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JOINT MASS SPECTROMETRY CENTRE

HICE • Aerosols and Health
Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health

Progress Report

Summer Term **2015** – Winter Term **2017**/2018

Joint Mass Spectrometry Centre (JMSC)

JMSC comprehends the cooperation unit Comprehensive Molecular Analysis – CMA at the Helmholtz Zentrum München and the Chair of Analytical Chemistry – CAC at the University of Rostock

Virtual Helmholtz Institute HICE

Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – Aerosols and Health (HICE)

→ The JMSC reports from 2008–2018 can be downloaded here:
www.helmholtz-muenchen.de/cma/publications

Foreword

Dear reader,

I'm very happy to present you the sixth progress report of the Joint Mass Spectrometry Centre (JMSC) as well as the second progress report of the Virtual Institute of Complex Molecular Systems in Environmental Health- Aerosols and Health (HICE).

The JMSC operates since 2008 as a cooperative, joint research initiative of the University of Rostock (Chair of Analytical Chemistry at the Institute of Chemistry) and the Helmholtz Zentrum München (cooperation unit: Comprehensive Molecular Analytics, CMA) based on a perpetual cooperation contract between the Helmholtz Zentrum München (HMGU) and the University of Rostock (UR). The main research fields of JMSC are located in areas of Environmental Health (and here in particular in the field of Aerosol and Health) and of Analytical Chemistry (and here in particular in Enabling Technologies, i.e. in the field of mass spectrometry, chromatog-raphy, laser spectroscopy and in-vitro cell exposure approaches).

Prof. Zimmermann with a newly developed Single-Particle Aerosol Laser Mass Spectrometer at newHICE-Measurement campaign in Feb. 2018 in Kuopio, Finland.

The virtual Helmholtz Institute HICE is a multidisciplinary research programme for elucidating the biological and health effects as well as the physico-chemical properties of aerosol emissions from combustion sources (e.g. ship engine exhaust, car emissions, wood combustion etc.) with 9 main partners, which was funded by the Helmholtz Association (HGF) from 2012-2017. After the end of the HGF-funding period, the HICE-concepts were perpetuated in a newly focused manner at JMSC by the HMGU ("newHICE").

As in the preceding JMSC reports, the actual concepts and the organisational structure of JMSC are briefly in-troduced. In this context it is to mention, that recently a new organisational structure was implemented at JMSC, introducing new JMSC deputy heads at the HMGU (Prof. Dr. T. Adam, CMA) and the UR (Dr. T. Streibel, CAC) as well as a topic leader structure. In the report also selected highlights, the actual PhD students and se-lected scientific reports on research projects are given. The JMSC co-workers are introduced and last but not the JMSC least performance parameters (cooperations, publications, lectures, acquired third-party funds etc.) are listed.

The second part of the report states about the HICE research and activities performed in the last half of the funding period. It includes HICE research highlights, reports on the educational aspects of the HICE programme, selected dissemination activities, including a section on the press and other media (e.g., TV) coverage of the HICE activities. At last, a brief outlook on newHICE is given.

I'm convinced that in the progress report at hand, the achievements and capabilities of the JMSC-cooperation between the Helmholtz Zentrum München and the University of Rostock as well as the advances made in HICE are well summarised.

Finally, I have to thank the rector of the University of Rostock, Prof. Dr. W. Schareck, and the scientific CEO of the Helmholtz Zentrum München, Prof. Dr. G. Wess as well as the administrations at UR and HMGU for the ongoing support of JMSC and HICE. Without the excellent and super engaged work of all the JMSC co-workers and PhD students as well as without the support by the co-operational partners of JMSC and HICE, the success of the last years would not have been possible. Finally I like to thank all JMSC members for their input and Dr. B. Schloter-Hai for compiling this current progress report.

I close with the hope that the following years will be as motivating, interesting, surprising and successful as the preceding ones and I'm very happy that finally "after HICE actually means before (new) HICE".

Prof. Dr. Ralf Zimmermann

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Joint Mass Spectrometry Centre

This is the JMSC

Since April 2008, the University of Rostock (Chair of Analytical Chemistry) and the Helmholtz Zentrum München (Comprehensive Molecular Analytics) are cooperating in the general area of environmental health research (e.g. human health-related ambient and emission aerosols research) as well as in the area of development and application of mass spectrometric and chromatographic analytical techniques for the characterization of complex molecular mixtures.

A joint research unit of University of Rostock and the Helmholtz Zentrum München (HMGU), the "Joint Mass Spectrometry Centre" (JMSC), was founded for this purpose. The JMSC is headed by Prof. Dr. Ralf Zimmermann, who concurrently holds the Chair of Analytical Chemistry (CAC) at the University of Rostock (UR) and directs the independent cooperation unit "Comprehensive Molecular Analytics" (CMA) at the Helmholtz Zentrum München (HMGU). From 2012 on, the cooperation was further intensified by the successful application, funding and implementation of the "Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – Aerosols and Health (HICE)". HICE is an international research consortium with 8 funded partner institutions, with a funding period of 5 years by the Helmholtz Impulse and Networking Funds (INF) of the Helmholtz Association (HGF), and supported financially by HMGU and UR. Prof. Dr. Ralf Zimmermann acted as the speaker of HICE. After the end of the HGF funding in 2017, a part of the HICE was permanently taken over by HMGU (newHICE). In addition to JMSC (i.e. UR and HMGU) also the University of Eastern Finland (UEF) is a funded partner of newHICE. The long-term aims of newHICE is to extend the concept of HICE, namely to investigate the biological and health impact of emissions from combustion sources, to the analysis of ambient air. This includes the development of more sensitive technologies to address the impact of the polluted ambient air onto human lung cells, the investigation of the effects of bioaerosols (allergy) and studies with artificially photochemically aged emission aerosols.

JMSC Research Areas

The scientific activities of the JMSC are currently structured in two general research areas, Aerosol & Health and Enabling Technologies. The objective of the first research field is to study the impact of aerosols and air pollution on human health (i.e. environmental health research). Environmental factors which are directly or indirectly relevant for human health and well-being are studied. A pronounced activity in this research field is the investigation of health effects of ambient and emission aerosols. The second general research field comprehends the area of development and application of mass spectrometric and chromatographic analytical techniques for the characterization of complex molecular mixtures. The work in the two general research fields is organized in eight corresponding and interlinked research topics at UR and HMGU, respectively (Fig.1).

The respective 8 topic leaders are indicated in the figure. The research topic of **Aerosol Chemistry** occupies itself with the chemical characterization of all kinds of aerosols, enveloping ambient aerosols as well as combustion aerosols and secondary aged aerosols, while **Aerosol Physics** is working on size distributions, questions of aerosol dosage and work place aerosols. The research topic of **Aerosol Toxicology** deals with biological effects on different omics-levels by investigating cell culture models, which are exposed to aerosols on an air-liquid interface. **Bio-Analysis** is engaged in the analysis of biomarkers

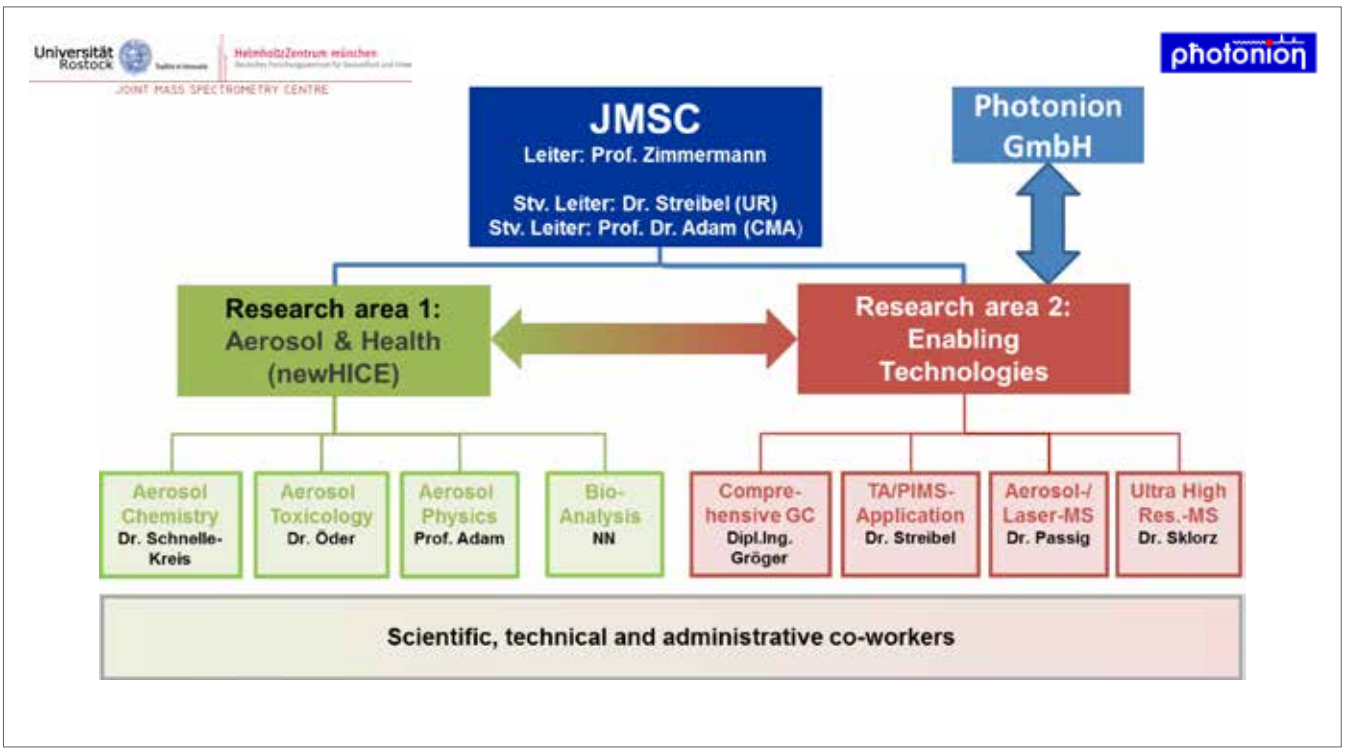


Fig.1: Organisation chart of the JMSC depicting the two general research areas and eight research topics with the respective topic leaders

Fig.2: a) Research Building of University of Rostock at Dr. Lorenzweg (till 2020) where the Chair of Analytical Chemistry/JMSC has its main research and teaching premises. Main large equipment are several photoionisa-tion mass spectrometers, partially in hyphenation with different separation and pyrolysis devices.

b) Research Building LLM of University of Rostock (since 2016) where the Chair of Analytical Chemistry/JMSC operates the Mass Spectrometry with a high resolution MS laboratory (FTICR-MS, Orbitrap MS), a short-pulse (fs) laser mass spectrometry laboratory, an aerosol mass spectrometry laboratory as well as a more routine anaylsis laboratory (LC-MS/MS, GC-MS).

c) Construction site of the new "Chemistry extension" building of University of Rostock, where Chair of Analyti-cal Chemistry/JMSC will move to in 2019/2020

of exposure utilizing chromatographic methods. In the **Topic Comprehensive GC** the development and application of sophisticated multidimensional comprehensive chromatographic separation methods, often coupled with high-resolution mass spectrometry, is conducted. The research topic **TA/PIMS-Application** busies itself with hyphenated analytical techniques between thermal methods and mass spectrometry as well as with online mass spectrometric monitoring of thermal processes. In the research field **Aerosol/Laser-MS** single particle mass spectrometry and Femto-second laser spectroscopy is performed. Finally the topic of **Ultra High Resolution-MS** is occupied with development and application of high resolution mass spectrometry utilizing Fourier-Transformed Ion Cyclotron Mass Spectrometry and Orbitrap-Mass Spectrometry.

Facilities and Equipment

At the University of Rostock the JMSC is represented by the Chair of Analytical Chemistry. It is located in buildings of the University of Rostock in the Dr.-Lorenz-Weg and in the new Research Building of the "Life, Light & Matter Department of the Interdisciplinary Faculty (Albert Einstein Straße). Currently 16 scientists and students (senior scientists, postdocs, PhD-students) are working at the Chair of Analytical Chemistry. Four scientists occupy permanent academic positions, while twelve scientific members of CAC have temporary third-party funded employment contracts or are scholarship holders. Furthermore there are 3.5 technical staff positions located at CAC (2 technicians, one secretary and 0.5 electronic engineer position). A new building is currently under construction next to the Research Building, to which instruments and staff at Dr.-Lorenz-Weg will move in 2020. (Fig.2).

The JMSC research equipment and instrumentation in Rostock include six photo-ionisation time-of-flight-mass spectrometers and one proton transfer mass spectrometer for online analyses. For the ultra-high mass resolution application and developments a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR-MS) system is available. The system is based on a 7T superconducting cryomagnet and has two FTICRMS carts

Fig.3: High resolution MS laboratory in the Research Building LLM of University of Rostock where the Chair of Analytical Chemistry/JMSC operates a FTICR-MS System. The 7 T FTICR exhibits two carts allowing MALDI, ESI, GC-/TA-APCI, APPI, APLI ionization experiments

(Solarix and APEX III, Bruker GmbH, Germany). The system can be used with MALDI, ESI and GC-APCI ion sources and interfaces and reaches mass resolutions of up to 500.000. Furthermore CAC has an Orbitrap high resolution mass spectrometer with ESI ion source. A laser laboratory is available for the application and development of photoionisation techniques (Nd:YAG laser, tunable OPO and dye laser, CO_2 laser, various excimer lasers, rare-gas excimer light sources), two LCMS systems and several GC-MS are used for method development. Two laser desorption-resonance enhanced multiphoton ionization-single particle-time-of-flight mass spectrometer (LD-REMPI-SP-TOFMS) for the online characterization of aerosol particles are in use.

For applications of analytical pyrolysis, combustion research and pyrolysis research, a pyrolysis furnace with two chambers and a pyrolyzer that is inter-connectable with a GC/ MS are available. For development and application in thermal analysis, three thermo balance systems are available, of which one is additionally equipped with a Fast-GC coupling unit. A Thermal/ Optical carbon analyzer is available to study carbon content in solid samples, which is in addition coupled to a time-of-flight mass spectrometer and a quadrupole mass spectrometer. The cooperation unit "Comprehensive Molecular Analytics" (CMA) at Helmholtz Zentrum München in Neuherberg and Sendling consists of 16 scientists. Nine scientists are permanently employed at Helmholtz Zentrum München. 18 PhD students are employed on a temporary basis with contracts through third-party funding or are stipend-holders. The cooperation unit also has five technical staff members and two scientists serving as associated scientific consultants. The CMA laboratory rooms are currently dispersed in two separate locations, one on the main campus of the Helmholtz Zentrum München in Neuherberg and the other at Gmunder Straße in München-Sendling.

The CMA cooperation unit operates two HPLC-MS/MS systems, two HPLC systems equipped with a diode array and fluorescence detector. Four instruments for the multidimensional analysis of highly complex samples in bioscience and environmental science are currently available in CMA: one system for multi-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS), one system for multi-dimensional gas chromatography fast quadrupol mass spectrometry (GCxGC-QMS), a multi-dimensional gas chromatography high resolution multi reflection time-of-flight mass spectrometer GCxGC-HRTOFMS (cooperation with LECO GmbH, Germany), a multidimensional comprehensive HPLCxGC System coupled to quadrupole MS (cooperation with Shimadzu GmbH, Germany).

Furthermore four GC-MS systems (partially equipped for thermal desorption of aerosol loaded filters) and an FTIR gas analyzer are available. Physicochemical characterization of particulate matter and aerosol particles is performed using a high resolution aerosol mass spectrometer (Aerodyne-AMS), two scanning mobility particle size spectrometers (SMPS), two electric low pressure impactors (ELPI), an aerodynamic particle size spectrometer (APS), a white light optical particle size spectrometer (WELAS) and diverse particle sampling equipment (several Berner impactors, a rotating-drum impactor, a MOUDI impactor and several low volume samplers). As a rather new research topic at CMA/JMSC the Aerosol Toxicology was established from 2015 on. This topic was expanded during the establishment of the permanent newHICE funding at CMA. The topic Aerosol Toxicology is equipped with 3 automated air liquid interface (ALI) cell exposures stations with in total 60 exposure places, facilities for cell culture work (incubators, clean benches etc.) a fluorescence microscope and a real-time PCR unit. Furthermore it operate the mobile S2 biosafety laboratory of CMA (HICE MobiLab)

The Joint Mass Spectrometry Centre cooperates in framework of the HICE extension ("newHICE") with the University of Eastern Finland in Kuopio in the field of aerosol and health. The joint research activities are regulated by a cooperation contract. At Kuopio, extensive measurement facilities for aerosol research are available, including state-of-the-art appliances for wood combustion and diesel generators as well as an aerosol chamber and flow tube reactors for aerosol aging experiments. Fur-ther HICE partners) nowadays are included via third-party funding (MDC, University of Luxemburg, Photonion GmbH) and further partner are joining for joint Aerosol and Health research

Fig.4: a) Building 24 at the main campus of the Helmholtz Zentrum München in Neuherberg where the CMA/JMSC operates aerosol chambers and aerosol characterisation devices, partly in cooperation with the spin-off Photonion GmbH

b) Main research premises of CMA/JMSC at Gmunder Straße in München-Sendling (2nd floor)

Fig.5: Multi-dimensional gas chromatography high resolution multi reflection time-of-flight mass spectrometer GCxGC-HR-TOFMS with experimental inlet systems for high-bowling samples (direct insertion probe-DIP and thermal-analysis-TA coupling). Cooperation with LECO GmbH

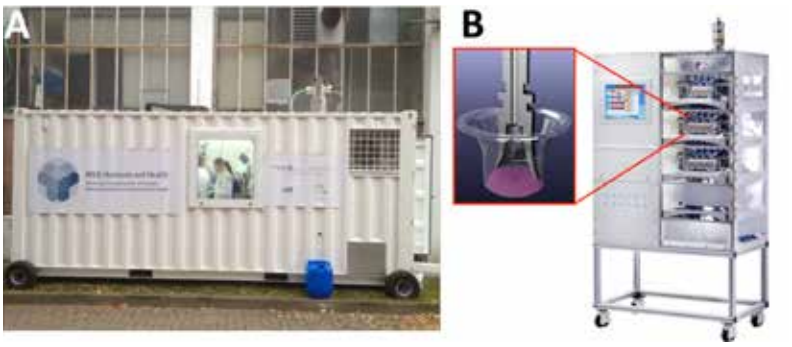


Fig.6: A) HICE MobiLab (mobile S2 biosafety laboratory) B) One of the three mobile automated air liquid interface (ALI) cell exposures unit with a sketch of the ALI cell exposure setting (purple= lung cell layer).

Technology Transfer: Photonion GmbH

Ongoing developments in online photoionization mass spectrometry (PIMS) in our cooperation unit have led to a number of patents and third party projects, often carried out with direct industrial support. To satisfy the growing demand, a spin-off company was founded in 2009, the Photonion GmbH. It is closely connected to scientific research and aims at the further development of innovative trace gas analysis instruments based on the JMSC photo ionization-mass spectrometry techniques and expertise. Measurement devices with both, single photon ionization (SPI) and resonance multiphoton ionization (REMPI) techniques are developed and marketed. Photonion is also engaged in fundamental and applied research projects together with JMSC, which will prospectively lead to new products (e.g. for single particle mass spectrometry and food technology). At Photonion 4 scientists are employed, working together with the JMSC scientists in Munich and Rostock on joint projects in the research field “Aerosol & Health” and “Enabling Technologies”.

Highlights

„Deutscher Zukunftspreis“ for C³ Consortium

The project C³-Carbon Concrete Composite, in which the JMSC is incorporated, was awarded with “Der Deutsche Zukunftspreis 2016” by the German president Joachim Gauck. The project C³ analyses carbon concrete as the building material of the future including more than 150 partners from research and industry. Within the consortium the JMSC investigates the health effects of working with carbon concrete in construction areas. “Der Deutsche Zukunftspreis” is one of the most prestigious scientific awards in Germany. The President of Germany annually honors single persons or consortia that transfer excellent innovations in engineering or natural sciences into marketable products for the good of society.

C3 Zukunftspreis

New Labs for CMA in Munich

The group Complex Molecular Analytics (CMA) moved from the Campus of the Helmholtz Zentrum München to a new location in the south of Munich in October 2015. The group has now 1700 m² work place available including five biology and analytics laboratories, eight offices and one spacious room for conferences and seminars. The new location was inaugurated on 2nd of December 2015. More than 60 colleagues, neighbors and guests participated in the event at Gmunderstrasse 37 in Munich. The research of CMA includes the creation of aerosols and the analyses with state-of-the-art mass spectrometry and chromatography methods as well as the study of effects of aerosols on human lung cells.

Gebäude Gmunder Str. und Einweihungsfeier

Media Coverage: Health effects of ship diesel

In June 2015 the Helmholtz Virtual Institute HICE published the results of the research on the effects of ship diesel and heavy fuel oil on human lung cell cultures in the renowned journal for interdisciplinary science PLOS ONE. The media followed with a broad response: The magazine “Der Spiegel” published an op-ed article, the newspapers “Zeit” and “Hamburger Abendblatt” covered the topic in their online issues, the programme “Report München” showed an interview with Prof. Ralf Zimmermann on the German broadcasting station ARD.

Experiments on car and wood emissions in Finland and Germany

The research of the Helmholtz Virtual Institute HICE focuses on the effects of emissions from ships, wood stoves and cars on human health. Therefor, two main measurement campaigns took place at the University of Rostock in 2015 and at the University of Eastern Finland in 2016. In Rostock the scientists analyzed the effects of gasoline and ethanol on human lung cells as well as on primary cells. In Finland the effects of wood as spruce and pine as well as of pellets were analyzed and compared to Diesel. The scientists also investigated the ageing process of emitted aerosols and its effects on human lung cells and animals. First results are expected in 2017.

Kuopio 2016

New cooperation project of CMA and ASG

On June 1st 2016 CMA and the company ASG Analytik-Service Gesellschaft started a new cooperation project. The project named "Entwicklung eines Screening-Verfahrens für fossile und biogene Schwerflüchter zur erstmalig validierten Bestimmung von spezifischen Parametern in Bitumen-Matrizen zur qualifizierten Alterungsprognostik und Schadensanalytik" is founded by the Federal Ministry for Economic Affairs and Energy as part oft he program "Zentrales Innovationsprogramm Mittelstand (ZIM)". Uwe Käfer, PhD Student in collaboration with ASG, will focus on chemical characterization of Bitumen and other distillation residues from petroleum. The project will run until May 2019.

