds at the earth's surface, thereby providing valuable information that complements model development activities in the Atmospheric Chemistry Department at the MPIC.

HONO is rapidly photolyzed during daytime and constitutes a significant source of OH radicals in the planetary boundary layer. The formation mechanism of HONO has been the subject of ongoing discussion but remained a mystery up to now. In a joint study with the research group of U. Pöschl, we performed measurements using a laboratory dynamic chamber and observed that HONO is released from soil nitrite as a function of temperature and soil water content, comparable to typically observed soil biogenic NO emissions (Figure 2).

While for managed ecosystems fertilizer input probably largely controls the soil nitrite content (via pH, NO₃⁻ and NH₄⁺, nitrification and denitrification) and hence, HONO emission, in natural ecosystems the Nr deposition fluxes to vegetation and soils influence the release of HONO. In this way deposited Nr is re-cycled to the atmosphere.

Results of NO-NO2-O3 and NH3-HNO₃-NH₄NO₃ triad exchange fluxes measured in situ above a montane Norway spruce forest stand (Fichtelgebirge/Germany) emphasize that the magnitude and direction of Nr fluxes are controlled by physicochemical and/or surface characteristics of forest vegetation and by the interaction of turbulent transport and chemical reactions of trace compounds in and above the forest canopy. The high roughness of the forest and the large receptor surfaces of coniferous trees (needles) resulted in surface resistances of total NH_4^+ and total NO_3^- close to zero. Dry deposition fluxes of total NH_4^+ and total NO_3^{-} exceeded those of NO and NO_2^{-}

by an order of magnitude. Simultaneous HONO measurements in and above the forest indicate that HONO was emitted from the ground. When the forest canopy was fully coupled to the air layer above, differences in the HONO mixing ratios varied around zero despite large differences of photolysis frequencies below and above the canopy. This may indicate that soil-emitted HONO was transported at least partially out of the forest and contributed to OH radical production.

We are currently measuring fluxes of individual Nr species including those of PAN and ozone at a nutrient-poor steppe-like grassland ecosystem complex in Rhine Hessen (Germany) using different micrometeorological methods, such as dynamic and static chambers, the aerodynamic gradient method, relaxed eddy accumulation and eddy covariance (Figure 1). The near-surface turbulent transport at the soil-vegetation-atmosphere interfaces is characterized by measuring vertical profiles of ²²²Rn and ²²⁰Rn. The simultaneous application of all methods will allow an assessment of the scalar similarity theory, the determination of the emission and uptake by surfaces and deposition velocities as well as an investigation of chemistry-turbulence interactions within the grass canopy.

Our future studies will focus on the investigation of fluxes of Nr compounds in the Amazon Basin. We are currently establishing a research station in the Amazonian rainforest encompassing a suite of specialized measurement towers. Our research will be supported by studies of the atmospheric oxidant cycle and the life cycle of the Amazonian aerosol involving a number of other international research institutes.

"Exchange fluxes of reactive nitrogen are influenced by turbulencechemistry interactions at the soilvegetation-atmosphere interfaces."

76 **_ 77**

Figure 2: Gas phase HONO (NO) mixing ratio measured in the exit of the dynamic chamber as a function of temperature and gravimetric soil water content. Soil samples were collected at a nutrient-poor grassland ecosystem in Rhine Hessen (Germany).

SELECTED PUBLICATIONS

Su, H., Cheng, Y., Oswald, R., Behrendt, T., Trebs, I., Meixner, F. X., Andreae, M. O., Cheng, P., Zhang Y., Pöschl, U.: Soil nitrite as a source of atmospheric HONO and OH radicals. Science 333(6049), 1616–1618 (2011).

Wolff, V., Trebs, I., Foken, F, Meixner, F. X.: Exchange of reactive nitrogen compounds: concentrations and fluxes of total ammonium and total nitrate above a spruce forest canopy. Biogeosciences (7), 1729–1744 (2010).

Trebs, I., Bohn, B., Ammann, C., Rummel, U., Blumthaler, M., Königstedt, R. Meixner, F. X., Fan, S., Andreae, M. O.: Relationship between the NO₂ photolysis frequency and the solar global irradiance. Atmos. Measure. Tech. (2), 725–739 (2009).

Trebs, I., Lara, L. L., Zeri, L. M., Gatti, L. V., Artaxo, P., Dlugi, R., Slanina, J., Andreae, M. O., Meixner, F. X.: Dry and wet deposition of atmospheric inorganic nitrogen compounds in a tropical environment (Rondônia, Brazil). Atmos. Chem. Phys. (6), 447–469 (2006).

Trebs, I., Metzger, S., Meixner, F. X., Helas, G., Hoffer, A., Rudich, Y., Falkovich, A. H., Moura, M. A. L., da Silva, R. S. (Jr.), Artaxo, P., Slanina, J., Andreae, M. O.: The NH_4^+ - NO_3^- - Cl^- - SO_4^{2-} - H_2O aerosol system and its gas phase precursors at a pasture site in the Amazon Basin: How relevant are mineral cations and soluble organic acids? J. Geophys. Res-Atmos., 110 (D07303), doi:10.1029/2004JD005478 (2005).

NONMICROBIAL METHANE FORMATION IN THE **BIOSPHERE**

FRANK KEPPLER JUNIOR RESEARCH GROUP

Figure 1: Plants produce methane: how significant is it for the atmosphere?

Methane (CH₄), 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 CH₄ budget including all its sources and sinks and the parameters that control its emissions is a precondition to simulate past and future scenarios of its atmospheric concentration. Traditionally, biogenic CH₄ was thought to be formed only by microorganisms (methanogens) under strictly anaerobic conditions in wetland soils and rice paddies, the intestines of termites and ruminants, and human and agricultural waste.

Until our discovery of methane emissions by plants in 2006, only combustion processes were considered to form CH₄ in aerobic conditions. Independent observations from several research fields now indicate that in addition to

terrestrial plants, soils, fungi, animals, and marine vegetation also produce CH4 under aerobic conditions. However, the mechanisms involved in its formation have not yet been elucidated and remain the subject of debate and speculation. This is particularly true for the recently identified vegetation source. Nevertheless, mounting evidence suggests that aerobic CH₄ formation may not be "exotic," but could be widespread in nature. Additional investigations are needed to identify CH₄ sources and fully understand the global biogeochemical cycling of CH₄.

One main focus has been the reaction pathways that lead to the formation of CH₄ in living and dead plants, and also the environmental factors affecting their fluxes. For example, CH₄ is released from dead plant matter when exposed to ultraviolet radiation and from intact living plants when they are wounded. In this context it was suggested that reactive oxygen species (ROS) might play an important role in the formation of CH₄ in plants. The requirement of specific ROS to generate CH₄ from plant material might be the key to understanding the functional mechanisms of nonmicrobial CH4 emission and could explain the divergent results of published CH₄ emission data from plants. All environmental stresses, both biotic and abiotic, as well as cellular signaling processes involve ROS formation. Thus, CH₄ formation in living plants may be an integral part of cellular responses towards changes in oxidative status present in all eukaryotes.

Next to the vegetation sources we have recently collected the first evidence that soils, fungi, marine algae, and even extraterrestrial matter such as meteorites might be sources of nonmicrobial CH₄ formation. Particularly ultraviolet radiation appears to strongly affect the release rates of CH₄ from terrestrial

soils and meteoritic material. These results have yet to be published and are the subject of further detailed investigations of our group.

We will continue to explore the reaction pathways involved in nonmicrobial CH₄ formation in the biosphere and solar system employing a stable isotope approach. The concept of nonmicrobial CH₄ formation in different environmental compartments of the biosphere is schematically illustrated in Figure 2. Once major pathways (both abiotic and biotic) in the different compartments have been identified, enhanced emphasis will be placed on their role

in global change, notably in view of the expectation that biospheric emissions of CH₄ may respond to climate warming. This will require the identification of major sources of biospheric CH₄ and the environmental parameters affecting their fluxes, in support of developing future scenarios.

Furthermore, investigations of extraterrestrial matter, such as meteorites, will be conducted. For example CH₄ may form by the exposure to ultraviolet irradiation. The implications of these findings may help explain formation of CH₄ on Mars, other planets, planetoids, and asteroids.

"Quantifying individual processes that release methane is key to understanding atmospheric methane, as previous understanding of the total source and sink have provided false confidence."

78 **79**

SELECTED PUBLICATIONS

Keppler F., Hamilton J. T. G., Braß M., Röckmann, T.: Methane emissions from terrestrial plants under aerobic conditions. Nature 439, . 187–191 (2006).

Keppler F., Hamilton J. T. G., McRoberts W. C., Vigano I., Braß M., Röckmann, T.: Methoxyl groups of plant pectin as a precursor compound for atmospheric methane: Evidence from deuterium labelling studies. New Phytol. 178, 808-814 (2008).