Flyer Cooperation Project

New Science Building for Interdisciplinary Research at the University of Rostock

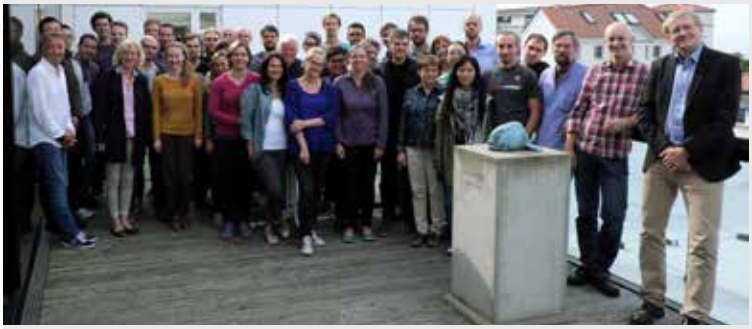
The new science building of the Department "Life, Light and Matter" of the University of Rostock was inaugurated in July 2015 after five years of construction. The JMSC runs four laboratories in the building. High resolution mass spectrometers as well as gaschromatography-MS systems were moved in November 2015 from the former laboratories of the Division of Analytical and Technical Chemistry to the new science building. An fs-laser Mass Spectrometer, granted by the Deutsche Forschungsgemeinschaft, will follow 2017. The science building incorporates highly interdisciplinary research combining essential elements of the basic sciences of physics, mathematics and chemistry with the application fields of mechanical engineering, electrical engineering, biology and medicine.

Forschungsbau

JMSC annual get-togethers: from the sea to the highest mountain

The JMSC members from the cooperation group CMA at the Helmholtz Zentrum München and from the Division of Analytical and Technical Chemistry at the University of Rostock meet once per year for scientific interchange. From 2015 to 2017 they picked very special locations for their get-togethers: the beach of the Baltic Sea and the summit of Germany's highest mountain, Zugspitze. The historical site "Prora" on the island of Rügen hosted the group in September 2015. In October 2016 the JMSC members were guests at the Environmental Research Station "Schneefernerhaus" on top of the Zugspitze. The latest meeting took place in Rostock which provided e.g. one of our conference sites, the Leibniz Institute for Baltic Sea Research Warnemünde, but also various highlights in close vicinity such as the Baltic sea spa Kühlungsborn or the impressive church Doberan Minster.

Aufm Boot Prora



Warnemünde

Zugspitze

Focus on education: Biological lab technicians

In 2016 CMA started to support the education of biological lab technicians at the Helmholtz Zentrum München. In the newly established cell culture lab the apprentice is trained in cell culture techniques, methods of cell exposure and viability testing and extraction of biomolecules like nucleic acids, proteins and metabolites. The first apprentice of the group is Alexander Wendler, who is already in his 3rd year of education. He joined CMA in October 2016.

Biolabor Gmunder Str.

Foundation stone for the new Institute of Chemistry building

The Institute of Chemistry at the University of Rostock started preparations for a new building: The laying of the foundation stone took place at the beginning of December 2016. Prof. Dr. med Wolfgang Schareck, the rector of the University of Rostock, and Mathias Brodkorb, Finance Minister of the Federal State of Mecklenburg-Vorpommern, headed the ceremony. The new building will include an area of 2.700 m² and will host six academic work groups. The finalization is planned for 2019. The Federal State and the European Union support the construction with 17 Million Euros.

Grundsteinlegung

“Quo vadis petrochemical analysis?“

Bayerischer Abend

Prof. Ralf Zimmermann chaired a GDCh (Gesellschaft Deutscher Chemiker) session on “Energy and Fuel” in the course of the “25th International Trade Fair for Laboratory Technology, Analysis, Biotechnology and analytica conference 2016” in May 2016. Fifteen international speakers gave state-of-the-art lectures about current and future trends in the analyses of petrochemical matrices. For a deeper discussion an additional workshop titled „Quo vadis petrochemical analysis?“ with about 40 participants from industry and science was hosted by CMA at the Helmholtz Zentrum München.

LECO Gas Chromatograph-High Resolution Mass Spectrometer for CMA

In the course of the ongoing cooperation with LECO, an US based analytical instrumentation developing company, a second Gas Chromatograph-High Resolution Time-of-flight mass spectrometer (GC-HRT) was installed at the CMA facilities in Munich. The work will focus on the transfer of already established high throughput analysis methods for aerosol research from nominal mass spectrometer to the new high resolution mass spectrometer to take advantage on the accurate mass information for the identification of marker compounds. The installation took place at the Helmholtz Zentrum Campus at the end of 2015 and the instrument was then shifted successfully to the new laboratories of CMA.

New installed LECO-CMA Cooperation System: LECO Pegasus GC-HRT

Tomsk warm

Workshop on wildfire aerosols in Russia

The JMSC participated in two workshops on “Wildfire Aerosols and Health” at the Institute of Atmospheric Optics (IAO) of the Russian Academy of Sciences in Tomsk, Russia in July 2015 and March 2016. The workshops (partly funded by the DFG) were focused on initiating a joint project on health effects of aged wildfire aerosols. For this purpose it is foreseen to use the Large Aerosol Chamber at the IAO for simulating wildfires of wood and peat and for ageing the emitted aerosols. Next to the JMSC the Technical University Munich and Max Delbrück Center Berlin took part in the German-Russian workshops.

PhD Students

Xin Cao

Xin Cao studied Forestry Chemical Industry at the Beijing Forestry University and received his master diploma degree in July 2016. His research is concerned with the separation and analysis of natural drugs from plants with the help of High Performance Liquid Chromatograph. Now his research focuses on the separation and analysis of modified base, nucleoside and nucleotide from radical oxidated DNA. The cell cultures are cultivated under special air condition in order to find the potential effect about haze on human health.

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Christian Gehm

Christian Gehm studied Chemistry at the University of Rostock and received his bachelor and master degree in September 2012 and October 2014. His research is concerned with the development of a new membrane inlet mass spectrometer (MIMS) for the online and on-site analysis of (poly)aromatic and halogenated compounds in natural water samples of the Baltic Sea and its catchment area draining rivers. The main focus lies on the development of the membrane inlet and the hyphenation with a laser mass spectrometer. For MIMS analytes are transported selectively from the liquid phase through a semipermeable membrane into the vacuum of the mass spectrometer, removing the matrix in the process. Advantages, especially by coupling membrane inlets with time-of-flight mass spectrometers and resonance enhanced multiphoton ionization, are the fast analysis as well as the improvement of sensitivity and selectivity for the desired analytes.

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Christoph Grimmer

Christoph Grimmer studied chemistry at the University of Rostock and received his Master's degree in 2015. The goal of his research is to identify the composition of petrochemical substances, which are analyzed with difficulty by usual methods. Using thermogravimetry, substances can either be evaporated or broken down to volatile fragments. Resulting heat flow or typical reaction temperatures may allow conclusions on the initial structures. Subsequently, the gaseous substances are ionized by laser radiation with defined wavelength and energy density and measured by a mass spectrometer. Switching between selective ionisation (resonance enhanced multi photon ionisation) or universal ionisation (single photon ionisation) yields further information about the analytes.

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Frank Hauser

Frank Hauser studied forensics at the Hochschule Bonn-Rhein-Sieg and at the Robert Gordon University in Aberdeen and received his bachelor degrees in 2014. After that he studied Analytical and Forensic Chemistry at the University of Hull and received his MSc in September 2015. He is working at the Federal Criminal Police Office (Bundeskriminalamt) and his research is about the illegal synthesis of amphetamine. He is looking at ways to use waste produced during the illegal amphetamine synthesis to support forensic police work using a variety of analytical techniques. The research is embedded in the Horizon 2020 EU project ‚microMole'. The main focus of this project lies on the detection of synthesis waste discharges inside the sewage system. For this the waste has to be characterised and analytical methods have to be developed which are able to detect prominent substances from the waste in the harsh environment of the sewage system.

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Jan Heide

Jan Heide studied Chemistry at the University of Rostock and reached his master degree in September 2016. His research topic is the online analysis of coffee roast gases. Coffee roasting is a very complex process being influenced by the used beans, roaster technique and various conditions. The aim is to obtain an understanding of the roasting process and to achieve a model for different coffee roasters and roasting conditions. Due to the high complexity of the investigated matrix, especially soft photoionization techniques such as SPI as well as REMPI will be used combined with the fast and reliable TOF-MS technology to achieve time resolved information of the roasting process.

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Yuting Huang

Yuting Huang is a Ph.D. student of University of Rostock, and does graduate research at Helmholtz Zentrum Muenchen. The research work is concerned with gaseous and particulate emission characterization from a Euro 5 vehicle engine under different driving conditions. The current study is in the framework of the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health Aerosols and Health (HICE), which addresses the health effects of anthropogenic combustion aerosols. The main focus of the Ph.D. study is on the emission profiles from high speed driving, and type approval test – New European Driving Cycle (NEDC), in order to gain more clarity on the emission characteristics and change under high speed driving mode, as well as temporal emission profile under transient condition in NEDC test.

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Uwe Käfer

Uwe Käfer completed his Master Degree in chemistry at the University of Regensburg in 2014. Afterwards he worked for ASG Analytik-Service GmbH, a company that is specialized in analysis of petroleum products. In June 2016 he started his PhD at the group CMA at the Helmholtz Zentrum München. His research is focused on the chemical Analysis of petroleum vacuum residues and bitumen. The work is part of an AiF research project for bitumen characterization, which is carried out together with cooperation partner ASG. Because of the complex nature of heavy petroleum samples, multiple techniques are combined for a comprehensive analysis. LC-fractionation and High resolution Mass spectrometry take key roles in the studies. Different ionization methods and sample inlet systems for High resolution mass spectrometry are combined to investigate important mechanisms in the chemistry of heavy petroleum compounds.

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Mohamed Khedr

Mohamed Khedr studied Chemistry in Tanta University (Egypt) and worked in the field of generic pharmaceuticals' formulation and quality control. In 2017, he received his Master's degree at the University of Siegen (Germany); majoring in Analytical Chemistry with a focus on applications of Gas Chromatography-Mass Spectrometry (GC-MS) in investigating trace analytes (down to the ranges of ng/kg) within a diversity of matrices, such as biological samples, beverages, foodstuff and food contact materials. His current research is concerned with developing sensitive methods for determining volatile and semi-volatile organic compounds involved in personal exposure to particulate matter in ambient air,. In order to validate the measurements recorded by the various instruments involved in the SmartAQnet project; and to perform source apportionment for detectable species. The SmartAQnet project aims at characterizing air quality in the urban part of Augsburg and is funded by the German Federal Ministry of Traffic and Digital Infrastructure – Bundesministerium für Verkehr und digitale Infrastruktur (BMVI).

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Vesta Kohlmeier

Vesta Kohlmeier studied Chemistry at the Technical University of Munich, with focus on inorganic, organometallic and polymer chemistry. Since December 2014 she is doing her PhD in aerosol sciences at the Helmholtz Zentrum in Munich, where she is running an aerosol experimental facility. Her main research interest is the characterization of dynamic aerosols generated from semi-volatile organic compounds (SVOC). The investigation of denuders as gas-particle partitioning tools for SVOC aerosols and their inclusion in personal aerosol samplers play an important role in her studies.

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Fengxia Li

Fengxia Li was majored in Preventive Medicine for bachelor degree and Occupational and Environmental Health for master degree at Peking University Health Science Center. She received her bachelor degree in July 2009 and master degree in July 2011. Her research topic is regarding long term sampling, chemical speciation, source apportionment and temporal spatial variability of nanoparticles in Augsburg. The research is done within the framework of the Ultra III (UIII) project (ENVIRONMENTAL NANOPARTICLES AND HEALTH: Exposure, Modeling and Epidemiology of Nanoparticles and their Composition within KORA) in cooperation with the Institute of Epidemiology II at Helmholtz Zentrum München. To achieve unattended weekly field sampling of size-segregated atmospheric particles, she verified the feasibility of a Rotating Drum Impactor (RDI) combined in series with a filter sampler in laboratory as well as in the field. Samples were collected at five locations in all seasons across the year 2015. Actually Fengxia Li is on parental leave.

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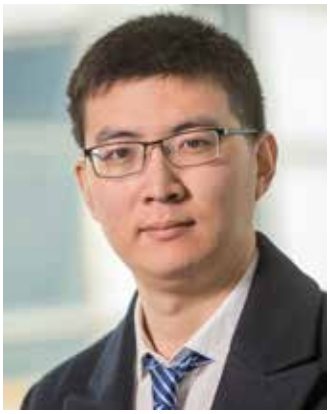

Xiansheng Liu studied Environmental Science at the Nanjing Normal University (Nanjing, China) and received his master degree in June 2017. His research topic comprised the ecological restoration of water, in particular odorous compounds, using Gas Chromatography – Mass Spectrometry. His PhD project focusses on the spatial variability, source contribution and influencing factors of ambient particulate matter composition, answering key questions concerning the ambient air pollution. The main goal of the project is the investigation and characterization of organic constituents of ambient particulate matter for health-related epidemiological and toxicological studies.

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Toni Miersch

Toni Miersch studied chemistry in Rostock and received his Master's degree in 2014. The DFG project he is involved in together with the Desert Research Institute in Nevada (DRI) is called "Brown Carbon". Within this project, soft photoionization time-of-flight mass spectrometry hyphenated to a modified thermo/optical carbon analyzer is used to investigate the chemical nature of the carbonaceous fraction of ambient particulate matter (PM) and those originating from combustion processes. A 7-wavelength laser is utilized to gain an insight into optical properties of particles and the reactions taking place during thermal analysis. Furthermore the installation of an EI-QMS system will provide the elemental composition (C, H, N, and S) of PM and so enhances the comprehension of aerosol properties.

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Sascha Münster-Müller

Sascha Münster-Müller received his bachelor degree in applied chemistry in 2013 and his master degree in bio- and pharmaceutical analysis in 2014 at the Fresenius University of Applied Sciences in Idstein. Currently he is working on the EU-funded project "SPICE-PROFILING" at the forensics department of the Federal Criminal Police Office (BKA) in Wiesbaden in cooperation with the Medical Center – University of Freiburg. Within this project he is developing a new impurity profiling method for synthetic cannabinoids via UHPLC-MSn and multivariate data analysis (mainly PCA). With this method, a wide range of "spice-product" test-purchases will be profiled to reveal underlying distribution networks. Furthermore, outgoing from the found impurities in seized samples, the synthesis of synthetic cannabinoids is postposed, aided by the organic chemistry department of the University Mainz.

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Anika Neumann

Anika Neumann studied chemistry at the University of Rostock and received her Master of Science degree in September 2016. Her research is focused on the characterization of combustion aerosols and their corresponding fuels using high resolution mass spectrometry. Fossil fuels and their combustion products are known as high complex mixtures. The main objective of her doctorate is developing a method for the chemical characterization of aerosol particles using ultra-high resolution Fourier-transform ion cyclotron resonance mass spectrometry. For ionization, atmospheric pressure photoionization (APPI) is used, which is able to ionize a broader chemical space than other atmospheric pressure ionization techniques such as electrospray or atmospheric pressure chemical ionization. In contrast to common spray techniques, thermal desorption is applied for evaporating volatile and semi-volatile molecules adsorbed on aerosol particles direct in the ion source. The optimization of several ionization parameters such as applying VUV-lamps of different wavelengths and the use of dopants are also part of her work.

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Dac-Loc Nguyen

Dac-Loc Nguyen is from DaNang, a coastal city of Vietnam. He graduated from Danang University of Polytechnich in 2009, then left for Taiwan to absolve his master degree at Aerosol laboratory in National Central University. He is interested in the fields of particulate matter pollution and aerosol chemistry, focusing on measurements of inorganic and organic aerosol composition and quantifying emitted source contribution on aerosol loadings. He has joined and conducted assessment of air quality and potential sources of adverse particulate matter (PM2.5 and PM10) in the north of Vietnam via grass-root 7SEAS project. At the moment, he is working with GC-GC TOF MS technique to characterize and determine comprehensively a wide range of both target and non-target organic components from combustion processes from Vietnam, which helps to elucidate the source apportionment studies.

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René Reiss

René Reiss had done his Bachelor in Analytical Chemistry at the Applied University Aalen and his Master in Applied Chemistry at the Nuremberg Institute of Technology. His work is part of the overall project SEMFreS from the Federal Office of Civil Protection and Disaster Assistance (BBK). His task within this project is to develop a measurement system that can be used for the fast and reliable detection of low volatile security relevant substances on surfaces. Advantages of this technique will be direct (without sample pre-treatment) results and the possibility to measure even at difficulty accessible places through a mobile measurement system. The measuring principle is based on the sample desorption from a surface with laser light pulses at the nanosecond timescale and is called ambient pressure laser desorption (APLD). Iontrap mass spectrometer and ion mobility spectrometer as well as other techniques will be used as detection systems.

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Julian Schade

Julian Schade studied Chemistry at the University of Rostock and received his Master of Science degree in September 2016. His research is focused on photo ionization time-of-flight mass spectrometry (PI-TOFMS). The main focus lies on the technological development of an optimized laser based light source for single photon ionization (SPI). Therefore the non-linear tripling process of light from a laser source has to be optimized and the within the scope of the master thesis developed ionization detector has to be refined to quantify the essential vacuum-ultra-violet (VUV) photons. This setup gives the opportunity to obtain basic and fundamental information about SPI and could help to lower the limit of detection during on-line gas phase analysis with TOFMS.

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Theo Schwemer

Theo Schwemer studied Chemistry and received the diploma degree at the University of Rostock in September 2012. His work contributes to the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health: Aerosols and Health. The topic of his research is “High Resolution

Mass Spectrometry coupled to Atmospheric Pressure Chemical Ionization Gas Chromatography”. His doctorate is focused on the development and application of a GC-APCI FTICR system for the characterization of volatile and semi-volatile compounds in emission aerosols. Therefore he is using the high resolution and accurate mass spectrometry to get compositions and retention times of compounds.

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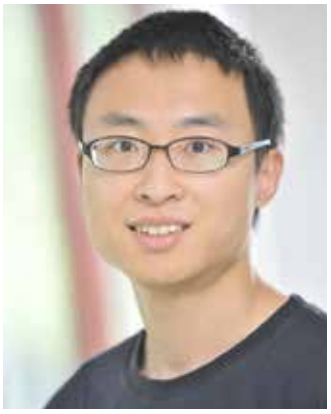
Xiao Wu



Xiao Wu studied Environmental Health and Occupational Health at the Shandong University and received his master degree in 2012. As a PhD student, he is in the cooperation group CMA at Helmholtz Zentrum München. The main goal of his research is to investigate the oxidative stress induced by particulate matters (PM) exposure on human body with LC/ LC-MS methods. The work runs in the frame of the “Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – HICE” and “Cooperative Health Research in the Augsburg Region – KORA”. Robust LC/ LC-MS methods to determine oxidative stress related biomarkers have been developed, optimized, and established. They could be successfully applied on three different projects: 1) a cohort of travelers has been recruited. Urine

samples were collected before and after travel and analysed to investigate the effects of air pollution; 2) Urine samples from volunteers of Augsburg region have been collected and analysed to investigate the association between the long term ultrafine particulate matters (UFPM) exposure and human health (KORA cohort); 3) samples from cigarette smoke exposed mice were collected and oxidative stress burden was investigated.

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Elias Zimmermann

Elias Zimmermann completed his master degree in molecular microbiology, microbial ecology and immunobiology at the University of Vienna in 2017. He is interested in cellular mechnisms and their responses to different (unfavourable) conditions induced by e.g. pathogens or aerosols. Since Jannuary 2018 he is doing his PhD in aerosol sciences at the Helmholtz Zetrum Munich, where he is investigating cellular responses at the air liquid interface (ALI). The main focus lies on responses of in vitro mammalian cells, especially lung cells, to ambient (bio-)aerosols with a particular focus on allergens. By working with ALI-systems, the effects of allergenes and other ambient particles can be assessed in a more realistic scenario, illustrating their role in sensitization of lung cells and thus the development of allergic diseases.

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Dipl.-Lebensmittelchem. Jana Diab

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M. Sc. Christopher Rüger

- Finished in January 2018
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- Finished in January 2018
- Thesis title: “Applying quantitative mass-spectrometry based proteomics on relevant questions of combustion gas-induced health effects”

Research Projects

Characterization of Combustion Aerosols from a Ship Diesel Engine by Direct Thermal Desorption Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Anika Neumann (UR), Christopher Rüger (UR), Martin Sklorz (UR), Ralf Zimmermann (UR/HMGU)

Abstract

Fossil fuel and its derived combustion aerosol are high complex mixtures. The ultra-high resolution of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is a powerful tool for addressing their chemical composition on molecular level. Direct thermal desorption (TD) combined with atmospheric pressure ionisation (APPI) FT-ICR MS is applied for characterization of different feed fuels and their primary combustion aerosol particles (PM) emitted by a ship diesel engine. TD-APPI was realized via a home-built in-source desorption unit equipped with a Kr lamp (10.0 and 10.6 eV). Using a defined heating ramp, temperature-resolved spectra are generated. The PM, sampled on aluminium foil, can be used without prior treatment. It was shown that TD APPI FT-ICR MS enables the chemical characterization of primary combustion aerosol particles and differences between fuels and particles were revealed.

Introduction

Global shipping is a source of combustion aerosols containing health and climate relevant pollutants and particulate matter [1,2]. In international waters, only few limitations of emission exist which is why low quality feed fuels such as heavy fuel oils (HFO) are often used. Near the coast, sulphur control areas (SECAs) limit ship emissions due to the negative health effects related to high particle concentrations. Although physical properties of aerosol particles are well investigated, there is little work which addresses the chemical composition on the molecular level of organics adsorbed. Because of high complexity of ship diesel combustion aerosol, ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in combination with atmospheric pressure photoionization (APPI) is a powerful tool for its characterization. [3,4] In contrast to other atmospheric pressure ionization techniques, such as electrospray and atmospheric pressure chemical ionization, APPI is able to ionize a broader chemical space. The aim to this study is the chemical characterization of different combustion aerosol particles emitted by a ship diesel engine and their related feed fuels.

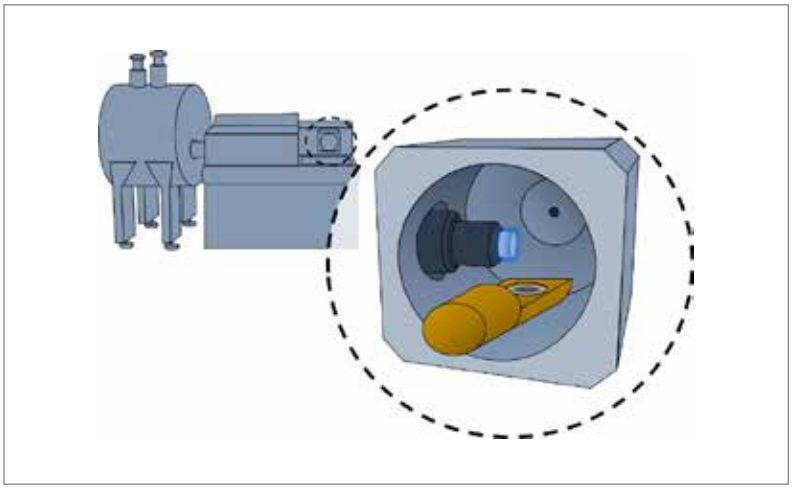

Fig. 1 Schematic illustration of the ion source with the thermal desorption unit equipped. Samples could be measured without prior preparation.

Material and Methods

Particle samples were taken during a measurement campaign in 2015 at the Faculty of Mechanical Engineering and Marine Technology at University Rostock. The experiments were performed at a four-stroke one cylinder ship diesel engine with three litre cylinder capacity driven with heavy fuel oil (HFO), marine gas oil (MGO), and diesel fuel (DF). Particles were collected after appropriate dilution by impaction on aluminium foil.