Keppler F., Boros M., Frankenberg C., Lelieveld J., McLeod A., Pirttilä A. M., Röckmann T., Schnitzler I.-P.: Methane formation in aerobic environments. Environ. Chem., 6, 459-465 (2009).

Althoff F., Jugold A., Keppler F.: Methane formation by oxidation of ascorbic acid using iron minerals and hydrogen peroxide. Chemosphere, 80, 286-292 (2010).

Wishkerman A., Greiner S., Ghyczy M, Boros M., Rausch T., Lenhart K. Keppler, F.: Enhanced formation of methane in plant cell cultures by inhibition of cytochrome c oxidase. Plant Cell Environ., 34, 457-464 (2011).

Figure 2: A conceptual scheme of nonmicrobial methane formation in the biosphere and from extraterrestrial matter.

THEORETICAL ANALYSIS OF OXIDATION MECHANISMS, REACTION RATES, AND PRODUCTS

LUC VEREECKEN INDEPENDENT RESEARCH GROUP .

Figure 1: Volatile organic compounds such as isoprene emitted from vegetation in remote forests help in buffering the oxidative capacity of the atmosphere.

The theoretical analysis of chemical processes can be powerful and applicable to a wide range of questions. By combining quantum chemical characterizations of chemical reactions with theoretical-kinetic analysis of the reaction rate and product yields, one can gain a deeper understanding of the underlying chemistry. Our group aims to intertwine with research efforts at the institute, for example by supplementing laboratory experiments and extending the results to wider reaction conditions, by studying the chemistry of compounds observed in the field, or by providing kinetic parameters for reactions needed in chemical kinetic models when insufficient information is available. In addition, stand-alone theoretical predictions are very useful to identify and quantify novel chemistry.

NF₃ is a potent anthropogenic greenhouse gas with a steadily rising con-

centration in the atmosphere. Supplementing the extensive experimental investigation in the Kinetics and Photochemistry Group (Crowley), we studied the reactions of NF₃ with excited $O(^{1}D)$ atoms and with OH radicals using theoretical methodologies. The reaction with O(¹D) was found to be an important oxidation process, though slower than typical $O(^{1}D)$ reactions due to an entropic bottleneck in forming the rigid ONF₃ adduct. The observed formation of F-atoms was confirmed, disproving previous theoretical work that only examined formation of OF radicals. These latter radicals were shown to be formed in a new but minor abstraction reaction. A number of reactions were examined in the NF₃+OH system; the theoretical prediction of the reaction rate found a very slow reaction, many orders of magnitude below the experimentally obtained upper limit (Figure 2).

Improvements in mass spectrometric resolution allowed the Organic Reactive Species Group (Williams) to identify the presence of the exotic carbon suboxide, C₃O₂, in ambient air, launching a joint effort to describe its tropospheric processing. Experimental work by the Crowley and Williams groups revealed rather slow rates of reaction with OH and ozone, the prime atmospheric oxidants. Ultraviolet spectra indicated a modest photolytic removal rate. A theoretical analysis of the reaction with ozone revealed a large reaction barrier, yielding a slow reaction rate, in good agreement with experiments. The chemistry was found to proceed through the formation of complex cyclic carbon oxide and carbonyl oxide intermediates, quickly leading to the full oxidation to CO and CO₂. The reaction mechanism with OH radicals involves multiple alkylperoxy and alkoxy intermediates, yet ultimately generating HOCO in

oxidative conditions. No evidence for the formation of highly reactive C₂O radicals was found.

Since the field campaign conducted in Suriname, it has been clear that OH radicals in the pristine atmosphere are regenerated in isoprene oxidation processes (Figure 1). The most viable chemical pathways leading to this regeneration have been controversial, predicted by theory yet difficult to reproduce in experimental setups. Recent modeling work by the Atmospheric Modeling Group (Lawrence) rigorously completed the isoprene oxidation in a new model called MIME (Mainz Isoprene Mechanism – Extended), which is an extension of the MCM (Master Chemical Mechanism) and the theory-based LIM (Leuven Isoprene Mechanism), and then simplified this to the MIM3 mechanism for inclusion in global models. Using these models, seemingly contradictory experimental data sets could be reconciled, showing that the OH concentration is buffered. Thus, new reaction pathways have been discovered, which are also relevant for other classes of atmospheric VOC, for example aromatics. Our group provided supporting calculations for the underlying kinetic model; this included a detailed comparison of two discordant experimental data sets on the key alkylperoxy radical rearrangements, providing further support for the MIM3 model validity.

"Theoretical calculations complement and extend experimental work, and aid the integration of laboratory work, field observations, and modeling studies."