The measurements were carried out by a SolariX Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 Tesla superconducting magnet. Mass resolution was set to about 300,000 @ m/z = 400. For ionization, a krypton VUV lamp (PhotoMate, Syagen Technology Inc., USA) with emission maxima at 10.0 and 10.6 eV was used. The set-up was completed by a home-built in-source thermal desorption unit (Fig. 1) which has the advantage, that no prior sample preparation is required.

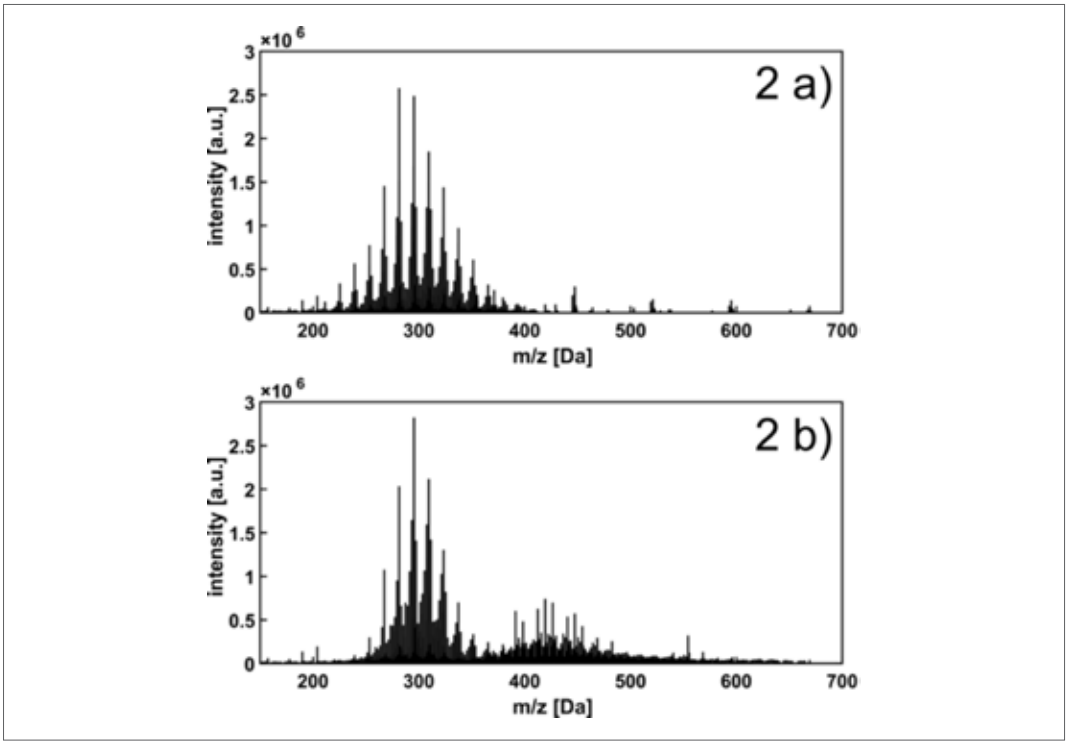

Fig. 2 Averaged mass spectra of 2 a) diesel fuel and 2 b) diesel PM.

A PAH standard was measured for evaluating source-specific parameters such as lamp position and ionization pathways. Sample foils were cut into six parts for measuring. Each aliquot was heated up from 50 to 250 C within 9 minutes. Feed fuels were diluted 1:1000 in dichloromethane and 10 µl of the solution was heated up with the same procedure.

Data were analysed via Bruker Data Analysis and in-house MATLAB routines.

Results

Initial measurements with a standard mixture of 11 different poly aromatic hydrocarbons (PAHs) showed that desorption of the species depends on their boiling point. For PAHs, mostly radical cations were detected but protonated and oxygenated ion species were present with lower intensity as well.

Three different types of feed fuels (DF, MGO, and HFO) and their combustion aerosol particles were compared using the approach described. The time resolved spectra contain hundreds of distinct signals covering a mass range from 200 to 450 Da for feed fuels and 200 to 600 for particle samples (Fig. 2). It has to be marked that detection of high boiling compounds is limited by the low upper desorption temperature applied. Therefore, the main part of signals of HFO refers to blending with lighter fuels.

Due to high resolution and high mass accuracy, elemental compositions can be assigned to mass signals measured. Spectra interpretation was based on component classes and time resolved double bond equivalents (DBE) plots. Feed fuels showed mostly protonated ions of the O1-O6 class with DBE range of 1.5-4.5, whereas particle samples showed a broader component class distribution. For the particles, also O-classes were found. However, particle spectra revealed the NO_2 and the SO class as well as a higher abundance of the CH and S class. CH species forming radical cations were mostly found during the end of the thermal desorption process of the particle samples.

Conclusion

TD-APPI-FT-ICR MS was successfully applied for characterization of feed fuels and their derived aerosols on the molecular level. Differences between fuels and particle samples were shown. Further investigation should be done on model compounds for a better understanding of APPI ionization mechanisms. It is also planned to enhance the maximum desorption temperature, to compare various engine conditions, and the impact of several feed fuels towards the chemical composition of the combustion aerosols.

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Petrochemical analysis with TA-(GC)-PIMS

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Thermal analytical methods (TA) are broadly used to determine thermal dependent properties of materials. A defined temperature program allows gaining information about mass loss (thermogravimetry, TGA) or energetic changes (e.g. differential scanning calorimetry, DSC) of solid or liquid samples. For the characterization of evolving compounds thermal analysis can be coupled to another analytical technique, e.g. infrared spectroscopy or mass spectrometry[1].

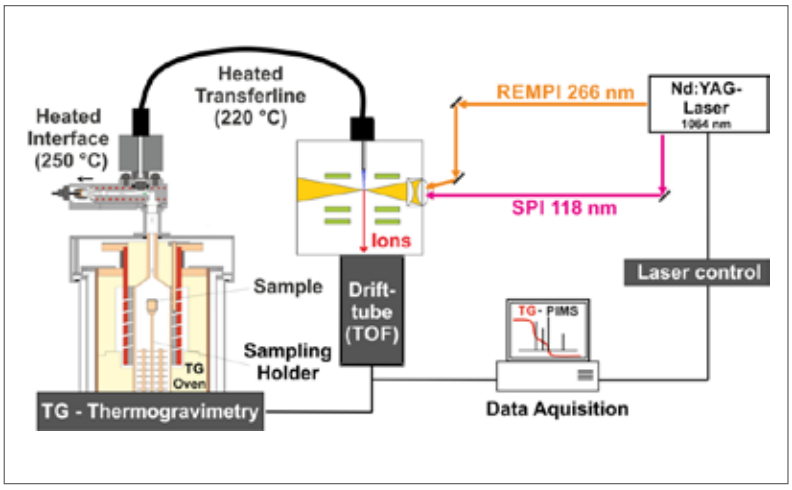

Fig. 1.Thermobalance (Netzsch Group, Selb, Germany) coupled to Photoionization Time-of-Flight Mass spectrometry setup (Photonion GmbH, Schwerin, Germany)

Thermal analysis coupled to mass spectrometry

For establishment of a TA-MS-hyphenation the gaseous analytes should be transferred to the mass spectrometer without change or condensation at hot or cold spots, respectively. Another technical challenge is the decrease in pressure of eight to nine orders of magnitudes that occurs when gases flow from atmospheric pressure of the TA into vacuum inside the mass spectrometer. A heated transfer capillary is a proven technique to achieve this[1b], and is also installed in our systems described here (Fig. 1).

The often implemented electron ionization (EI) highly fragments molecules, which is a big drawback if complex mixtures are analyzed. Aliphatic compounds fragment easily, hampering the analysis of complex mixtures of hydrocarbons such as crude oils or its products. Fragment ions and intact molecule ions of different molecules superpose each other, while other substances do not form molecule ions at all. Additionally, related compounds may break into similar fragments as well, all together resulting in hardly interpretable spectra.

Photoionization

Soft ionization minimizes or suppresses fragmentation. Several soft ionization technologies such as chemical ionization[2], field ionization[3] or photoionization are available. Our concept is focused on the usage of two photoionization techniques, namely resonance enhanced multi photon ionization (REMPI)[4] and single photon ionization (SPI)[5].

REMPI ionizes organic compounds with intense UV-laser pulses. At least two photons are necessary (Fig. 2). The first absorption of a photon converts the molecule into an electronic intermediate state (M*). If this state is stable for a certain time, absorption of a second photon of the same energy is possible and may lead to ionization if the targeted molecules' ionization energy is exceeded. The necessary high photon densities can be achieved with intense nanosecond laser pulses. Since only compounds with a stable intermediate state can be ionized, REMPI is a very selective ionization method. Furthermore, REMPI is also very sensitive, its limits of detection can reach values in the ppb or even ppt range.[6] The herein shown wavelength of 266 nm selectively addresses aromatic substances.

In contrast, SPI is a more universal soft ionization method. As shown in Fig. 2 SPI ionizes molecules with just one photon. Thus the single photon has to exhibit sufficient energy to transfer an electron into the ionization continuum, which can be achieved by using vacuum ultra-violet photons at 118 nm.

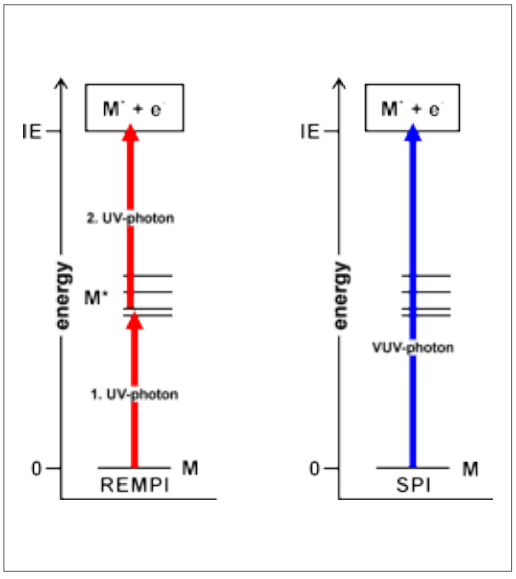

Fig. 2. Ionization energy (IE) is reached via REMPI (left) or SPI (right)

All compounds with an ionization energy lower than the energy of the photon of 10,5 eV are ionized. Besides aromatic molecules many aliphatic hydrocarbons, carbonyls, nitrogen or sulfur containing compounds are addressed as well.

Thousands of components

Crude oil consists of thousands of hydrocarbons. Main components are alkanes, cycloalkanes and aromatic hydrocarbons. To a minor degree, there are compounds containing heteroatoms, whereas sulfur containing compounds are the most abundant species.

Up to date crude oil is one of the most important energy sources. To keep up with the rising need, non-conventional crude oils with increased amounts of heavy, high molecular fractions are exploited. As a consequence higher requirements for pumping, storage and refinery are expected.

Oil companies are economically interested in the constitution of crudes. Furthermore, since non-conventional oils contain more carcinogenic poly aromatic compounds, detailed information obtained from novel analytical approaches can help in the prediction of impacts on the environment or health of humans.

Volatile substances and decomposed products

The TA-MS system with photoionization (TA-PIMS) separates the components of a crude. Volatile substances are separated by boiling point. [7]Thermal fragments of high molecular constituents can be detected and identified as the temperature of the TA rises. TA measurements can be compared to a simulated refinery process: during heating some kind of distillation takes place and at high temperature non-volatile fractions are thermally cracked (pyrolyzed) to smaller fragments.

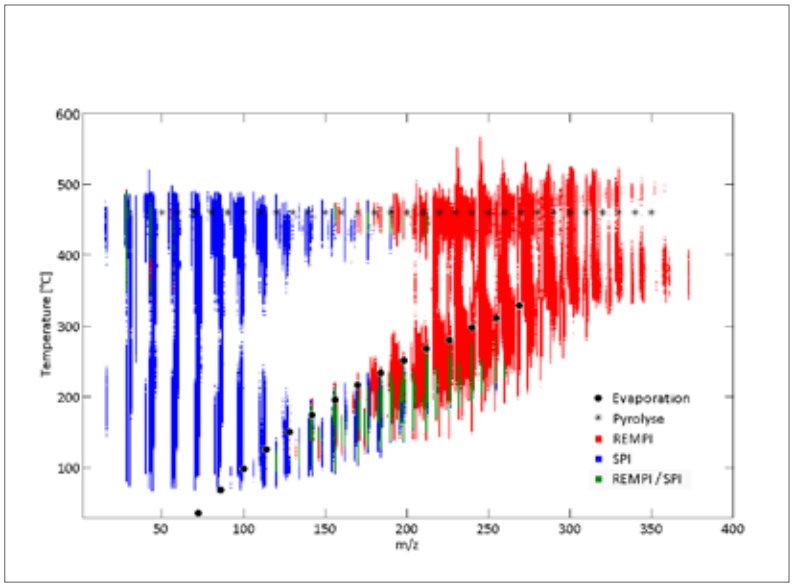

Fig. 3. Contour plot of a crude oil ionized with SPI and REMPI

Fig. 3 shows a two dimensional contour plot, which presents an overview of the whole mass spectrometric characterization of a volatilized crude oil sample. Here the mass to charge ratio (m/z) is plotted against the stepwise raised temperature (with a heating rate of 10 K/min).

REMPI was used to investigate the aromatic fingerprint (red) of the oil, while the blue depiction was produced by single photon ionization. Even though SPI detects aromatic and aliphatic compounds, large aromatic systems are considerably less intense than in REMPI and therefore depicted in red. Both ionization methods together show two distinct temperature regions. In the first region up to 350°C mainly hydrocarbons evaporate and homologous series of aliphatic and aromatic hydrocarbons appear successively by their rising molecular mass and thus their boiling point. Between 350 and 500°C smaller species appear. Those are pyrolytically formed fragments of non-volatile structures.

To gain further insight, mass spectra at every temperature can be investigated. During evaporation homologues of phenanthrene can be observed by REMPI (Fig. 4, A). At lower temperatures derivatives of naphthalenes are present. With SPI homologous series of alkanes and naphtenes can be seen (Fig. 4, C). Since the naphtalenes are already evaporated at this elevated temperature, isobaric nonane and other paraffins can be assigned.

At 460°C pyrolytical processes can be witnessed. The REMPI-MS spectrum still shows low-volatile aromatics, but also naphtalenes, which have been absent during evaporation (Fig. 4, B). They emerge from high molecular aromatics.

With SPI-MS the homologous series of alkenes, beginning with propene, are visible at 460°C (Fig. 4, D). Alkenes are typical thermal fragments of saturated hydrocarbons.

Tar sand, bio fuels, polymers and charcoal

TGA-PIMS measurements also show the loss of mass of distillable or gaseous hydrocarbons inside of tar sands or oil shales, which can be used for yield determination. A fast gas chromatography coupled between TA and PIMS enables the separation of isobaric compounds.[8]

Besides crude oils, tar sands or oil shales also refined products such as fuel oil or diesel with or

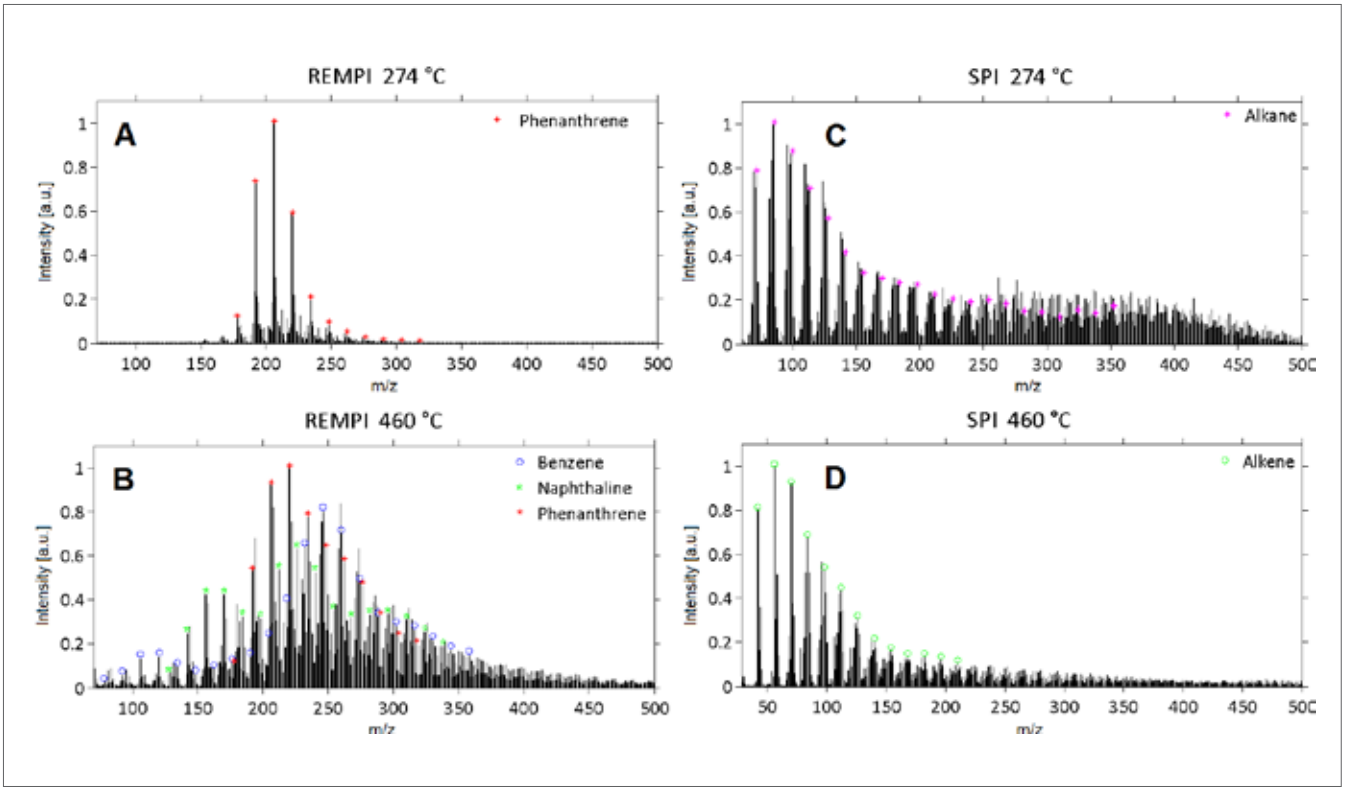

Fig. 4. Mass spectra of different temperatures: REMPI at 274°C (A), REMPI at 460°C (B), SPI at 274°C (C), SPI at 460°C (D)

without bio fuel can be investigated. Further subjects of interest are food[9], polymers[10], wood and charcoal[11].

Funding

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Coupling of fast gas chromatography with Thermal Analysis/Mass Spectrometry (TA-GC-MS)

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The coupling of mass spectrometry to Thermal Analysis is a well established analytical technique for investigating evolved gases from solid and liquid samples, when they are subjected to a controlled temperature ramp. Electron ionization (EI) is the commercially most applied ionization method. Single photon ionization (SPI) has been introduced by our group as a potential alternative method. However, both methods have limitations concerning the exact determination of single molecular structures. In the case of EI this is mainly due to the formation of fragment ions, with SPI the distinction of isobaric compounds can be very difficult depending on the mass resolving power of the used mass spectrometer. To overcome these restrictions, the introduction of a gas chromatography separation is a possible solution, whereby the GC-column is inserted between the thermal analysis device and the mass spectrometer. A crucial prerequisite hereby is the demand for a relatively fast separation time, for otherwise many evolving compounds may be missed during a GC run. Two analytical concepts for fulfilling this task have been compiled.

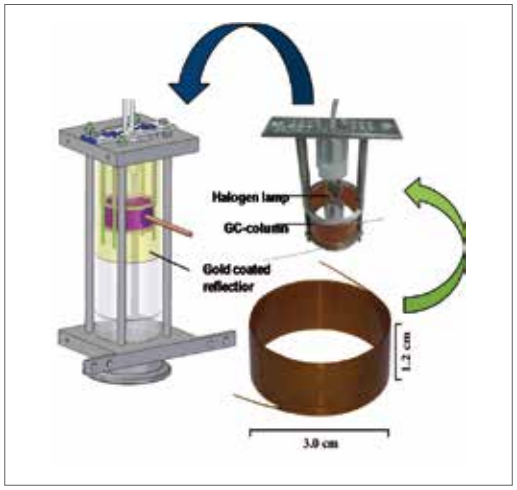

Fig. 1 Scheme of the optically heated fast GC cycling module

The first approach is based on fast temperature cycling by applying a halogen lamp as the heat source. The scheme of this setup is shown in Fig. 1. Inside a metal framework a gold-coated glass cylinder is placed, which encases the GC column stack with a halogen lamp at its centre to provide fast heating of the column. The transfer capillary is guided through a hole in the glass cylinder. Fast cooling is carried out by an air blower. With this setup, one complete heating/cooling cycle could be realized within 30 seconds.

The module was implemented in an evolved gas analysis setup consisting of a thermal analytical device (STA 449 F3 Jupiter by Netzsch-Gerätebau, Germany) and an orthogonal time-of-flight mass spectrometer (Tofwerk, Switzerland) with electron ionization. A standard mixture containing among other species the isobaric substances nonane and naphthalene was taken for a test measure. Fig. 2 depicts the separation properties of the fast GC-module in comparison with the measurement of a diesel sample, for that a continuous temperature ramping was applied (see Fig. 2A, Fig. 2B displays the fast temperature cycles of the new device). With the continuous ramping, the separation of nonane and naphthalene is clearly depending on the TA oven temperature (Fig. 2C) while with the new module the separation stays constant over a wide range of oven temperatures.

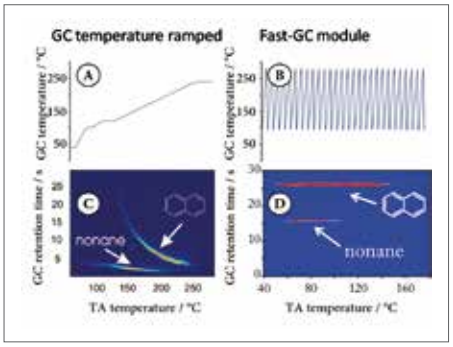

Fig. 2 The left part of the figure depicts a measurement of a diesel sample (above: GC temperature ramping, below: Separation of nonane and naphthalene. The right part shows the same sample with the new Fast-GC device.

The second approach is shown in Fig. 3. It consists of a consumable-free dual-stage thermal modulator. Evolved substances from the thermally analysis device are led to the 3m long GC column (4), which runs inside a stainless steel capillary (2). The capillaries are sandwiched by two opposing Peltier elements (1), which have a hot and a cold side (A/B). Welding wire (3) provides the electrical connection, and the contact area is increased by layers of Kapton film (5). This allows cooling down to –60°C for trapping the evolved species, which are subsequently released by overcompensating the cooling, resulting in a hot pulse of about 300 °C for three seconds. Modulation cycles of thirty seconds are possible with this setup.