80 **_ 81**

SELECTED PUBLICATIONS

Peeters, J., Nguyen, T. L., Vereecken, L.: HOx radical regeneration in the oxidation of isoprene. Phys. Chem. Chem. Phys. 11, 5935–5939 (2009).

Nguyen, T. L., Vereecken, L., Peeters, J.: HOx regeneration in the oxidation of isoprene III: Theoretical study of the key isomerisation of the Z- δ -hydroxy-peroxy isoprene radicals. ChemPhysChem 11, 3996–4001 (2010).

Dillon T. J., Vereecken L., Horowitz A., Khamaganov V., Crowley J. N., Lelieveld J.: Removal of the potent greenhouse gas NF₃ by reactions with the atmospheric oxidants O(¹D), OH and O₃. Phys. Chem. Chem. Phys. 13, 18600-18608, doi: 10.1039/c1cp22230a (2011).

Taraborrelli D., Lawrence M. G., Crowley J. N., Dillon T. J., Gromov S., Groß C., Vereecken L., Lelieveld J.: Hydroxyl radical buffered by isoprene oxidation over tropical forests. Nat. Geosci. (submitted) (2011).

0.0 0(¹D)+NF₃ -4.6 F₂NF--0 -36.2 F+N0+F₂ -42.3 NF₂+OF -50.8 0(³P)+NF₃ -60.7 FN0+F+F -63.8 0NF₂+F -74.6 -80.0 F₂NOF -94.5 FN0+F₂ -113.0 0NF₃

Figure 2: The reaction with excited $O({}^{1}D)$ atoms was shown to be an efficient removal process of the greenhouse gas NF_3 . The theory-based analysis confirms and extends the experimental work.

CENTRAL SERVICES

CENTRAL SERVICES

Administration, Library, Electronics Group, Information Technology, Workshops and Public Relations

20 EURO

THE SCIENTIFIC WORK OF THE INS-**TITUTE IS SUPPORTED BY VARIOUS CENTRAL SERVICE**

Competent staff assists the scientists with practical issues such as instrumentation or in research applications. Besides the administration, the central

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 250 employees, the implementation and monitoring of procurement policies, the administrative execution of projects and third party funding, the bookkeeping and accounting of the institute's budget, the accounting of travel expenses and the support of visiting scientists and

research fellows. Consequently, the administration is divided into the areas Staff, Purchasing, Accounting, and

LIBRARY

The library provides the scientists with media and scientific information in many forms. While the collections of printed material (books, journals) remain a valuable source of information, the importance of electronic media (especially online journals) has been steadily increasing in recent years. Literature databases (Georef, Web of Science, etc.) represent another important

ELECTRONICS GROUP

The main task of the group is the hardand software development needed to support scientific experiments and the maintenance of existing electronic equipment. Commercially available equipment rarely meets the specific needs of scientific work, e.g., of field measurements. To stabilize an instrument's process parameters, despite changing environmental conditions, additional process controls for temperature, pressure or flux need to be implemented.

tems are often newly developed and modified, there has been an increasing

services include the library, an electronics and an IT group, facilities management, the mechanical workshops, and public relations.

82 **83**

International Management Office. Affiliated to the institute's administration are all provision and support facilities such as the central building management, building maintenance services, the library, the reception gate and the post office. In 2010 and 2011 audits of the Max Planck Society and the Landesrechnungshof (Audit Office of the State of Rhineland-Palatinate) have shown that the institute's administration with a total of twelve employees is lean, effective and efficient.

source of information, as do various document delivery services.

The library collections cover various subject areas (physics, chemistry, biology, mathematics, meteorology, geosciences, astronomy, ecology, nuclear physics) and contain approximately 28,000 volumes (periodicals, monographs, reports, theses), as well as various microfiche forms CDs and video tapes.

demand for highly flexible and scalable process control hard- and software. Although primarily needed for control, data management, archiving and visualization, the equipment is also used in automated process control, i.e. without an operator. Such applications are based on a modular system consisting of various processors, input/output modules and software Since these sysmodules.

IT-GROUP

The group provides the institute's central information technology needs, data processing systems and ensures smooth operation of the servers, PCs and the network. Four staff members currently provide support to some 300 users, approximately 400 clients and network devices, about 30 servers (a number that is continually growing) and the operating systems Windows, Linux, Mac OS, Solaris. This includes the challenging task of supporting scientists during measurement campaigns in very remote locations.