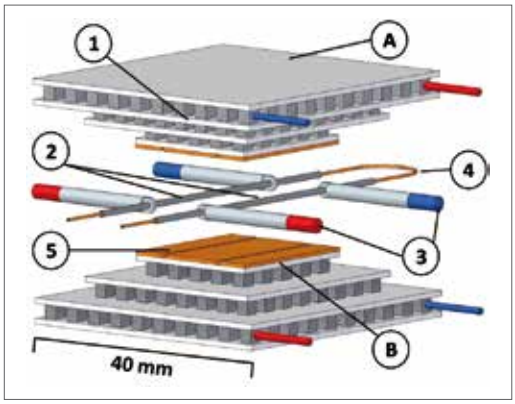

Fig. 3 Scheme of the Fast-GC consumable free modulator

Characterization of Asphaltenes by Ultra-High Resolution Mass Spectrometry (FT-ICR-MS) equipped with Atmospheric Pressure Photoionization (APPI) – Structural Insights utilizing Infrared Multiphoton Dissociation (IR-MPD)

Christopher Rüger (UR), Mark P. Barrow (University of Warwick), Simon Andersen (Schlumberger Limited), Ralf Zimmermann (UR/HMGU)

Abstract

Asphaltenes, defined as soluble in toluene and insoluble in small paraffins, are referred to be one of the most complex mixtures and the heaviest crude oil fraction. In this study ultra-high resolution mass spectrometry equipped with atmospheric pressure photo ionization (APPI) was utilized for a chemical characterization of a variety of asphaltene samples via direct infusion and without further separation. Structural insights were obtained by infrared multiphoton dissociation (IR-MPD). As a result it could be shown that asphaltenes precipitated with different paraffins exhibit mostly the same chemical species, but differ in chemical pattern. Furthermore, the aromatic building blocks of different parts of the molecular asphaltene distribution are similar, but vary in abundance. The find-ings approve the petroleum continuum theory – the Boduszynski model – and support the island model in the scientific debate about the asphaltene structure.

Introduction

The partitioning of petroleum into different fractions based on its solubility in various solvents is a common approach in petroleum research and technology. One established method is the so called SARA fractionation, which will generate four fractions: saturated, aromatics, resins and asphaltenes.

Asphaltenes, the toluene soluble and heptane insoluble fraction of petroleum, referred to be one of the most complex mixtures on earth and are the heaviest fraction of crude oil. They are highly aromatic, polar and contain various heteroatoms, e.g. sulphur, oxygen, nitrogen and metals (nickel, vanadium etc.). Their comprehensive chemical characterisation improves strategies to use them in the refining process stream. Furthermore, innovative approaches to minimize problems during the exploration of heavy crude oil with high asphaltene content are enabled. Besides the feedstock material, the asphaltene yield and chemical composition is strongly influenced by the precipitation solvent, temperature, contact time, solvent-to-petroleum ratio, pH and other factors. A more in depth characterisation of the structure of asphaltenes allow a linkage between their properties and certain structures. [1-2]

The aim of this study is the chemical characterization of asphaltenes precipitated with different sol-vents from different crude oils on the molecular level. Ultra-high resolution mass spectrometry was applied to address the high complexity of the mixture and separate the species on the m/z axes. The high mass accuracy enables the assignment of elemental compositions to the peaks. Fragmentation – the main concept in mass spectrometry for structural information – was further applied by photo dissociation in the ICR cell.

Material and Method

Eight asphaltene samples (kindly provided by Schlumberger Limited) precipitated with different sol-vents (Heptane, Hexane and Pentane) and originating from different feedstock heavy oils (HO_1, HO_4 and HO_8) were investigated (Fig. 1. a). The solid material was dissolved in dichloromethane to a stock solution concentration of 2 mg/ml. The stock solution was further diluted in 2-propanole/toluene (80/20) to 0.1 mg/ml obtaining the final spray solution applied for mass spectrometric measurement.

The measurements were carried out by a solariX Fourier transform ion cyclotron-resonance (FT-ICR) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 12 Tesla superconducting magnet and an atmospheric pressure photo ionization (APPI) source in positive ion mode at the University of Warwick, Great Britain (Fig. 1. b). APPI was realized utilizing a krypton lamp with emission peaks at 10 and 10.6 eV. The flow rate was set to 1,200 µl/h, the dry gas flow to 4 l/min, the dry gas temperature to 250 °C and the nebulizer pressure to 1.2 bar.

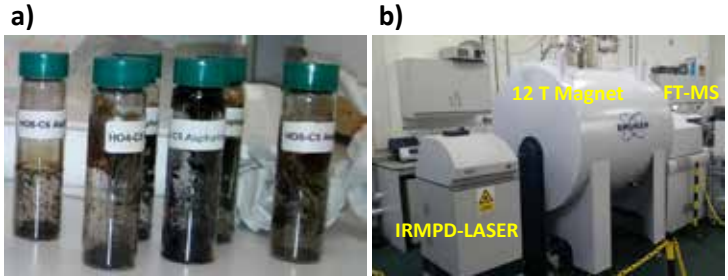

Figure 1. a) Black-brownish solid asphaltene sample material. The appearance and color of the fractions varied in-between the heavy oil origin and applied solvent for precipitation. b) Fourier transform mass spectrometric set-up at the University of Warwick equipped with high field magnet (12 T) and IR-MPD laser.

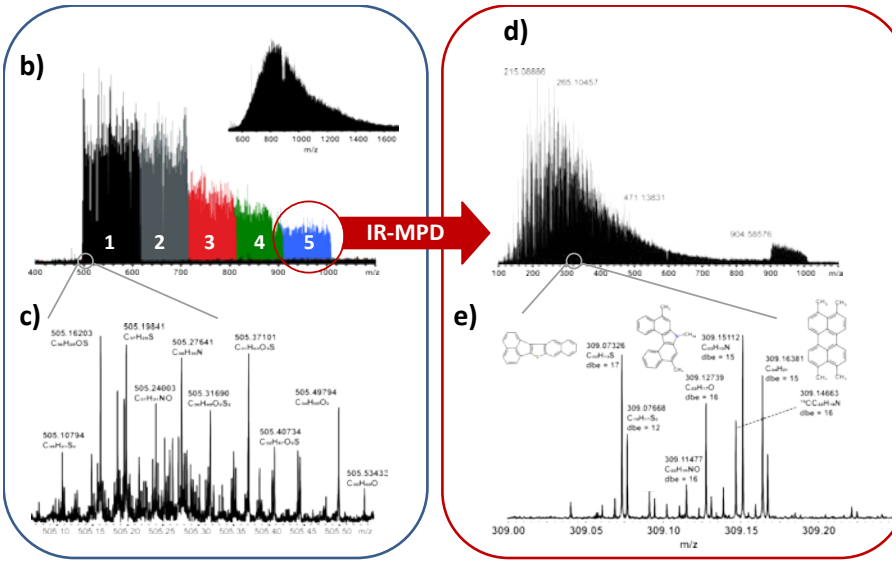

Figure 2. Outline of the mass spectrometric experimental work-flow with exemplary results for the heavy oil HO4 and Pentane as precipitation solvent. a) Low resolution overview mass spectra – the well-known m/z distribution for petroleum sample material is easily visible. b) Stitched segmented ultra high resolution mass spectra of the asphaltene. c) Zoom-in to nominal mass m/z 505 – over 35 peaks can be observed. d) IR-MPD spectra for the fragmentation of the 5th segment (900-1000 m/z). The fragment distribution is observable in the range from 100 to 800. A non-dissociated rest of the parent species remains. e) Zoom-in to nominal mass m/z 309 – highly aromatic core structure species can be observed.

Different mass spectrometric experiments were carried out. Initially, an overview scan with a lower resolving power (512 K transient) from m/z 200–2000 was acquired. Afterwards, segmented scans (based on the spectral stitching approach) with a width of m/z 100 from m/z 500–1000 (5 segments) were recorded in ultra high resolution mode (8 M transient). Additionally, fragmentation experiments in the ICR cell were conducted utilizing infrared multiphoton dissociation. For this purpose a carbon dioxide laser (10.6 µm wavelength) at 50 % laser power and 0.5 s irradiation time was ap-plied. Three segments (500-600, 700-800 and 900-1000 m/z) were more in detail characterized with this approach for all samples.

Data analysis was done using Bruker Data Analysis software and MATLAB applying the typical protocols for petroleum analysis.

Results and Discussion

The mass spectra revealed different pattern for the different crude oils as well as for the different precipitation methods. As example, heavier paraffins for precipitation lead to a broadened m/z distribution with a higher number of species observed. Briefly, the influence of the precipitation method is stronger compared to the change in pattern between the different crude oil feed stocks.

In Fig. 2 the general results of the different mass spectrometric experiments are combined. Fig. 2.a shows the overall asphaltene distribution, which ranges from 500 to above 1600 m/z. The selected segment scans are shown stitched together in Fig. 2.b. Fig. 2.c nicely visualizes the complexity of the asphaltene mixture. More than 35 peaks on one nominal mass can be resolved at m/z 505. The signals can be mainly attributed to highly aromatic hydrocarbon species with at least one het-eroatom. Pure CH-class species are only observed with low abundance, whereas sulphur containing species are dominant.

IR-MPD generates a high number of fragments, which could be assigned to various alkylated aromatic core structures (Fig. 2.d and 2.e). The compound class distribution for the IR-MPD scans for m/z 100 – 400 (“smaller core structures”) exhibit a high contribution of CH-, CHS- and CHN-class species. CHO-class compounds are less abundant in the fragment spectra. This reveals that oxygen is mainly present in side chains rather than in the aromatic core. Different fragmented segments from one crude oil feed reveal slightly different distributions, indicating the higher abundance of certain aromatic structures in the lower, middle and higher mass range of the asphaltene molecular continuum. Nonetheless, the assigned elemental compositions are similar to a high proportion between the segments.

Comparing the double bond equivalent (DBE) values, a quantity for aromaticity, between the species observed in the fragmented spectra and the nondissociated species revealed that only a slight shift in average DBE occur. This aspect is an argument for the island theory in the debate about the as-phaltene structure.

Conclusion

FT-ICR-MS equipped with APPI can be used for asphaltene characterisation and the differentiation of their method of precipitation as well as the origin of the crude oil. Since IR-MPD leads to a high number of fragments and reveals a good fragmentation yield the authors believe that IR-MPD in combination with ultra-high resolution mass spectrometry is a promising tool for petroleum characterisation and in particular for the characterisation of asphaltenes.

Dose Determination in Air Liquid Interface Exposure Experiments

Erwin Karg (HMGU), Jürgen Orasche (UR/HMGU), Stefan Stanglmaier (HMGU), Sebastian Öder (HMGU), Ralf Zimmermann (UR/HMGU), Marco Dilger (KIT)

Introduction and objective

Health impacts from the inhalation of aerosol particles have been documented in Europe since a long time. The main sources for airborne particles in a European capital are – based on a measurement campaign followed by matrix-factorization of the data – traffic, biomass burning and cooking[1].

The nature of the emissions is currently changing. Due to modifications in fuel use, in fuel composition and in the mix of fuels used in the society the type of emissions and therefore also the inhaled aerosol will be changed. It is important to recognize these changes and to document them by comparable data in order to provide a data base for legislative or political reaction. This requires simple, timesaving and reproducible methods which effectively combine both biological and physico-chemical analytics.

Methods

This necessity can be addressed by the exposure of immortalized cell lines from the human respiratory tract at the air-liquid-interface (ALI) [2]. In an ALI system adherent cell cultures are exposed under controlled conditions while being supplied with culture medium from below and being exposed to airborne particles and gaseous pollutants from above. The structure of an ALI exposure system is displayed in Fig. 1. It consists of a closed housing stabilized at 37°C and 85 % relative humidity, an aerosol reactor to adjust the aerosol to temperature and humidity, and the cell exposure units. A relative humidity of 99.5% as found in the lungs is technically not achievable, but cell integrity, stability and confluence have been demonstrated in numerous exposure experiments. Commonly, biological effects are correlated with exposure parameters like mass or number concentration. However, it is more accurate if the dose of the agent at the cell site would be known, i.e. if the deposition probability of the airborne particles onto the cells' surface area could be calculated or measured.

Results

For standard deposition situation and for particles close to unit density (1 g/cm³) deposition functions are available from literature saying that about 1.5 – 2 % of the airborne particles are deposited almost independent of particle size onto a flat underlying surface [3]. In this case, the dose of particles deposited on the Transwell surface area C_{tw} can be calculated from the airborne concentration C, deposition probability W, exposure duration time t_e, exposure flow rate Q

$$C_{tw} = \frac{C\,W\,t_e\,Q}{\pi\,R_{tw}^2}$$

and the radius of the Transwell area R_{tw}:

Efforts have been made to characterise the deposition function more precisely. Comouth et al. developed a size resolved deposition function for the Transwell area [4] using polystyrene latex (density ≈ 1 g/cm³) and silicate (density ≈ 2 g/cm³) particles and fitted a theoretical deposition function to the data (Fig. 2A). The curve sets show similar shape and deposition probability like the results from the lung deposition model calculations [5] (Fig. 2B) do for the defined size range

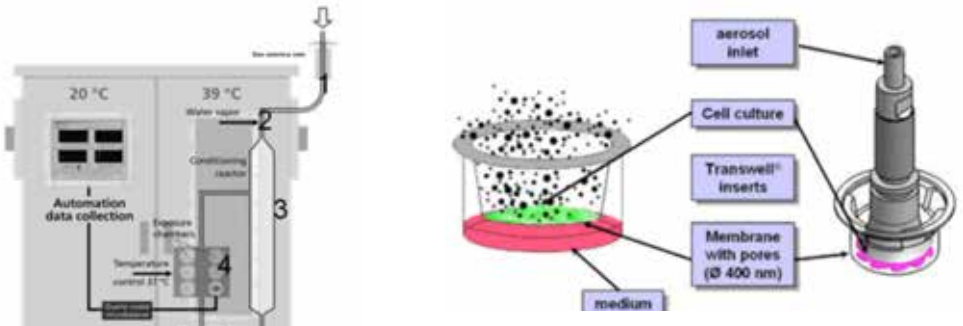

Fig. 1 Left Schematic setup of the air-liquid-interface exposure system: aerosol inlet (1), humidifier (2), aerosol reactor (3), exposure unit (4) and flow control (5); right: an exposure unit consists of: aerosol inlet into a transwell insert and cell medium[2]

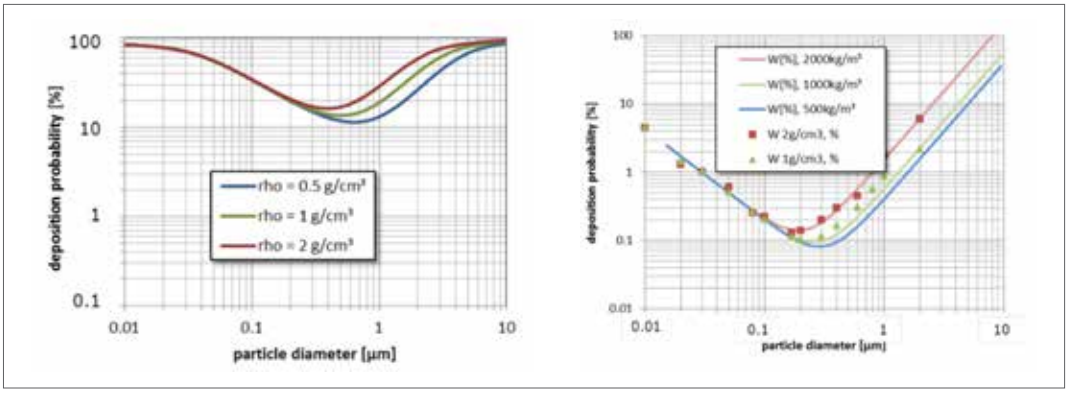

Fig. 2A Surface deposition probability of particles with varying density calculated by the ALI deposi-tion model [4]. Measured data were available for 2 and 1 g/cm³ only

Fig. 2B Lung deposition probability of particles with varying density calculated by the hygroscopic lung deposition model [5] which is accessible via the internet [6]

(≈ 40 nm to 2 µm); however, they bear unrealistic results especially for micron-sized particles, where the curves should converge to a deposition probability of 1 like in the lung deposition model, while the postulated functions rise infinitely.

Techniques to analyse the deposited particles directly at the Transwell surface area have been performed using a quartz crystal micro balance (QCM) with a resolution of 10 ng/cm² and fluorescein detection method [2]; but commonly within a four hour exposure duration, data were close to the limits of detection. Alternative methods have been developed using parallel filter samples, one at the aerosol inlet and the second one at the Transwell area. Particles were generated by a propane fired diffusion flame with a molar oxygen to fuel ratio of 0.96. A number of organic substances was analysed from the filter pair and a deposition dose was calculated (Fig. 3) for each substance. However, the variability in the results is high and so is the inter-substance variation. Reasons therefore may be found in differences between sampling positions, low filter loads, humidity effects at 85 % r.h., a particle size dependent load and deposition of organics or matrix effects from the filters' quartz fibres.

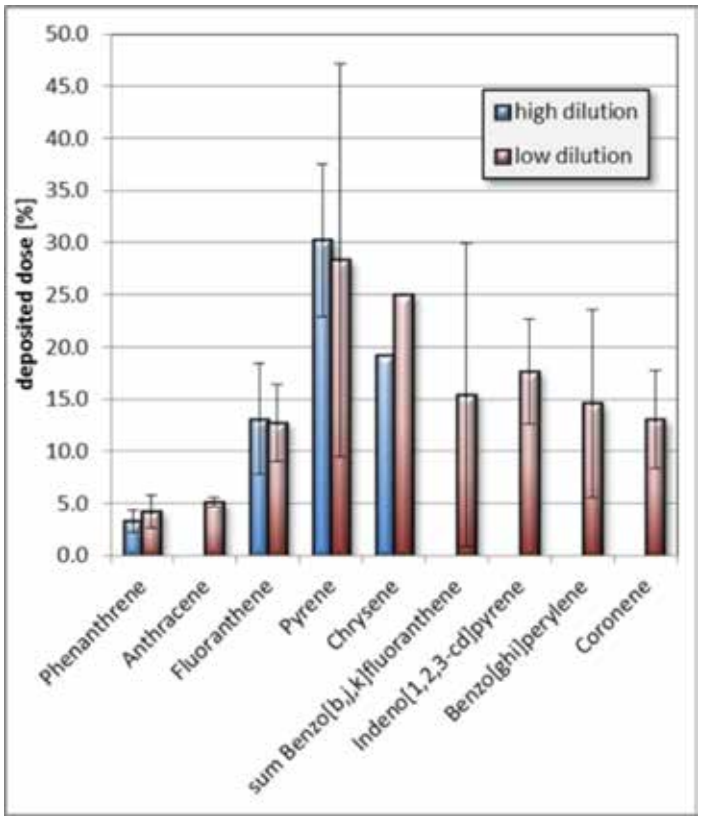

Fig. 3 Results from deposition analyses using soot particles from diffusion flame generator at two different dilutions. Analyses from filter samples taken at the inlet and the membrane in a Transwell insert

Conclusions

Several methods were developed and tested to characterise particle deposition onto the cells' surface area in an ALI Transwell position. Necessity was found to improve the theoretical deposition model for the ALI system and to set up advanced methods for the direct analysis of deposited particles.

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Biological effects of combustion emission gas phase components

Erwin Karg (HMGU), Sebastian Öder (HMGU), Ralf Zimmermann (UR/HMGU), Marina Depré, Jeroen Buters (TUM)

Introduction

The air we breathe is not a pure gas but an aerosol, i. e. a mixture of gases and particles in solid or liquid state. While our body is adapted by evolution to most of the natural aerosols, effects of detrimental health impact were ascertained for many emissions from anthropogenic combustion sources. Thereby the major health impact is ascribed to particles and not to gases, as clean air dilution reduces their number but not their potential for health implications. For gases, on the other hand, turbulent spatial dilution during transport implies a rapid risk reduction with distance to the source. But as the number of emission sources is high in urban environment (and is even rising), the exposure to gaseous pollutants may not be negligible any more. The rising exposure in cities to nitrogen oxide from internal combustion engines may serve an example therefore.

As both gases and particles show effects in biological substrates, knowledge of the gas phase impact is necessary when determining the aerosol potential. Especially in studies with emission aerosolsfrom internal combustion engines a significant proportion of gaseous agents such as carbon monoxide and nitrogen oxides is inevitable. Carbon monoxide, for instance, is a product of incomplete combustion and therefore is due to stoichiometric oxygen deficit or to competing oxidation processes in an engine's piston displacementvolume. Nitrogen oxides, on the other hand, result from high combustion temperatures when the nitrogen of the combustion air itself is oxidized. Knowing their impact onto the exposed bio target is indispensable. An experiment was set up to examine a number of agents separately and to determine a dose-response-relationship for each gas phase without particulate matter.

Methods

An „Air-Liquid Interface" (ALI)(1, 2) exposure system (Fig. 1), entitled to the HICE Project, has been used with two types of lung epithelial cell lines (BEAS-2B, A549). Cells were grown as a monolayer on a membrane, supplied with medium from the bottom and being exposed against the gas phase from above under controlled conditions. The ALI arrangement is commonly taken as the most convenient scenario to mimic the exposure conditions for cells of the human lung epithelium (1) and allows the control of both cell viability and exposure atmosphere. For the study, a mass flow controlled gas phase mixer was set up which allowed to combine the components nitrogen, oxygen and agent in the correct proportions to guarantee a stable gas flow and an oxygen content of 21 % in the air.

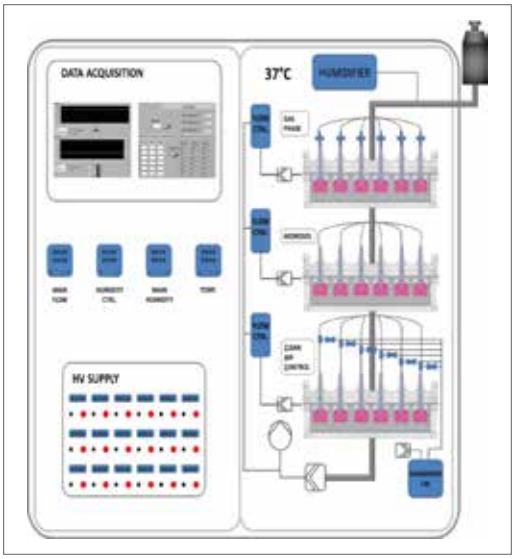

Fig 1 Scheme of the air liquid interface exposure system hosting 18 Transwell inserts for cell exposure

The cell lines used in the study originate from human bronchial (BEAS-2B) and alveolar (A549) lung epithelia. Intracellular ATP content was taken as the metric for cell viability and the integrity of the cell membrane, determined by the analysis of free lactate dehydrogenase (LDH) in the culture medium as the metricfor cell toxicity. Experimental duration was four hours and non-exposed, incubated cells served for control.

Dose-effect-relations were determined for the main noxious components carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxide (NO), nitrogen dioxide (NO_2) and sulphur dioxide (SO_2) to evaluate their influence in real emissions and possibly correct for their impact. Therefore, agent concentrations were varied from the relevant environmental concentration to about twenty times the occupational exposure limits.

Results

Effects of cell stress due to their insertion into the exposure system, the lower humidity in the ALI system (85 % instead of 100 %) and the air blow inside a Transwell resulting from the stagnation point flow was tested by a clean air exposure experiment with synthetic air (hydrocarbon free air of 79 % nitrogen and 21 % oxygen) and was found less than 8 %. For CO_2 no effect was found as expected, as the cells in the lungs are

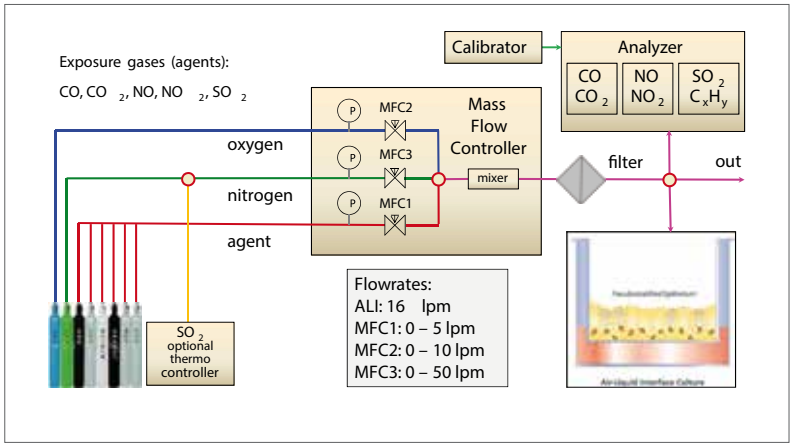

Fig 2 Scheme of the experimental setup. Gaseous components from cylinder are added to synthetic air, composed from pure nitrogen and oxygen

naturally confronted with CO_2 expired from the lungs in a concentration up to 5 % and as cells are kept in a 5 % CO_2 atmosphere in the incubator. CO, known as inhalational toxin with significant lethal risk during prolonged inhalation, showed no cellular effect (3); the lethal inhalation risk for humans is known to be related to the blockage of oxygen transport by haemoglobin in the blood, which is not relevant for cells.

NO showed a significant reduction of ATP turnover combined with an increasing LDH cytotoxicity for the highest level of concentration (520 ppm) but only mild effects for lower ones. This corresponds to the fact that NO is an endogenous substance, synthesized in the lungs by the enzyme L-arginine and is used for therapeutic purposes.

While exposing to NO_2, cell viability (ATP) is depressed to less than 50 % and cytotoxicity rises to more than 50 % of damaged cells (Fig 3A). Note that significant effect levels occur already at low concentrations. The results are in line with studies referring limitations of lung function and inflammatory response in human subjects.

As fuel is desulphurized in Europe, SO_2 can hardly be found in in vehicle combustion emissions. The combustion of heavy fuel oilin ship engines, however, generates significant concentrations of SO_2 in the exhaust gas. While the cells inside the ALI system tolerated low gas concentrations, an almost 100 % lethality was found for the more sensitive BEAS-2B cells at the highest concentration (Fig 3B).

Conclusions

The effect of gaseous agents in combustion emissions was investigated for individual emission gas species in dose-response experiments. While no cell-damaging effect was found for CO_2 and CO, mild effects were found for NO at higher concentration. Even at low concentrations, NO_2 leads to considerable cell damage. SO_2 shows the clearest effects, but only at high concentration. We conclude that in toxicological studies with combustion emissions, the unavoidable accompanying gaseous agents may not be disregarded and have to be carefully controlled by appropriate dilution.

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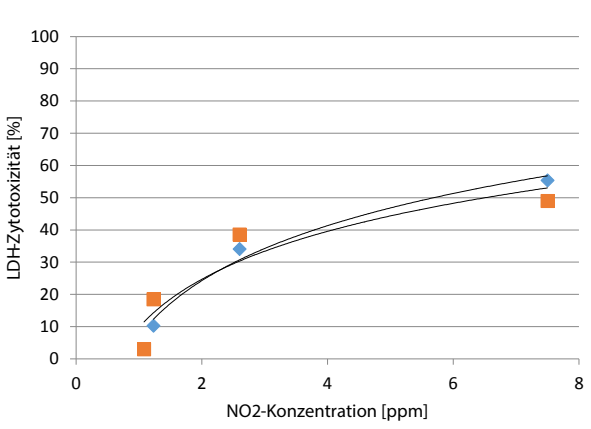
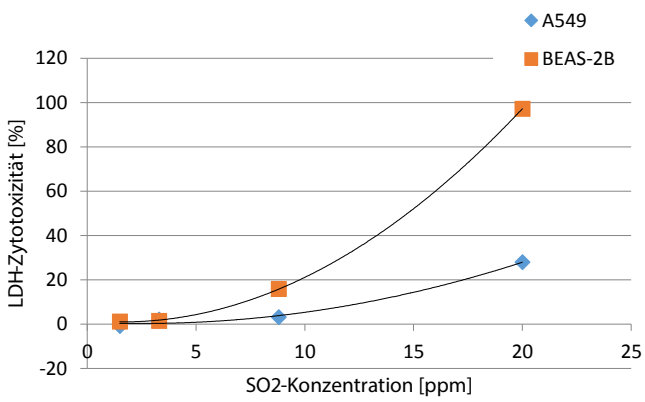
Fig 3A LDH-Cytotoxicity of nitrogen dioxide for A549 and BEAS-2B cell lines

Fig 3B LDH-Cytotoxicity of sulfur dioxide for A549 and BEAS-2B cell lines





Seasonal and spatial variation of organic composition and source contributions of ambient particulate matter in the ultrafine and accumulation mode size range

Fengxia Li (HMGU), Erwin Karg (HMGU), Jürgen Orasche (UR/HMGU), Annette Peters (HMGU), Gülcin Abbaszade (HMGU), Josef Cyrys (HMGU), Ralf Zimmermann (UR/HMGU), Jürgen Schnelle-Kreis (HMGU)

Ambient particulate matter (PM) in the accumulation mode (< 500 nm) and ultrafine (< 100 nm) size range is discussed to be involved in adverse health effects. Long term studies are needed to study their behavior, properties and potential health effects. In this study we present the seasonal and spatial variation of composition and source contributions of the organic fraction of ambient particulate matter in the size range < 360 nm ($PM_{0.36}$).

To achieve unattended continuous long term sampling of size-segregated 24-hour ambient particulate matter (PM), a sampling strategy of a modified 3-stage rotating drum impactor (RDI) in series with a sequential filter sampler was introduced, tested in the laboratory and verified in a field campaign. Laboratory experiments were conducted to find out the collection characteristics of the 3rd stage of the RDI using the quartz fiber filter (QFF) as substrates. The measured cut point of the last stage is 0.36 µm, which is larger than the nominal value 0.1 µm given by the manufacturer (Li, 2015).

A short pilot field campaign and a long term field campaign of semi continuous sampling of daily $PM_{0.36}$ were conducted successively. In the pilot campaign, two sets of combined samplers were operated side by side at a reference site in the urban background (Cyrys, 2006) to verify the feasibility of weekly unattended field sampling and comparability of two sampler sets. The long term campaign was carried out from April 2014 to February 2015 in Augsburg, Germany. Samples were collected at the same reference site and in parallel at one of three traffic influenced sites (T1 to T3) or an additional urban background site (B1) in the Augsburg region. Sampling at each of these satellite sites was carried out for 2 weeks each in summer, spring or fall, and winter.

In situ derivatization thermal desorption Gas Chromatography Time of Flight Mass Spectrometry (IDTD-GC-TOFMS) was applied to the analysis of the 24-hour ambient samples. Analysis of organic species was done for all size fractions (< 0.36 µm, 0.36 – 1 µm, 1- 2.4 µm, and 2.4 – 10 µm) of pilot campaign. A total of 294 $PM_{0.36}$ long term campaign samples were analyzed (i) for carbon fractions using a thermo-optical carbon analyzer and (ii) for organic composition using IDTD–GC–TOFMS.

The comparability of two such sampler sets was verified with respect to PM collection profile of two RDIs as well as measured concentration of chemical compounds in each sampled size fraction. This warranted the comparing of parallel daily samples is not biased by systematic instruments difference, so that spatial variability could be investigated and the epidemiological study could be carried out.

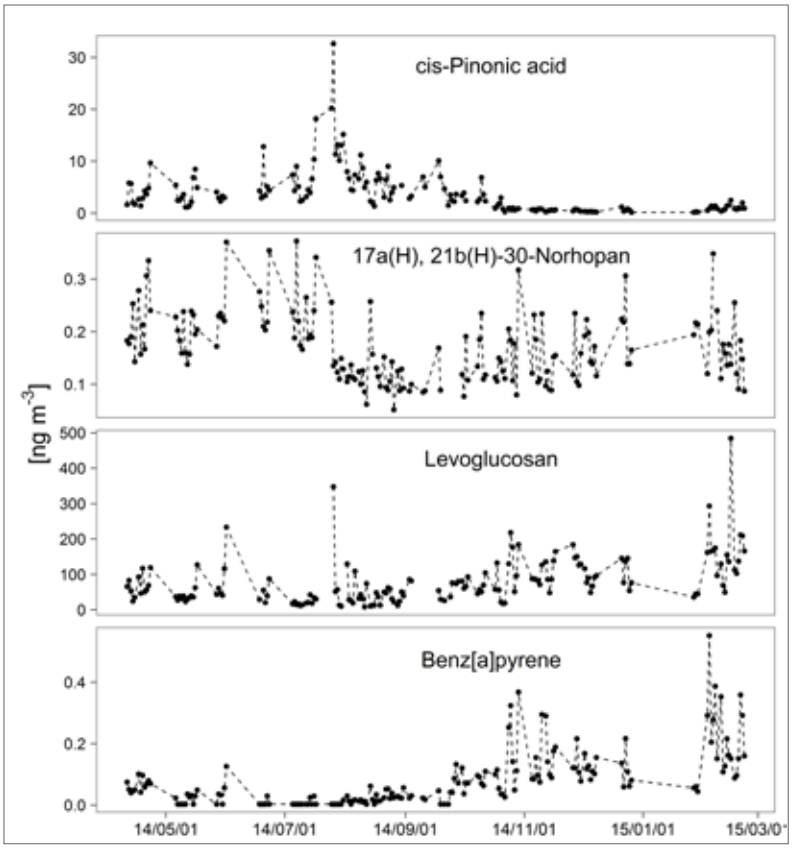


Fig. 1 Seasonal variation of concentrations of selected compounds at the reference site

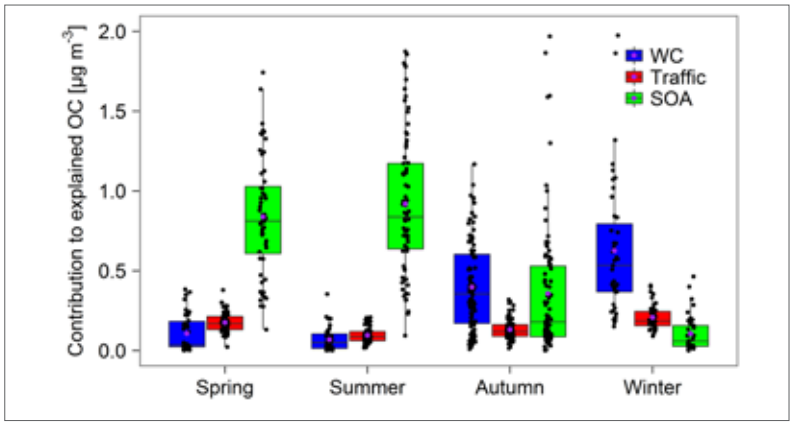
Concentrations of representative measured compounds are show in fig. 1. Some compounds such as cis-pinonic acid show strong seasonality with high concentrations during spring and summer, while norhopane shows more stable concentration during the whole sampling period. EPA PMF 5.0 was applied to determine the contributions of the main sources to the OC in the collected $PM_{0.36}$. The preliminary denotation of source factors from PMF analysis was based on factor profiles as well as seasonal variation of the factor contributions. Three factors have been separated which were interpreted as domestic heating (factor 1), biogenic SOA (factor 2),

and traffic (factor 3). Factor 1 was dominated by higher molecular weight PAHs, levoglucosan and dehydroabietic acid. Factor 2 was characterized by high contributions of cis pinonic acid, OC2 and OC3. Factor 3 was dominated by hopanes.

Seasonal variation of the factor contributions at the reference site are shown in fig 2. Factor 1 contribution decreased from spring to summer and then increased remarkably in autumn and winter which is consistent with the time period that people using domestic heating. Factor 2, in contrast, increased from spring to summer and then decreased substantially in autumn and further dropped to a very low level in winter. This could be explained by the abundance of precursors and a favored meteorological condition for SOA formation in spring and summer. Factor 3 contributed quite constantly to the OC with slightly lower values in summer and slightly higher values in winter.

Fig. 2 Seasonal variation of source factor contributions to OC in the $PM_{0.36}$ at the reference site

The ongoing evaluation of the spatial variation of the factor contributions did no show significant differences within Augsburg area so far (fig. 3).



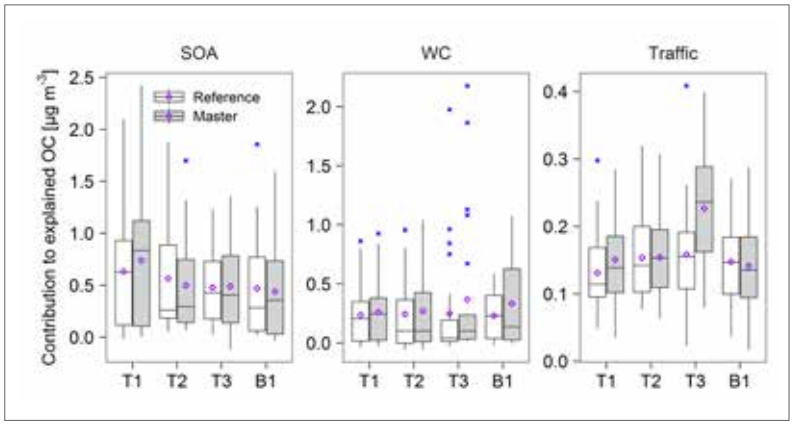


Fig. 3 Spatial variation of the source factor contributions to OC in the $PM_{0.36}$ in comparison to the reference site. Only results from parallel sampling at the two sites each are shown

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Coffee Roast Degree approved by Mass Spectrometry

Hendryk Czech (UR), Claudia Schepler (UR), Sophie Klingbeil (UR), Sven Ehlert (Photonion), Jessalin Howell (Smuckers), Ralf Zimmermann (UR/HMGU)

Roasting coffee is still regarded as more art than science: An under-roast of the coffee beans and the chemical reactions necessary to produce its characteristic flavour and colour do not occur at an adequate level; while over-roasting of the bean results in a bitter brew. However, coffee producers and their customers are interested in consistency, which can be achieved by photoionisation mass spectrometry (PI-TOFMS) through real-time monitoring.

On that account, 100 g green coffee beans of the two most common cultivars, Arabica (from Mexico) and Robusta (from Vietnam), were roasted in a small-scale drum roaster at different time-temperature profiles ('fast', 'medium' and 'slow'). Evolving volatile compounds out of the roasting off-gas were analysed by PI-TOFMS at four different wavelengths, either with single-photon ionisation (SPI at 118 nm) or resonance-enhanced multiphoton ionisation (REMPI at 266 nm, 248 nm and 227 nm), which were generated from the fundamental radiation of a Nd:YAG laser by SHG and THG crystals, an optical parametric oscillator (OPO) for REMPI and a VUV cell filled with xenon for SPI. The different photon wavelengths accompany to different analyte selectivities and relevance for the examination of the roasting process [Czech 2016]. On the one hand, SPI allows detecting every compound with ionisation energy below the applied photon energy of 10.49 eV (equivalent to a wavelength of 118 nm). This includes fatty acids, carbonyls, phenolic species and furans from Maillard and Strecker reactions as well as decomposition of carbohydrates. On the other hand, REMPI enables monitoring especially aromatic compounds (Fig. 1), such as caffeine, substituted phenolic species and furans, with high selectivity and sensitivity depending on their absorptivity at the applied UV-wavelength [Boesl 2000, Hertz-Schünemann 2013]. In particular, the degradation of chlorogenic acids, such as 5-feruloylquinic acid, is responsible for the formation of phenolic species, such as 4-vinylguaiacol (m/z 150), that are known as key species for the determination of the roast degree [Dorfner 2003].

The temporal evolution of all detected evolving compounds in the roasting off-gas is systematically grouped by non-negative matrix factorisation (NMF). NMF refers to a matrix decomposition technique which partitions a m/z-by-t matrix M into a k-by-t score matrix H and an m/z-by-k loadings matrix W by minimising the functional $f(W,H)_k$ with a combined approach of alternating least-square and multiplicative update algorithm[Berry 2007]:

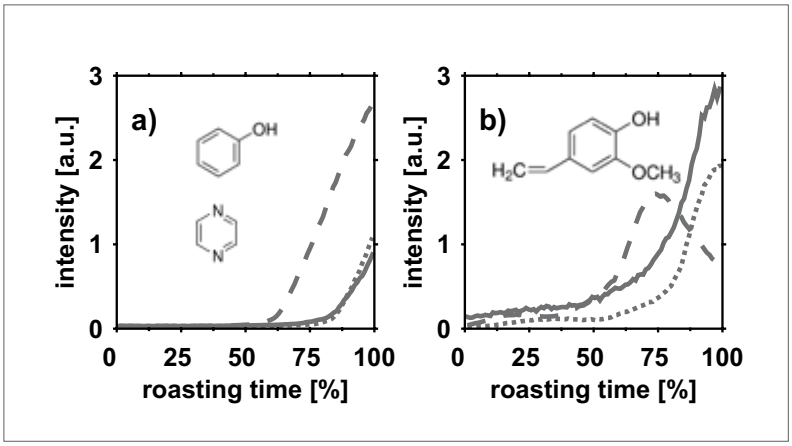

Fig. 1 Time profiles of a) m/z 94 and b) m/z 150 analysed at 266 nm, corresponding to pyrazine/phenol and 4-vinylguaiacol under 'fast' (solid line), 'medium' (dotted) and 'slow' (dashed) roasting conditions for Arabica beans

$$f(W,H)_k = \frac{1}{2}\|M - WH\|_F^2$$

The missing dimension k, also called the rank of f(W,H)k, to complete the matrix decomposition can be regarded as the number of single processes to identify in M. On that account, the k rows in H can be interpreted as the contribution of k single sub-processes with corresponding representative mass spectra in the k columns of W. Because k was unknown, increasing ranks k starting from k = 2 were evaluated in terms of a meaningful solution. Consequently, the scores of an NMF solution of the rank of four illustrated the temporal evolution of consistent roast degree phases named 'evaporation', 'early roast', 'late roast' and 'overroast', while the factor loadings gave chemically sound results to the phases (Fig. 2). For example, the factor loading 'evaporation' was dominated by palmitic acid (m/z 256) from early decomposition of coffee oils whereas 'overroast' contained the known overroast-marker pyridine (m/z 79). Subsequently, pairs of m/z were derived from the factor loadings by finding the maximum ratio of inter-class distance to inner-class dispersion (Fisher ratio) for best differentiation between subsequent roasting phase transitions. Finally, five linear classifiers were calculated using Fisher's linear discriminant analysis (LDA) for every roasting phase transition, that the stage of the coffee roasting process can be on-line monitored in real-time by PI-TOFMS for the perfect cup of coffee.

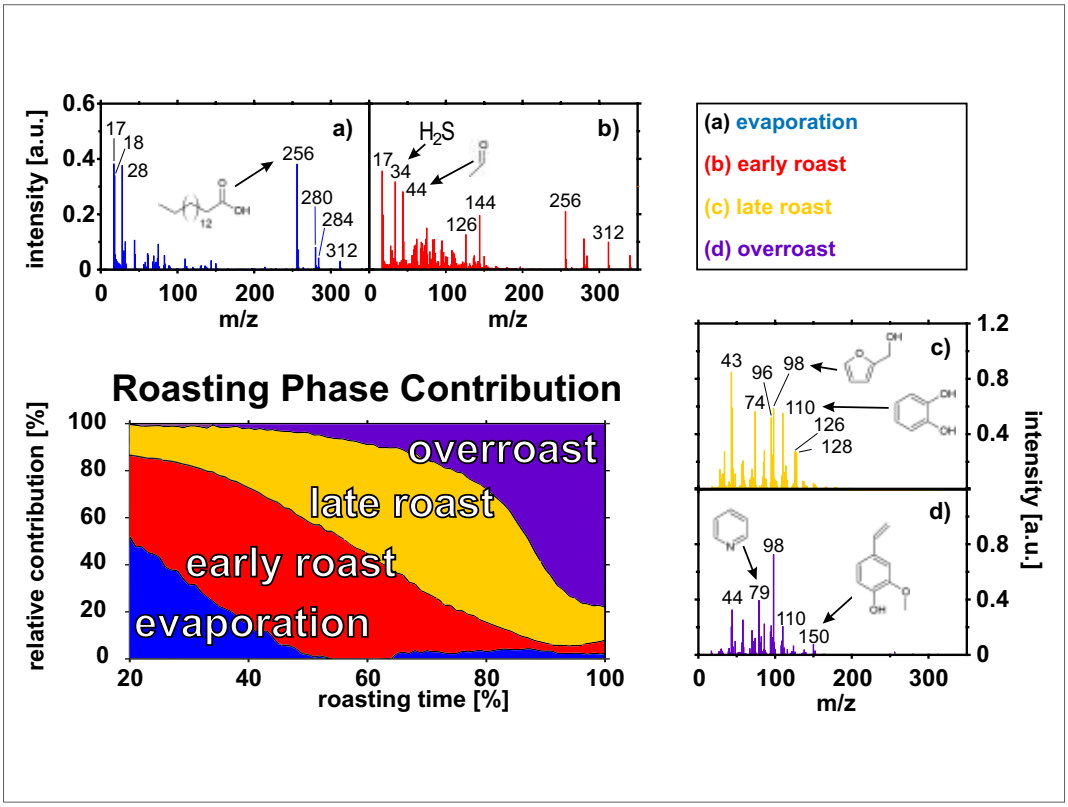

Fig. 2 Temporal evolution of the four roasting phase 'evaporation', 'early roast', 'late roast' and 'overroast' from the normalised NMF scores (centre left) surrounded by the NMF factor loadings (a – d) giving information about the molecular composition of the respective roasting phase

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Optimization of VUV-Light Generation for Single Photon Ionization in Mass Spectrometry

Julian Schade (UR), Johannes Passig (UR), Ralf Zimmermann (UR/HMGU)

Among the variety of ionization schemes in mass spectrometry, single photon ionization (SPI) stands out as near fragment free technique addressing many organic substances without producing interfering ions from the carrier gas. However, light sources for intense VUV-radiation are technically challenging. Typical VUV lamps [1] provide undirected emission from an extended emitter volume which restricts the focusing ability. As a result, the MS sensitivity suffers from limited light intensity in the ionization zone. Alternatively, pulsed laser radiation can undergo multiple frequency upconversions in nonlinear processes to reach the UV and VUV range. Since solid material transparency drops down approaching the VUV-region, harmonic generation is typically realized in rare gas cells, close to the mass spectrometer. Because of limited phase matching conditions, the conversion efficiency into these (odd) harmonics is generally very low [2]. The current project targets on the optimization of the third harmonic generation (THG) process in a gas cell in order to yield more VUV photons from the pump beam.