The tasks are:

- Ensuring availability of the IT Systems for a smooth workflow
- Safeguarding the IT infrastructure against technical faults and other security risks

- Supporting the scientific groups by optimizing IT-supported processes
- · Providing advice when new comput ers and network devices are beeing purchased
- Supporting users with hardware and software problems

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

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.

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, such as 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 mechanics training workshop has been highly successful in the competitions of the "Handwerkerjugend" with eleven prize winners at regional, ten at state and four at federal level contests.

The electronics technicians, who are trained for their qualification in the electronics group, are offered a basic education in metal techniques as well. In addition, the training workshop offers industrial courses for schools and various types of education.

PUBLIC RELATIONS

In 2011 the Max Planck Institute for Chemistry complemented the Minerva logo of the Max Planck Society with its own logo and corporate design. The different sizes of open and closed circles of the logo symbolize practical field research as well as model calculations. The circles represent research on molecules, nanoparticles as well as science on the entire Earth system.

Further, a new institute website was launched, which allows visitors to navigate within a clear information structure. It also offers additional features such as event calendars and search functions.

In 2011 Mainz was elected the "City of Science," and many science related activities took place in the public arena. The Max Planck Institute for Chemistry participated with hand-on science exhibits. The main attraction in Mainz was the science market in which our institute was represented by the "cloud memory" and the mobile laboratory from the Particle Chemistry department. In 2009 the institute participated with an exhibit about satellite remote sensing aboard the ship "MS Wissenschaft" (Motor Ship Science) - an interactive exhibition in form of a floating science center. About 30 cities were visited, with the target group being primarily school classes. In autumn 2009 the Max Planck Institute for Chemistry, representing the Earth System Research Partnership and the Mainz Geocycles

search Center, organized and hosted the "Klimazeitreise" (Climate time travel). The journey was based on virtual travel through the aspects of our climate in the form of public lectures. The institute also took part in the exhibition train of the Max Planck Society "Research Expedition Germany" which was part of the "Science Year 2009." The train was conceived in a way that makes it particularly suited to reaching the maximum possible number of citizens and young people over a wide geographical

Re-

84 **85**

area in a short period of time. As in previous years, the institute organized a Girl's Day. The aim of this nationwide event is to interest girls in pheric Chemistr scientific and technical professions.

> From 2009–2011 the PR team has published 38 press releases, often in close cooperation with the MPS 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.

A PR highlight in 2012 will be the celebration of the 100th anniversary of the institute. In addition to a history of science colloquium, the institute plans an exhibition and an anniversary publication in which the different research eras of the institute will be reviewed. There will also be a ceremony and an open house day in October 2012.

Another PR focus will be the Earth System Research Partnership. The three Max Planck Institutes involved are jointly developing and building a major exhibit which will represent atmospheric and climate research to be shown on the 2012 tour of the "MS Wissenschaft."

STAFF AND BUDGET

In early 2011 a total of 266 persons were employed at the institute, of which 66 scientists, 89 junior scientists, 3 scientific guests and 12 apprentices; 228 staff members were paid from institutional funds and 38 scientists were supported by third-party project funding. As is the case with other institutes of the Max Planck Society, 50% of the funding derives from the federal government and 50% from the states.

In 2010, the institute's total budget was €19.32 million.

CONTACT DATA

Max Planck Institute for Chemistry (Otto-Hahn-Institut)

Hahn-Meitner-Weg 1 55128 Mainz Germany

Phone: +49-6131-305-0 E-Mail: pr@mpic.de www.mpic.de

PUBLISHED BY

Max Planck Institute for Chemistry (Otto-Hahn-Institut), Mainz, Germany, January 2012

EDITOR-IN-CHIEF Susanne Benner

EDITORS T. W. Andreae, Wolfgang Huisl and le-tex, Leipzig

LAYOUT markenfaktur, Heidelberg

PRINTED BY Eubler Druck, Heidelberg

GRAPHICS AND PHOTO CREDITS

If not stated separately: Authors of the articles, Carsten Costard, Rosita Eckl, Rainer Königsstedt, Jochen Schöngart, Elmar Uherek, Florian Wittmann, Pictures from the Archive of the Max Planck Society and the Mainz Cloud Gallery.

The MPIC is continually growing and evolving. For up-to-date information please see our website: www.mpic.de

Copryright 2012 MPIC.

Max Planck Institute for Chemistry (Otto-Hahn-Institut)

Hahn-Meitner-Weg 1 55128 Mainz Germany

Phone: +49 (6131) 305 – 0 www.mpic.de E-Mail: pr@mpic.de