A Nd:YAG-laser (Spectra Physics Quanta Ray Pro-270, 355 nm, 36 mJ pulse energy) is used to generate the VUV light via THG. The laser is operating with a pulse length of 8 ns and a repetition rate of 20 Hz. Radiation focused (f=30 cm) into a gas cell filled with a mixture of Xenon and Argon at low pressure, see Fig. 1. High gas purity is achieved by getter devices absorbing residual molecules. Due to the high intensity of the laser light in the focus region, non-linear optical effects lead to the generation of collinear radiation of triple frequency (wavelength 118 nm) and a photon energy of 10.5 eV, respectively. In order to separate the VUV light (118 nm) from the typically 4 to 5 orders of magnitude more intense pump light (355 nm), the beams pass the edge of a MgF_2-lens at a certain incidence angle and chromatic dispersion leads to spatially separated light paths. Note that only VUV-transparent materials and media (e.g. MgF_2, N_2, vacuum) are allowed in the optical path of the VUV light. The MgF_2-lens also focuses the VUV-light into the vicinity of the mass spectrometers acceptance volume where it ionizes the analyte gas delivered by a needle inlet. The optimal focus position depends on the beam parameters, and reflects a favorable balance between sufficient photon flux, illuminated volume and potential multiphoton effects at higher intensities. The signal strength of the analyte is dependent on the VUV-light intensity. The setup allows for determining the sensitivity of the instrument in a realistic analytical setting. However, many parameters influence the signal strength, and VUV intensities cannot be determined using the mass spectrometer only. In order to obtain reliable information on the VUV generation process, an absorption cell was developed and installed as photon counter. The cell is filled with nitrogen oxide (NO) and nitrogen (N_2) at a pressure of few mbar. Due to its lower ionization potential, only NO is ionized by the VUV-photons and absorbs 91% of the incident VUV light in the current configuration. A homogenous electric field extracts electrons and ions. The resulting current is measured using custom electronics and an oscilloscope. For a certain ratio between electric field and mean free path length, the current, respective charge number, is equal to the number of absorbed photons (plateau in Fig. 2).

Fig. 3 shows the photocurrent in the absorption cell as function of the partial pressure of Xe for both clean gases (getter purification, blue) and gases of lower purity (5.0, grey). Obviously, the gas purity in the VUV-cell is crucial to reach high VUV-light intensities. This can be attributed to absorption, ionization and focus near phase distortion by the residual gases. The plots show pronounced optima of Xe-pressures that shift to higher values with increasing Xe/Ar ratios (3 mbar for Xe and 5 mbar for Xe @ Xe/Ar=1/6). This behavior originates from phase matching conditions within the THG process: Typically destructive interference and reconversion to the

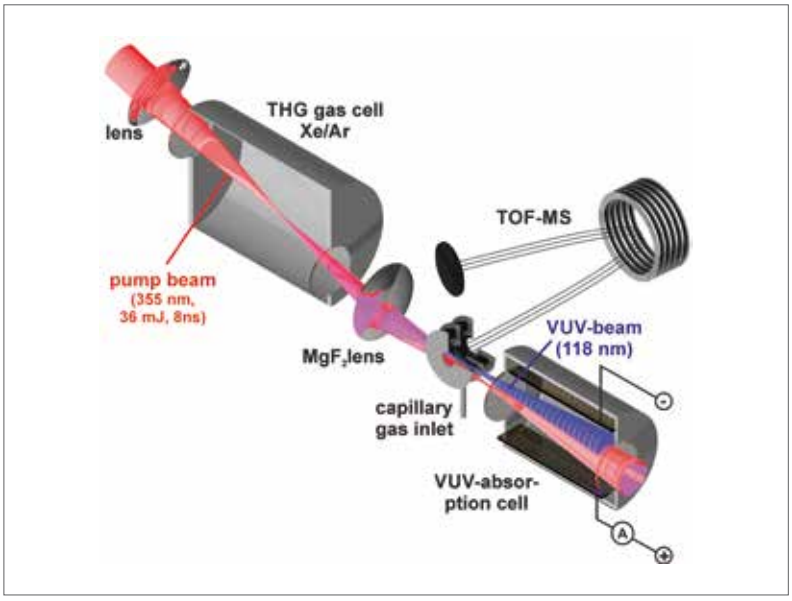

Fig.1 Schematic of the experimental setup

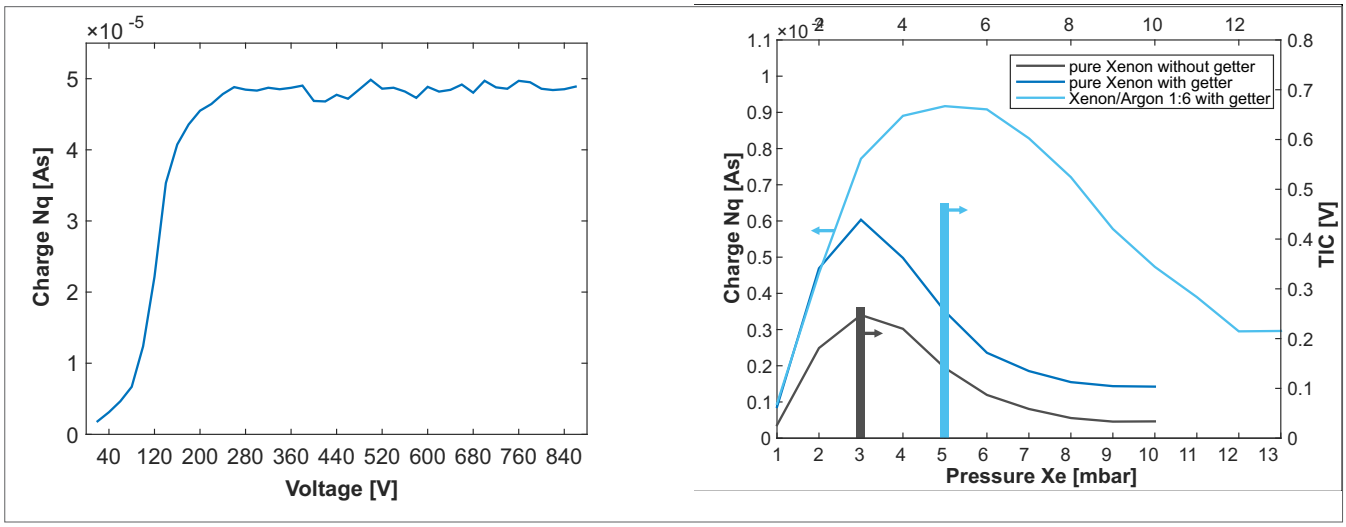

Fig.2 Photocurrent in the absorption cell as function of electric field. VUV-intensities were measured at 300V, where the current, respective charge number, is equal to the number of absorbed photons

Fig. 3 Photocurrent measured in the absorption cell, respective number of VUV-photons, as function of the partial pressure of Xe in the THG cell. Getter purification leads to higher VUV intensities and increased total ion currents (TIC) of the analyte gas in the MS. Mixtures with Ar shift the pressure optimum to higher values and allows enhanced VUV generation. This reflects optimized phase matching in the (THG-) focal region

pump light occurs throughout the focal region. The negative dispersion (n~1/ω) of Xe between 117.2 nm and 119.2 nm (transitions 5p-5d) allows for an extended region of phase matching between fundamental (355 nm) and third harmonic (118 nm), and thus for an energy transfer into the VUV light. By adding a second, positive disperse gas (n~ω), the mixtures dispersion can be tuned to enhance the phase matching region. Stronger VUV-pulses are also reflected by the ion signal from the mass spectrometer (bars in Fig. 3). With the current setup, absolute VUV-photon numbers can be measured. Moreover, they can directly be related to sensitivity values of a SPI-MS for the first time. Therefore, critical optical parameters can be evaluated providing a basis for future SPI setups. Ongoing experiments will be ready for publication in 2017.

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Single-Particle Aerosol Mass Spectrometry

Julian Schade (UR), Johannes Passig (UR), Ralf Zimmermann (UR/HMGU)

Anthropogenic aerosols from combustion and industrial processes are known to provoke serious health effects. A recent WHO report attributes more than 3 Mio. deaths per year solely to ambient air pollution [1]. Driven by global urbanization, mobilization, consumption and population growth, this value is expected to increase to more than 7 Mio. premature deaths within the next decades.

The high temporal and spatial variability of both particle emissions and weather conditions requires fast on-line techniques for particle detection and characterization. The aerosols are physically and chemically complex and undergo permanent changes in dynamic interaction with the surrounding atmosphere. Among a large variety of aerosol characterization techniques, the aerosol-time-of-flight-technique (ATOF)[2,3] allows for an on-line analysis of the chemical composition of individual, size-selected particles (see Fig. 1(a) for working principle).

In commercial ATOF-instruments, an ultra-violet (UV) laser pulse hits the particle in the ion source of a mass spectrometer, where it leads to simultaneous desorption and ionization of the plume (Laser Desorption & Ionization, LDI). Both positive as well as negative ions are detected in the bipolar spectrometer. With that method, mainly inorganic components of the particles are obtained. Their signatures are applied for source apportionment (for example high K+-peaks for wood/biomass combustion, Na+ with [Na2Cl]+ and Cl- for marine aerosols etc. Nevertheless, organic components, relevant for health effects (e.g. polycyclic organic hydrocarbons, PAHs) and atmospheric processes are indirectly specified by its fragments [4] or oligomers [5,6] with ambiguity in molecular identification.

With the ATOF research prototype developed in our group, thermo-desorption (TD)/laser ionization schemes were investigated [7]. Here, particles hit a hot surface in the vicinity of the ionization volume. Organic components are desorbed and subsequently ionized by an excimer laser pulse of 248 nm wavelength. This technique allows for the selective and sensitive detection of PAHs from the particles via resonance enhanced multiphoton ionization (REMPI). An alternative method to determine the PAHs from individual particles is the implementation of a laser desorption step prior to REMPI-ionization [8]. In contrast to TD, the residual particle remains accessible to further ionization steps. Timing and alignment of the desorbing IR-laser (typically pulsed CO_2) is very critical. The particle and the desorbed plume, must be hit twice at a definite space and time. Furthermore, the local intensity at the particles position governs the expansion velocity of the plume that travels with the particle. It must have an appropriate size and density in the mass spectrometer ion source when the ionization laser fires (at its correct time). In that way, intensity profiles, spatial alignment, laser timing, heating rate and expansion dynamics are convoluted. Within the last years, the method was intensively optimized so that the particle hit rate for successful single particle LD-REMPI went up from 5-10% to more than 50%, which is crucial for ambient particle analysis.

Recently, we developed a scheme detecting both the PAHs bound to an individual particle and the inorganic/elemental constituents [9]. Herein, a single particle is exposed to a sequence of three consecutive laser pulses of different wavelength to desorb and selectively ionize the health-relevant PAHs while the refractive elements from the particle core are exclusively ionized by the last, intense UV pulse corresponding to conventional LDI (Fig. 1b-e). In order to assign the resulting ions to the respective ionization process, the extraction electrodes polarity is reversed within a few hundred nanoseconds between the laser pulses leading to an opposite acceleration of the ions into one of the respective ion flight tubes of the mass spectrometer. Our approach provides both a fully-fledged mass spectrum of (carcinogenic) PAHs in a single particle (Fig. 2, red) and the elemental composition of its core via cations (blue). Consequently, the individual PAH-distribution of single-particles in aerosols and its assignment to specific pollution sources become accessible for the first time.

Current projects aim on the extension of the method to particles smaller than 200 nm by advanced optical detection and/or aerodynamic preselection. Moreover, the particles desorption/ionization dynamics are in the focus of our research in order to address a larger number of target molecules in ambient aerosols with increased sensitivity. In that context, we also prepare the application of ultrashort laser pulses in order to detect specific classes of molecules with particular relevance for health and climate on a single-particle basis.

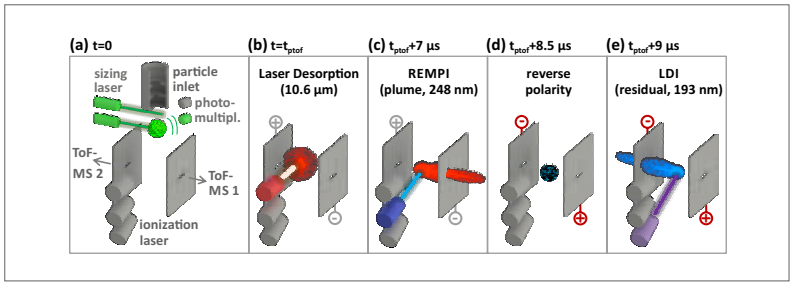

Fig. 1(a) ATOF-principle: Particles are aerodynamically accelerated and sized via laser velocimetry. Approaching the dual MS ion source, the multi-step pulse sequence is started: (b) The particle is heated by an IR-pulse. (c) The plume of desorbed PAHs is selectively ionized and analyzed in one MS tube. (d) Fast field inversion. (e) An UV pulse hits the particle for LDI of inorganic cations being detected in the second MS tube. Fig. modified from [9]

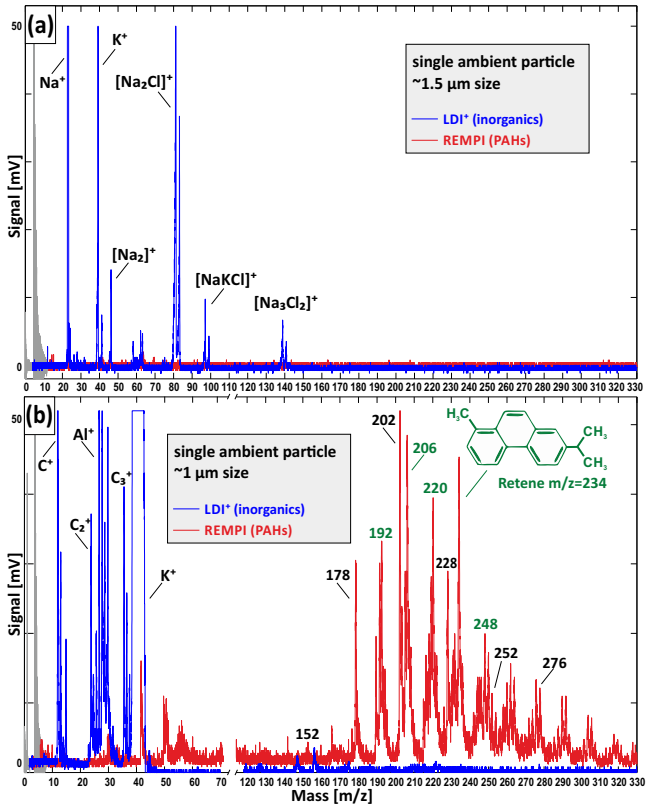

Fig. 2 Combined mass spectra of two exemplary ambient air particles: (a) Typical sea-salt particle (b) A PAH-containing particle. Combined LDI+ and REMPI information features the assessment of specific health risks, here by a high amount of (carcinogenic) PAHs. In this case, apportionment to wood or biomass burning is possible by a dominant K+ peak combined with retene (m/z=234). Fig. modified from [9].

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Ambient pressure laser desorption – ion mobility spectrometer for fast and sensitive detection of explosives

René Reiss (UR), Sven Ehlert (Photonion), Ralf Zimmermann (UR/HMGU)

Introduction

An ambient pressure laser desorption (APLD) ion mobility spectrometer(IMS) is introduced within this work which enables to measure substances on surfaces without sample pretreatment and gain ion mobility information of them. This coupling is especially useful for substances with low vapor pressure, which in turn are difficult to detect for common air sampling techniques. Especially drugs and explosives, relevant in forensic science, have two characteristics that make them hard to analyze but ideal for laser desorption (LD). Firstly, many explosives are thermal labile and thermal stress should be avoided. The thermal stress is lower by using a pulsed LD, instead of a continuous one1, and should therefore lead to less fragmentation and better detection limits for explosives. Secondly, most of the explosives have a very low vapor pressure e.g. RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine) 4.4·10-9 .

Experimental setup

One microliter sample solution was dropped upon a surface like a stainless steel sheet to prepare a sample. After the solvent was evaporated, the residue carrying surface was hold in front of the APLD head. Subsequently the carrier surface was scanned with the APLD system to detect the residue. Later on, when the measurement was done, the surface was cleaned with methanol and could be reused. The APLD operates by direct desorption of samples from surfaces with short laser pulses. At first the pulsed Nd:YAG laser produces an approx. 5 ns wide pulse of light with a pulse energy of about 3-5 mJ. The laser pulse is then transferred to the surface via laser fiber. Using the desorption head the laser fiber is hold in position with just a few millimeters distance to the surface. The pulsed laser light ablates the analyte from the surface which is then transferred through a capillary into the IMS. The desorption head was heated to 180°C to prevent the analyte from adsorbing at the surface. The practical aperture and a snapshot from an ongoing measurement can be seen in Fig. 1.

Results and Discussion

By measuring safety relevant substances under real conditions the practical usefulness was demonstrated. Within this experiment EGDN (nitroglycol), urea nitrate, PETN (pentaerythritoltetranitrate), HMTD (hexamethylenetriperoxide diamine), RDX (hexogen), Tetryl (2,4,6-trinitrophenylmethyl-nitramine) and of course TNT (trinitrotoluene) had been measured. The achieved limits of detection are in a range of 0,5 ng to 50 ng. These amounts represent a total amount measurable of substance on a surface and were measured from a single spot. Whereas actual APLD improvements as well as the coupled IMS leaded to these limit of detection. Fig. 2 shows the capabilities of the APLD-IMS system when measuring TNT. The amount of TNT is plotted against the total signal intensity for different levels of TNT. This means that all TNT signals from all spectra were accumulated and plotted against the used amount of substance. A good correlation between sample amount and signal intensity can be obtained and therefore shows the performance of this system.

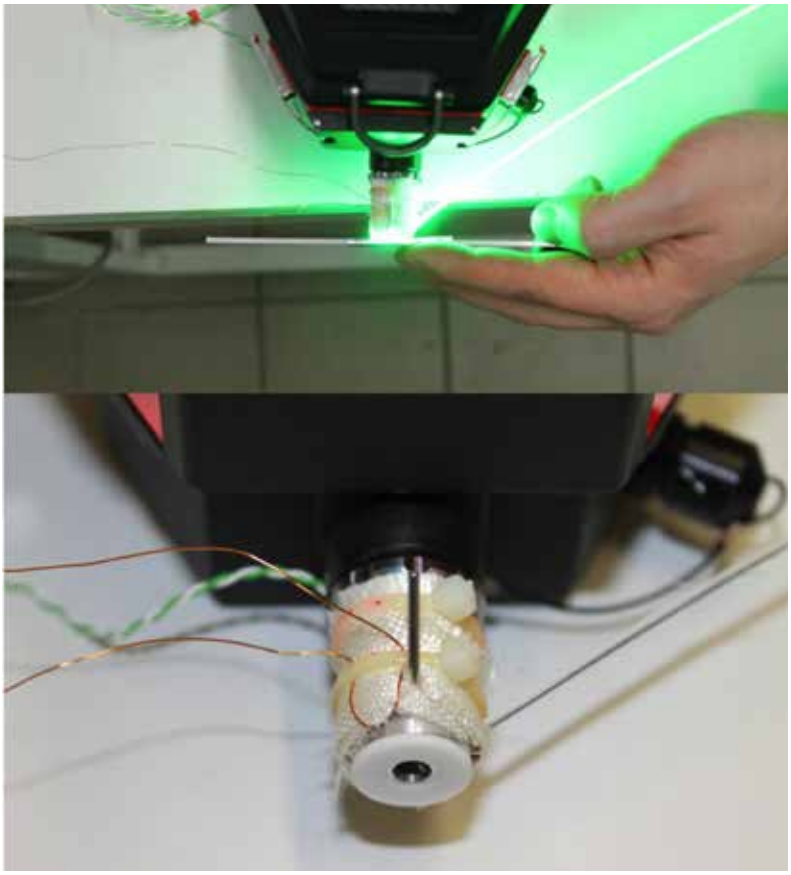

Fig. 1 Upper part: Desorption taking place from a surface. The green laser pulse ablates the analyte from the surface. The analyte is then transferred into the ion mobility spectrometer for detection. Lower part: Close up view of the ambient pressure laser desorption head seated on the ion mobility spectrometer (GDA-X). A PTFE ring is placed at the front to prevent thermal heating of the analyzed surface. At the right the laser fiber enters the APLD head and on the left a thermocouple and resisted heating can be seen.

The basic APLD qualification and performance also have been shown at laboratory and field experiments. These were done among others measurements in cooperation with the Federal Criminal Police Office Wiesbaden (BKA) were different explosives, drugs and drug precursors were analysed3. To mention an example, positively detecting TNT residues by probing a suitcase inner surface after TNT was stored inside it. Even

though the TNT was stored inside the suitcase for only about half an hour at room temperature and was shielded by a zipped plastic bag from the suitcase surface a positive detection was possible.

Conclusion

A fast and reliable detection of explosives can be crucial for first responders to allow correct decision-making. Powerful and flexible analytical tools are necessary to achieve the goal of measuring explosives fast and reliable. Beside these theoretical requirements there are also practical requirements like small geometrical size and flexibility. APLD-IMS allows such an easy and flexible sample collection of analytes on surfaces4. Because of the short pulse duration of only nanosecond, the thermal energy input can be minimized. The APLD is therefore an excellent alternative to measure surface adsorbed substances without the fear of thermal degradation.

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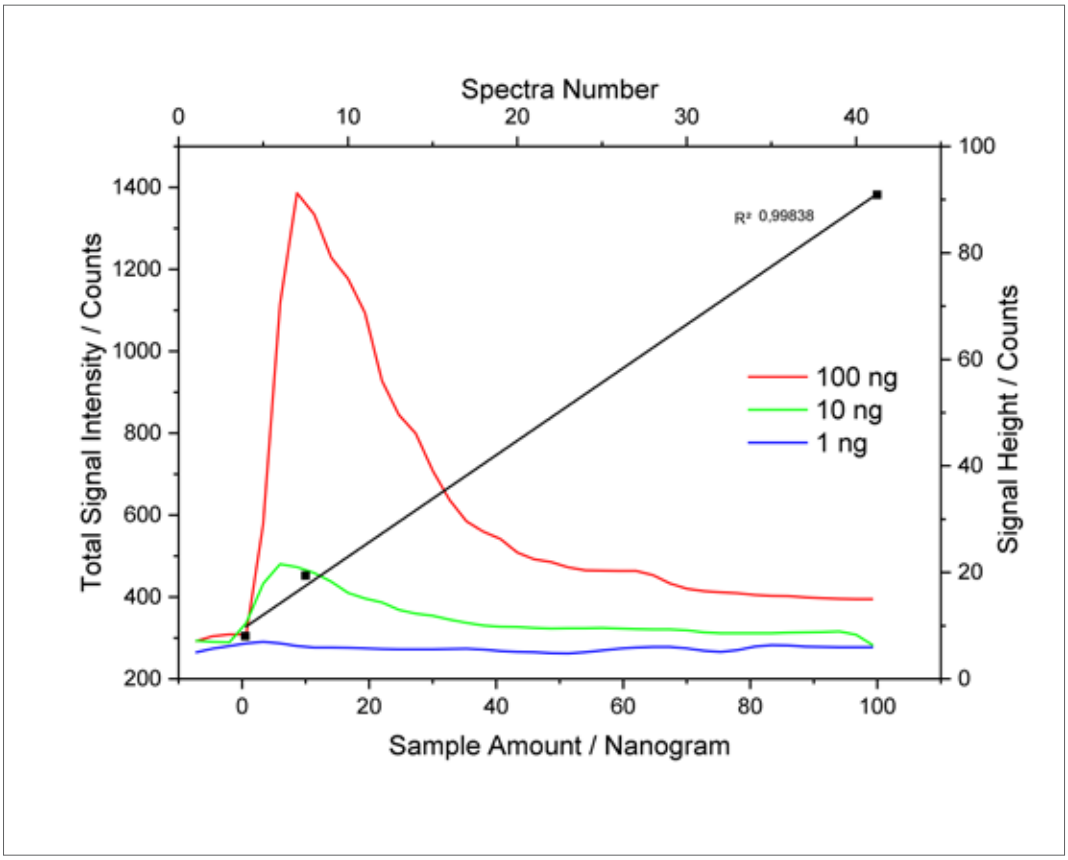

Fig. 2 Desorption of TNT from a prepared surface. The concentration is a total amount desorbed from a single spot. Quantification is done by high accumulation of all sample spectra achieved from this sot (black data points). The total signal intensity belongs to these black data points and to the best line if fit. The system response is also plotted for every total amount of substance used and can be seen as differently colored lines. These lines show the signal height as a detector response for every spectra recorded and belong to the signal height axis.

High flow gas chromatography mass spectrometry using atmospheric pressure chemical ionization

T. Schwemer (UR), C. Rüger (UR), M. Sklorz (UR), R. Zimmermann (UR/HMGU))

Abstract

The effect of high carrier gas velocities on gas chromatography (GC) in combination with APCI FT-ICR MS was investigated. Rising the carrier gas velocity from 29 cm/s (Van Deemter optimum) to 145 cm/s leads to a reduction of acquisition time, lower elution temperatures, and an extension of the detectable mass range. Doing high flow GC-MS of crude oil samples the mass range was enlarged from m/z 670 to 720. New compounds at higher carrier gas velocities mainly contribute to the CH-, CHO_2-, CHS_1- and CHO_1S_1-classes. Nevertheless, the signal-to-noise ratio as well as resolving power decreased and complicate the identification of isomeric species.

Introduction

Gas chromatography (GC) is one of the most important separation techniques. The hyphenation to mass spectrometry (MS) enables the detection and quantification of a large variety of substances. Typically the applied carrier gas velocity is set according the Van Deemter optimum to achieve the best chromatographic separation. For helium the optimum velocity is between 20 – 30 cm/s. However, Amirav et al. showed that high carrier gas velocity enlarges the observed compound range (Fialkov et al. 2003). Furthermore, the use of a programmed temperature vaporized injectors with a separated temperature program (PTV) enables the transfer of compounds on the GC column at lower temperatures and reducing thermal degradation during sample injection. As the applied APCI-source is not limited to low carrier gas flows (as e.g. most vacuum ionization sources), we investigate pros and cons of high carrier gas velocity for analysis of high boiling complex samples.

Materials and Methods

To investigate the effects of higher carrier gas velocity a polycyclic aromatic hydrocarbon standard and a Turkish crude oil sample were analyzed with a CP 3800 gas chromatograph equipped with a programmed temperature vaporizing injector. An aliquote of 2 µL was injected with a split ratio of 1:10 and separated on a 15 m BPX-5 column with 0.25 mm ID and a 010 µm film. The temperature programs of injector and oven was applied according the Fig. 1. Helium and nitrogen were used as carrier gas and the gas velocity was varied from 29 (Van Deemter optimum) to 93, 145 and 183 cm/s. Mass spectrometric measurements were conducted with an Apex Qe Series II FTICR MS system with a 7 Tesla magnet. For ionization a heated APCI source II was used, which was connectedvia a heated transfer line at 300 °C with the GC.

Results and Discussion

Higher carrier gas velocity revealed a reduction of separation time and elution temperature of substances. The number of detected m/z ratios, assigned elemental compositions and the mass range increase with rising velocity (fig.2 a). For example at the Van Deemter optimum approx.

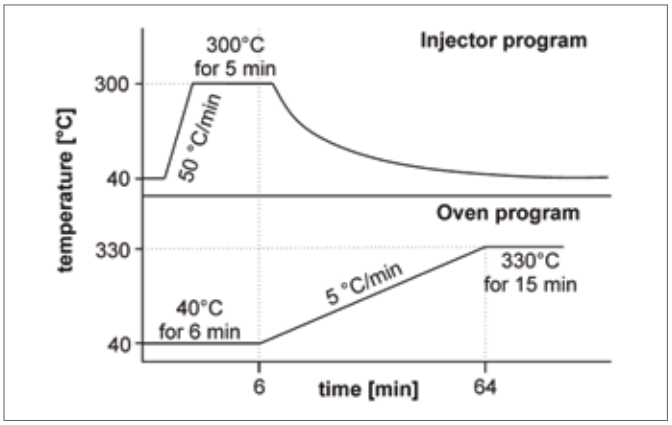

Fig. 1 Temperature program of PTV injector and GC oven

2,100 elemental compositions are assigned in the crude oil. For 145 cm/s approx. 2,300 elemental compositions can be assigned. Most of the detected compounds showed lower signal-to-noise (S/N) ratios at higher carrier gas velocity. The maximal total carbon number of detected compounds is increased from 48 to 52, which corresponds to an extension of mass range from m/z 670 to 720. The new appearing compounds mainly belong to the CH-, CHS_1-, CHO_2- and CHO1S1-class. Nevertheless, as the abundance of the new CH- and CHS1-class components is comparable low, the intensity weighted compound class distribution revealed only small changes between the different applied carrier gas velocities (fig. 2b).

Acknowledgement

Funding by the Helmholtz Foundation for the HICE virtual institute (www.hice-vi.eu) and the state scholarship program, which are funded by the European Social Funds (ESF), is gratefully acknowledged. Furthermore we thank the DFG for funding of the Bruker FT-ICR MS. The total

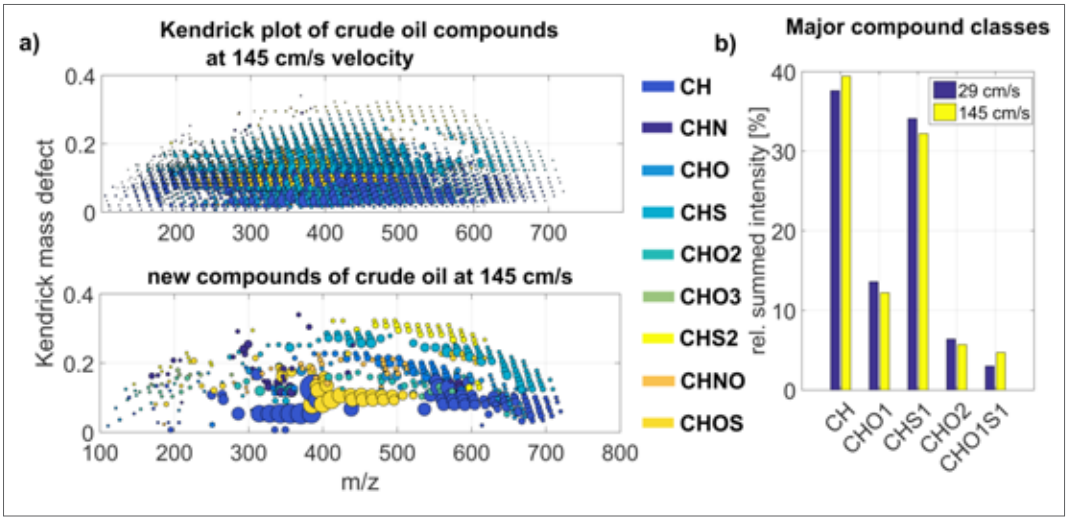

Fig. 2 a) Kendrick plot of assigned crude oil compounds at a carrier gas velocity of 145 cm/s with color coded compound classes and intensity weighted bubble size (up); and Kendrick plot of new elemental compositions (down), (scale of intensity coded bubble size normalized individually); b) major compound class distribution of all assigned elemental compositions of crude oil with selected carrier gas velocities

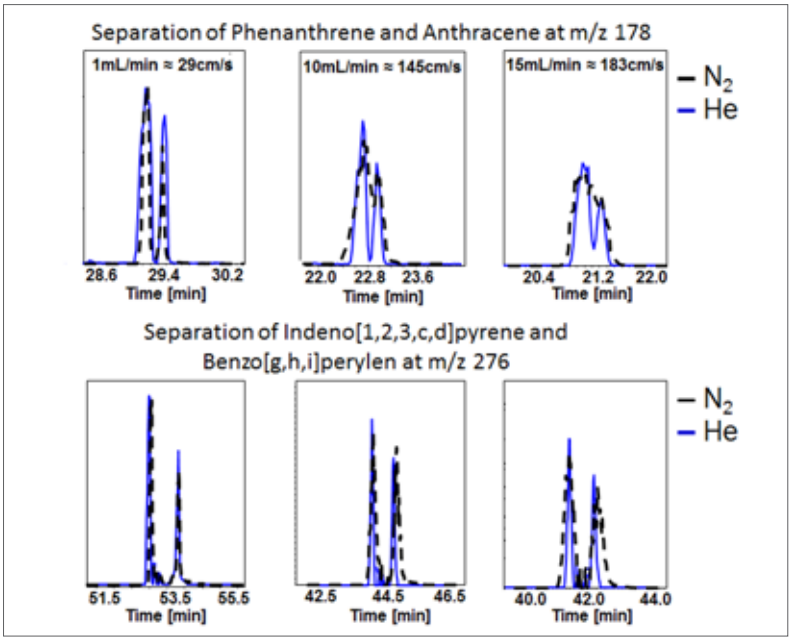

Fig. 3 Extracted ion chromatograms of selected substances for 3 different carrier gas velocities and two different carrier gases (nitrogen = black, helium = blue) in a PAH standard mixtur

ion count is not affected significantly by the gas velocity variation and the chromatographic peak areas of compounds are nearly the same. But GC peaks at higher velocities broadened, resulting in lower peak intensity and lower S/N ratios (fig. 3). That leads to decreased detection limits and make identification of isomeric species difficult. This gets even worse if switching the carrier gas from helium to the nitrogen (saving costs). Changing carrier gas velocity also slightly influenced the relative retention times: E.g. retention times ratio of methyleicosanoat to benz[a]anthracene shifted about 1.5 %.

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Characterization of Petroleum and Petroleum derived Matrices by comprehensive two-dimensional gas chromatography and/or high resolution time-of-flight mass spectrometry

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Abstract

Chromatography and mass spectrometry are classical key technologies for the investigation of complex petrochemical matrices. Nowadays, full refined petrochemical fuels like gasoline and diesel could be completely separated and quantified based on two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS). However, higher boiling point cuts and intermediates remain challenging. To overcome these obstacles, GCxGC-TOFMS has to be further extended towards high resolution mass spectrometer (e.g. High resolution time-of-flight mass spectrometry, HRT). In case of distillation residues, where gas chromatography is not applicable, HRT could be applied in combination with introduction systems working at ambient pressure like thermal analysis or the sample could be introduced directly with a direct insertion probe. We will demonstrate the application of (HR-)TOFMS for different distillation regions as well as distillation residues. Up to the distillation limit GCxGC-TOFMS/HRT will allow a very detailed qualitative and quantitative analysis which will be demonstrated on the examples of typical middle distillates and light crude oils. The capabilities of a direct mass spectrometric analysis of distillation residuals will be demonstrated on the example of bitumen.

Introduction

Gas chromatography (GC) is one of the most imIn 1987 Boduszynsky described the composition of petroleum as a continuum of chemical classes as a function of the atmospheric equivalent boiling points of the compounds (Fig. 1).1 Boiling point and molecular distribution are also crucial parameter for the choice of the analytical technique to determine the composition of such a petroleum matrix. In industry a wide range of standardized methods like ISO, ASTM or DIN/EN are applied to ensure a comparability of petroleum and petroleum derived products like fuels all over the world. In most cases a couple of different techniques have to be applied to gather qualitative as well as quantitative information's for different compound classes and/or boiling point distributions. Especially (gas-) chromatographic techniques are very well suited to break down the continuum of compounds to groups of classes or even individual compounds. An obstacle is often the isomeric complexity which increases according to the boiling point of the petroleum matrix. Isomeric compounds tend to overlap within classes but also with other classes, since they could elute over a wide boiling point range. To overcome some of these limitations so called comprehensive techniques could be applied and first methods based on comprehensive two-dimensional gas chromatography are already accepted by ASTM.2,3 Mass spectrometry further

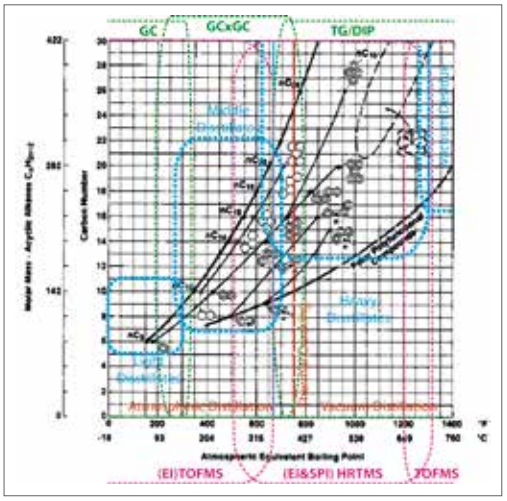
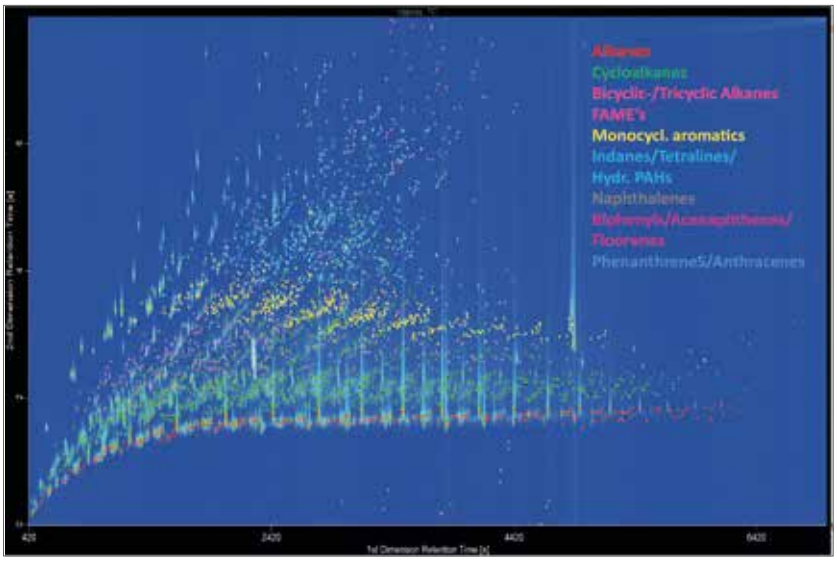


Fig. 1 The Boduszynsky continuum model for petroleum. The analytical techniques applied for this study are indicated.

enhances the selectivity of these technique and allows a spectral validation of the compounds of interest. This becomes especially important for cases were compounds or compound classes could not completely resolve even when GCxGC is applied. State-of-the-art mass spectrometry will further allow distinguishing nominal isobaric compounds based on accurate mass information. The derived elemental composition will also allow a localization of heteroatomic compounds as well as its aromaticity. However, at a certain boiling point limit, the application of gas chromatography is no longer suitable and direct mass spectrometric methods could be applied. In such cases the resolving power of the mass spectrometer becomes more and more important.

Beside high mass resolution also a soft and preferably uniform ionization technique will facilitate the spectrometric assignment of compounds and compensates, to a small extend, the lost chromatographic separation. Sample introducti-



n-Alkanes	iso-Alkanes	Monocyclics	Bicyclics	Tricyclics	alkyl. Benzenes	Indanes	Tetralines	Naphthalenes	Biphenyls	Fluorenes	Diphenylmethanes	Acenaphthenes	Tri aromatics	Poly aromatics	FAME	Total
0,01%	-	0,02%		-	0,03%	-	-	-	-	-	-	-	-	-	-	0,07%
0,14%	0,07%	0,28%	0,01%	-	0,19%	-	-	-	-	-	-	-	-	-	-	0,69%
0,78%	0,30%	1,06%	0,09%	-	0,64%	0,16%	-	-	-	-	-	-	-	-	-	2,99%
1,32%	0,89%	2,01%	0,76%	0,00%	0,93%	0,69%	0,69%	0,07%	-	-	-	-	-	-	-	7,79%
1,58%	0,91%	1,85%	0,69%	0,01%	0,91%	1,77%		0,17%	-	-	-	-	-	-	-	7,89%
1,45%	0,56%	2,00%	0,86%	0,02%	0,77%	1,99%		0,31%	0,03%	-	-	0,01%	-	-	-	8,00%
1,56%	0,94%	2,85%	0,73%	0,02%	0,82%	2,59%		0,34%	0,16%	0,01%	0,01%	-	0,02%	-	-	10,08%
1,64%	0,92%	3,01%	0,71%	0,01%	0,81%	2,11%		0,34%	0,44%	0,06%	-	-	0,11%	-	0,15%	10,30%
2,12%	1,21%	2,99%	0,46%	-	0,58%	0,84%		0,20%	0,35%	0,06%	-	-	0,14%	-	1,35%	10,50%
2,12%	1,53%	3,40%	0,38%	-	0,37%	0,76%		0,09%	-	0,11%	-	-	0,06%	0,04%	0,04%	8,92%
1,79%	0,89%	3,22%	0,36%	-	0,29%	0,18%		-	-	-	-	-	-	0,01%	0,28%	7,01%
1,01%	1,46%	2,72%	0,67%	-	0,26%	0,13%		-	-	-	-	-	-	-	3,32%	10,17%
1,01%	1,54%	1,55%	0,47%	-	0,16%	-		-	-	-	-	-	-	-	0,06%	6,81%
1,98%	0,58%	1,13%	0,18%	-	0,21%	-		-	-	-	-	-	-	-	0,41%	3,68%
1,20%	0,59%	0,60%	0,01%	-	0,08%	-		-	-	-	-	-	-	-	0,06%	2,53%
0,88%	0,22%	0,26%	-	-	0,04%	-		-	-	-	-	-	-	-	0,07%	1,16%
0,35%	0,36%	0,01%	-	-	-	-		-	-	-	-	-	-	-	0,02%	0,73%
0,13%	0,18%	-	-	-	-	-		-	-	-	-	-	-	-	0,01%	0,32%
0,06%	0,08%	-	-	-	-	-		-	-	-	-	-	-	-	-	0,14%
0,03%	0,02%	-	-	-	-	-		-	-	-	-	-	-	-	-	0,06%
0,02%	0,01%	-	-	-	-	-		-	-	-	-	-	-	-	-	0,03%
0,01%	-	-	-	-	-	-		-	-	-	-	-	-	-	-	0,01%
0,01%	-	-	-	-	-	-		-	-	-	-	-	-	-	-	0,01%
-	-	-	-	-	-	-		-	-	-	-	-	-	-	0,20%	0,20%
21,45%	13,27%	29,66%	6,38%	0,06%	7,08%		11,82%	1,01%	0,99%	0,26%	0,01%	0,01%	0,36%	0,04%	6,86%	99,90%

Fig. 2 (above) Analysis of Diesel by GCxGC-TOFMS. Spectral deconvoluted compounds are indicated by colored dots. The colors indicate the assignment to a class. (below) Detailed quantitative analysis of Diesel based on GCxGC-TOFMS. Almost 4000 individual peaks could be classified according to substance class and carbon number.

on could be performed at controlled atmospheric condition or at reduced pressure/vacuum conditions. Thermal analysis will allow the simulation of refinery distillation processes including thermal cracking and pyrolysis of heavy compounds. The distillation limit and cracking behavior of the matrix could be further shifted to higher temperatures if a direct evaporation of the matrix in vacuum is performed by e.g. a direct insertion probe. In this study LECO time-of-flight technology with unit and high mass resolution were combined with different frontends to investigate the different regions of the Boduszynsky continuum of petroleum matrices. Experimental setup

According to the complexity of the petroleum matrix unit- and high resolution time-of-flight

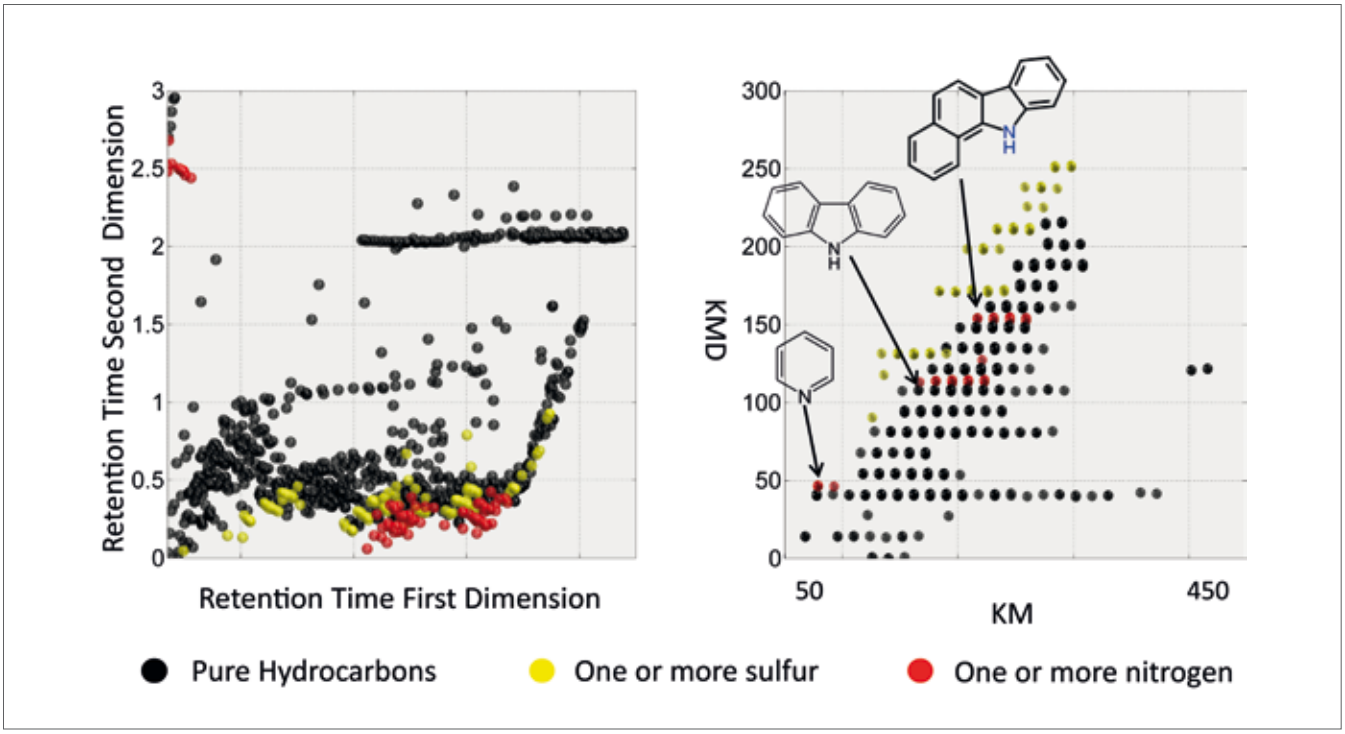


Fig. 3 Aromatic composition of heavy fuel oil represented as pseudo chromatogram (left). Accurate mass information is used to identify heteroelements and classes. Derived Kendrick mass defect plots facilitate the determination of compound classes (right).

mass spec-trometry technologies (Pegasus and Pegasus HRT, LECO) were applied (Figure1). Beside build-in 70 eV electron ionization also single photon ionization (SPI) was adapted for LECO HRT. Up to the atmospheric boiling point limit of petroleum GCxGC was applied as frontend and only adapted for higher tempera-ture if necessary. Beyond the boiling point limit GCxGC was either hyphenated to thermal analysis (STA Jupiter Serie, Netzsch) or completely removed. For the second case direct insertion probe (DIP) was applied to introduce sample material. Four different kinds of petroleum matrices were investigated: Diesel (middle distillate), heavy fuel oil (heavy distillate) and bitumen (vacuum residue). In addition also a light crude oil was analyzed. All matrices were diluted in DCM before injection.

Results and Discussion

Middle distillates like Diesel could be almost comprehensively analyzed by GCxGC-TOFMS. Unlike FID methods2,3, TOFMS also allows a reliable allocation of overlapping substance classes. Elution pattern information's from GCxGC were combined with MS fragmentation pattern information for scripting (Fig. 2). Quantification was performed due to the application of group specific MS response curves which were established for all shown substance classes. As a result more than 99% (m/m) of a middle distillate could be quantitatively assigned to substance classes and carbon numbers (Fig. 2).4With one analysis a couple of standard methods could be substituted and the results are in good agreement with results obtained by DIN/EN/ISO. However, for some parameter e.g. aromatic composition in jet fuels, deviations from standard methods were observed. Further investigation indicated, that compre-hensive methods are more suitable for the investigation of actual modern fuels.5 It was also possible to adapt the method for higher boiling matrices to analyze the volatile fraction of these matrices. As an example a light crude oil was analyzed and the substance classes were adapted to the non-processed petroleum matrix. The high temperature GCxGC-TOFMS approach allowed a quantitative assignment of approximately >80 % (m/m) of the matrix and a discrimination of several crude oils and blends from crude oils. The HT-GCxGC method could also be correlated with boiling point information to derive a simulated distillation model. With this approach the qualitative composition of boiling point cuts could be predicted.6 However, for some compound classes, no unambiguous allocation of substance classes could be done based on mass spectral patterns from unit mass resolution instrumentation and an allo-cation based on elution pattern will be empirical as long as no authentic standards were analyzed. To overcome this limitation unit resolution time-of-flight

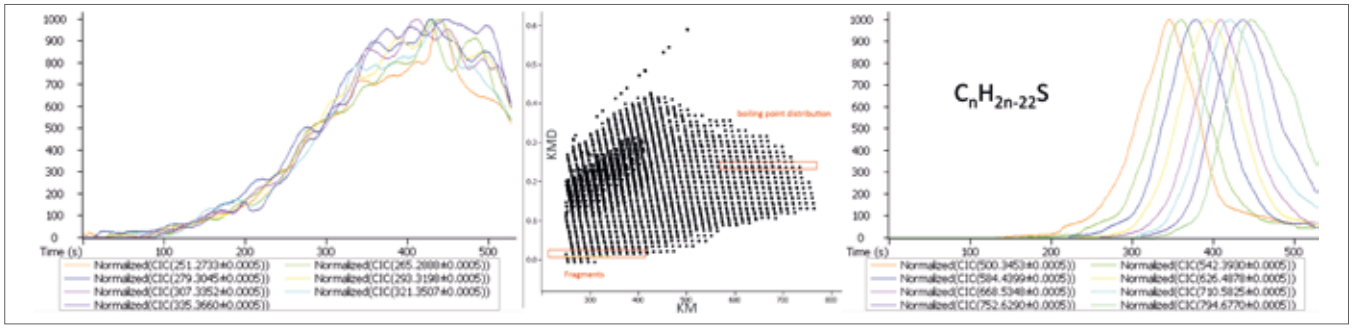


Fig. 4 According to the continuous composition of petroleum, the Kendrick mass defect plot shows a typical regular and periodically pattern for the analyzed bitumen (middle). Fragmentation pattern (left) and evaporation profiles (light) could be roughly distinguished. The exact mass information also allows the suggestion of elemental compositions.

technology was replaced by high resolution time-of-flight resolution with a mass resolution of up to 50.000 and a mass accuracy of < 2ppm. For demon-stration, heavy fuel oil with a high aromatic (pure hydrocarbon and heteroromatic) fraction was ana-lyzed. GCxGC-HRT allowed a non-targeted identification of heteroatomic nitrogen and sulfur species as well as an assignment of the aromaticity based on ring-and-double binding equivalents. Based on GCxGC also the isomeric composition could be derived and illustrated (Fig. 3). Petroleum matrices behind the boiling point were analyzed with direct insertion probe – high resolution time-of-flight mass spectrometry. Complete and SARA-fractionized samples were placed directly on a probe and inserted into the source of the MS. After a short drying step, the sample was continuously heated and evapo-rated directly into the ion source of the mass spectrometer. Calculated atmospheric equivalent boiling points of up to 700°C could be achieved and mass spectral analysis showed masses beyond 1000 m/z at these temperatures. The correlation of boiling point profiles with mass fragmentation pattern allowed a rough discrimination of boiling pattern vs. fragmentation pattern and different homologous classes could be assigned by their elemental composition (Fig. 4).

Acknowledgement

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Investigation of associations between air pollution-related biomarkers of exposure and harm in biological samples using liquid chromatographic and liquid chromatographic-mass spectrometric methods

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Our research is aimed at the long-term and short-term effects induced by exposure to air pollutants such as fine particulate matters and ultra-fine particulate matters. Robust liquid chromatographic and liquid chromatographic-mass spectrometric methods are developed in order to determine biomarkers of oxidative stress and biomarkers of exposure from collected biological samples such as urine, blood, bronchoalveolar lavage fluid, and tissue from human and mice. Associations between exposure and health effects are investigated. One of the current projects is described as follows:

Determination of air pollution-related biomarkers of exposure and harm in urine of travellers between Germany and China using liquid chromatographic and liquid chromatographic-mass spectrometric methods

Introduction

In the past several decades, China had notable success in terms of economic growth, as well as booming transportation and industry. However, these changes are accompanied by the impairment of air quality, which is caused by fossil fuel and biomass combustion [1-3]. Particularly in winter, heavy hazes often cover huge areas of north China, which has become a global concern. One of the major components of haze is particulate matter (PM) consisting of suspended solid or liquid particles. They can be inhaled and accumulated in the bronchus and pulmonary alveolar surfaces, inducing the formation of reactive oxygen species (ROS) such as peroxides, superoxide, hydroxyl radical, and singlet oxygen. These species disturb the natural oxidative stress balance. Furthermore, they can induce cell apoptosis. Their reactivity can be blocked by antioxidants or internal enzymatic processes of the cell. Particles with diameter < 2.5 µm ($PM_{2.5}$) have been proven to be more harmful because they can be inhaled into the deeper lung regions and are able to penetrate cell membranes. During phases of oxidative stress, bio-molecules, including phospholipids, proteins, and DNA, are oxidatively attacked. These biochemical processes, on one hand, can induce further development of diseases such as cancer. On the other hand, the formed oxidation products and metabolites can be used as indicators of air pollution exposure and harm. One strategy is to determine the biomarkers in urine samples, such as malondialdehyde (MDA) [4], $F_{2\alpha}$-isoprostanes [5], and 8-hydroxy-2'-deoxyguanosine (8OHdG) [6]. Due to the non-invasive character of urine sampling, such methods are appropriate also for studies of large populations. In environmental health studies and epidemiological studies, one problem researchers often encounter is that the subjects under study have usually been exposed to the same conditions or similar conditions for a long period. This can conceal or change characteristics related to acute injuries. Every year, millions of people perform long-distance travel. Among the places of travel, some have relatively „clean" air while others have relatively „unclean" air. Here, we propose the idea that travellers can provide an ideal model to investigate acute health effects due to their exposure to different environments during travel.

Instrumentation, results, and discussion

A pilot study was performed by focusing specially on individuals travelling to China from Germany. The studied population consisted of nine non-smoking "healthy" (no chronic diseases such as cardiovascular diseases, chronic obstructive pulmonary disease, or renal insufficiency) young male Chinese volunteers with a mean age of 29 (ranging from 26-34). The urine samples were collected. Analyses of oxidative stress biomarkers were carried out with a triple quadrupole mass spectrometer, API-3000 (AB Sciex, Darmstadt, Germany) equipped with an electrospray ion source (ESI), coupled with an HPLC system HP1100 (Agilent Technologies, Waldbronn, Germany). All analyses were performed in the multi-reaction monitoring (MRM) mode. The time trends of median values from the Boxplot are shown in Fig. 1. The concentration of $PM_{2.5}$ shows nearly constant and low values in the measurements after returning from China. The highest median concentrations of the oxidative stress biomarkers MDA (Fig. 1 B), the oxidative DNA damage biomarker 8OHdG (Fig. 1 C), and the polycyclic aromatic hydrocarbon exposure biomarkers OH-PAHs (Fig. 1 E) are found directly after returning from China (S1 samples). The decreasing trends lasted for 2-4 weeks for most of the biomarkers while the downtrends of OH-PAHs lasted for only 1-2 weeks till pre-travel

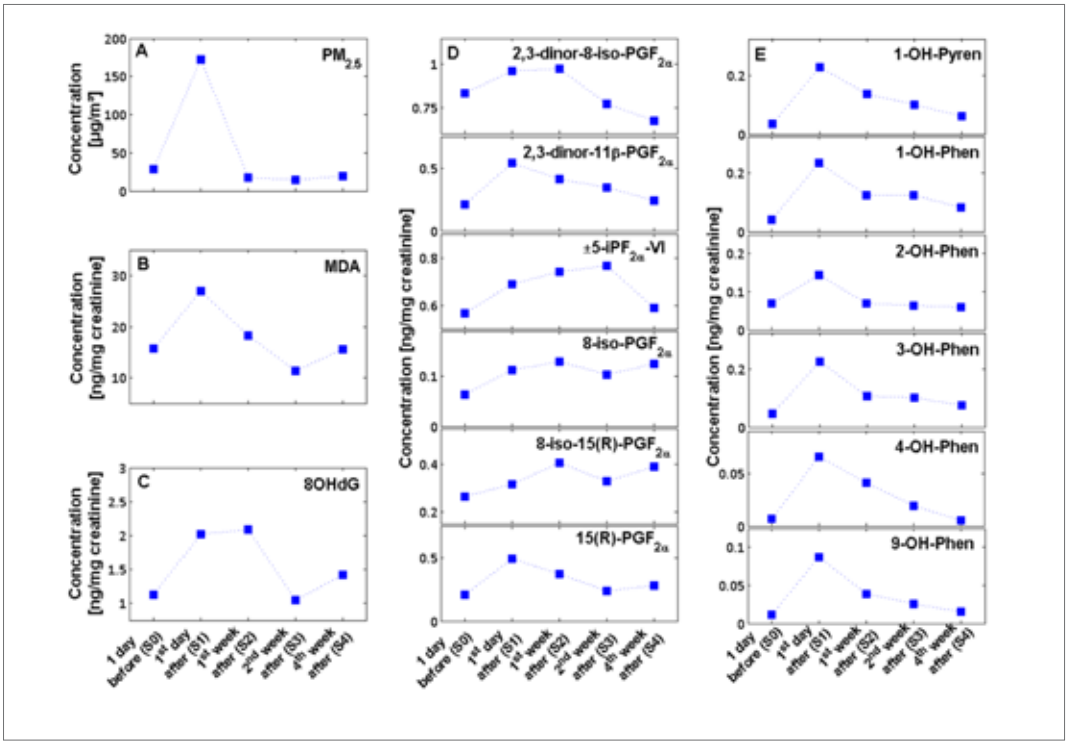

Fig. 1: Time trend curves for the median values of:

A) $PM_{2.5}$-concentration;

B) Concentration of malondialdehyde, a biomarker of lipid peroxidation (oxidative stress);

C) Concentration of 8-Hydroxy-2'-deoxyguanosine, a biomarkers of oxidative DNA damage (oxidative stress);

D) Concentration of isoprostanes, biomarkers of arachidonic acid oxidations (oxidative stress);

E) Concentration of hydroxylated PAHs, biomarkers of polycyclic aromatic hydrocarbon exposure in the urine of the travellers (valid cases A02, A03, A04, A05, A07) starting with before travel (S0), directly after travel (S1) and the 4 weeks after return (S2,S3,S4).

values were achieved. This indicates, in accordance with the literature [7], a faster removal pathway from the organism, for PAH. The differences in the $PM_{2.5}$ concentrations between China and Germany match the overall increasing (S0 and S1) and decreasing (S1 to S4) trends of oxidative stress biomarkers and PAH metabolites. The results show: (1) the selected methods are reliable and applicable for routine analyses; (2) the concept of using air-travellers as model is feasible and worth to be further performed within a larger cohort; (3) the investigated volunteers who were exposed to high levels of $PM_{2.5}$ conditions showed increased concentrations of biomarkers for PAH exposure; (4) high oxidative stress and oxidative DNA damages evolved fast and significantly.

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our-institute/about-us/index.html

Helmholtz Zentrum München
Research Unit Analytical BioGeoChemistry
Munich, Germany
Prof. Dr. Ph. Schmitt-Kopplin, Dr. M. Witting
www.helmholtz-muenchen.de/research-
unit-analytical-biogeochemistry/index.html

Karlsruhe Institute of Technology (KIT)
Institute of Catalysis Research and
Technology (IKFT)
Karlsruhe, Germany
Prof. Dr. E. Dinjus, PD. Dr. N. Dahmen
www.itc-cpv.kit.edu/english/index.php

Karlsruhe Institute of Technology (KIT)
Institute for Meteorology and Climate Research,
Atmospheric Aerosol Research (IMK – AAF)
Garmisch-Partenkirchen, Germany
Prof. Dr. S. Emeis
www.imk-ifu.fzk.de/institute.php

Karlsruhe Institute of Technology (KIT)
Institute of Toxicology and Genetics (ITG)
Karlsruhe, Germany
Dr. S. Diabaté, Prof. Dr. U. Strähle, Dr. C. Weiss
www.itg.kit.edu/index.php

Karlsruhe Institute of Technology (KIT)
Institute of Technical Chemistry (ITC)
Eggenstein-Leopoldshafen, Germany
Dr. H.-R. Paur, S. Mülhopt
www.itc-tab.kit.edu

Leibnitz Institute for Baltic Sea
Research Warnemünde
Warnemünde, Germany
Prof. Dr. D. Schulz-Bull
www.io-warnemuende.de

National Institute of Chemical
Physics and Biophysics
Tallinn, Estonia
Prof. Dr. U. Kirso
www.kbfi.ee/?id=56&lang=eng

Oel-Wärme-Institut GmbH
Herzogenrath, Germany
Dr. – Ing. K. Lucka, Dr.-Ing. R. Edenhofer
www.owi-aachen.de

Paul Scherrer Institute
Laboratory of Atmospheric Chemistry
Villingen, Switzerland
Prof. Dr. U. Baltensperger, Dr. A. Prévôt,
Dr. E. A. Bruns
www.psi.ch/lac

International and National Universities

Baku State University
Faculty of Chemistry
Baku, Azerbaijan
Prof. Dr. A. S. A. Azizov
www.chemistry.bsu.edu.az/en

Brandenburg University of Technology
Cottbus-Senftenberg
Chair of Inorganic Chemistry
Senftenberg, Germany
Prof. Dr. P. Schmidt, Dr. A. Efimova
www.b-tu.de/fg-anorganische-chemie/

Cardiff University
Cardiff Earth & Ocean Sciences
Cardiff, UK
Dr. T. Jones
www.cardiff.ac.uk/earth

Cardiff School of Biosciences
Cardiff, UK
Prof. Dr. K. BéruBé
www.cardiff.ac.uk/biosi

Ghent University
Department of Organic Chemistry
Ghent, Belgium
Dr. C. Walgraeve
www.orgchem.ugent.be

Hong Kong Polytechnic University
Research Centre for Environmental
Technology & Management Department
Kowloon, Hong Kong, China
Prof. (Frank) Shung Cheng LEE
www.cse.polyu.edu.hk/04environmental.php

Department of Civil & Environmental Engineering
Kowloon, Hongkong, China
Prof. Xiangdong Li
www.polyu.edu.hk/cee/web/lixiangdong

Leibniz Universität Hannover
Institute of Environmental Planning
Prof. Dr. C. von Haaren
www.umwelt.uni-hannover.de/
umweltplanung.html?&L=1

Nanjing University of Information Science and Technology
Yale-NUIST Center on Atmospheric Environment
Nanjing, China
Prof. Dr. Y. Zhang
www.yncenter.sites.yale.edu/research-team

Maastricht University
Department of Toxicogenomics
Maastricht, Netherlands
Dr. J. J. Briedè, Dr. T. de Kok
www.toxicogenomics-um.nl/

Middle East Technical University
Department of Petroleum and
Natural Gas Engineering
Ankara, Turkey
Prof. Dr. M. Versan Kok
www.pete.metu.edu.tr

Otto-von-Guericke University
Institute of Medical Engineering
Magdeburg, Germany
Prof. Dr. C. Hoeschen
www.imt.ovgu.de

Stellenbosch University
Division of Polymer Science
Stellenbosch, South Africa
Prof. Dr. H. Pasch
www.academic.sun.ac.za/polymer

Shandong University
Department of Environmental Health
School of Public Health, China
Prof. Jie Li
www.sph.sdu.edu.cn/zyjg/wsdlxx1/sy.htm

Technical University of Darmstadt
Institute of Applied Geosciences
Darmstadt, Germany
Prof. Dr. S. Weinbruch
www.geo.tu-darmstadt.de/iag/index.en.jsp

Technical University of Dresden

Arbeitsgruppe Mechanische
Verfahrenstechnik (MVT)
Dresden, Germany
Dr.-Ing. L. Hillemann
www.tu-dresden.de

Institut für Baubetriebswesen (IBB)
Dresden, Germany
Dipl.-Ing. C. Weller
www.tu-dresden.de

Technical University of Munich

Center of Allergy & Environment –
Zentrum Allergie & Umwelt (ZAUM)
Munich, Germany
Prof. Dr. J. Buters, R. Effner
www.zaum-online.de

Physics Department
Garching
PD Dr. A. Ulrich
www.ph.tum.de

Professur für Regenerative Energiesysteme
Straubing
Prof. Dr.-Ing. M. Gader
www.res.wzw.tum.de

Università degli Studi di Messina
Facoltà di Farmacia
Dipartimento Farmaco-Chimico
Messina, Italy
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www.farmacia.unime.it

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University of Augsburg

Chair of Resource Strategy
Augsburg, Germany
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www.mrm.uni-augsburg.de/de/gruppen/reller/

Institute of Geography
Augsburg, Germany
Physical Geography and Quantitative Methods
PD Dr. A. Philipp
https://www.geo.uni-augsburg.de/en/chairs_professorships/phygeo/

University of California, Davis

Department of Chemistry
Davis, California, USA
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Kuopio, Finland
Prof. Dr. M.-R. Hirvonen
www.uef.fi/intola

Fine Particle and Aerosol Technology Laboratory
Kuopio, Finland
Dr. O. Sippula, Prof. Dr. J. Jokiniemi Dr. P. Tiitta
www.uef.fi/en/web/fine

University of Ferrara
Department of Analytical Chemistry
Ferrara, Italy
Prof. Dr. C. Pietrogrande, Prof. Dr. F. Dondi
www.unife.it

University of Gothenburg
Gothenburg, Sweden
Prof. Dr. J. B. C. Pettersson
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University of Göttingen
Interdisziplinäres Zentrum für Nachhaltige Entwicklung (IZNE)
Geowissenschaftliches Zentrum
Göttingen, Germany
Prof. Dr. H. Ruppert
www.izne.uni-goettingen.de

University of Luxembourg
Luxembourg Centre for Systems Biomedicine
Esch-Belval, Luxembourg
Dr. K. Hiller
www.en.uni.lu/lcsb/people/karsten_hiller

University of Mainz
Organic Chemistry Department
Mainz, Germany
Prof. Dr. T. Opatz
www.fb09.uni-mainz.de/

University of Pretoria
Department of Chemistry
Pretoria, South Africa
Prof. Dr. E. Rohwer, Dr. P. Forbes

University of Rostock

Department of Anaesthesiology and Intensive Care Medicine
Rostock, Germany
PD Dr. J. Schubert
www.kpai-uni-rostock.de

Department of Chemistry
Rostock, Germany
Prof. Dr. U. Kragl, Prof. Dr. R. Ludwig
www.chemie.uni-rostock.de/en/

Department of Physics
Rostock, Germany
Prof. Dr. O. Kühn, Dr. S. Bokarev
web.physik.uni-rostock.de/quantendynamik/index.html

Department of Piston Engines and Internal Combustion Engines
Rostock, Germany
Dr. U. Schümann, Dipl.-Ing. C. Fink, Dipl.-Ing B. Stengel
www.lkv.uni-rostock.de/en

University of Warwick

Coventry, Great Britain
Prof. Dr. P. O'Connor
www2.warwick.ac.uk/fac/sci/chemistry/research/oconnor/oconnorgroup

Coventry, Great Britain
Dr. M. Barrow
www2.warwick.ac.uk/fac/sci/chemistry/research/barrow/barrowgroup

China University of Mining and Technology
Department of resources and Earth Sciences
Beijing Campus
Ph. D Prof. L. Shao
www.cumtb.edu.cn/

Peking University Health Science Center
Dept. of Occupational and Environmental Health
Professor Xiao-chuan Pan
http://english.bjmu.edu.cn/

Public and State Institutions

Aerosol academy e.V.
Neuherberg, Germany
H. Grimm
www.aerosol-akademie.de

Augsburg City
Augsburg, Germany
T. Gratza
www.augsburg.de

Bavarian Environment Agency (Bayerisches Landesamt für Umwelt)
Augsburg, Germany
Dr. H. Ott, Dr. M. Rössert
www.lfu.bayern.de/index.htm

Bavarian Research Foundation
Munich, Germany
Prof. Dr. S. Mayer
www.forschungsstiftung.de

Federal Criminal Police Office (BKA)
Wiesbaden, Germany
Dr. M. Pütz, Dr. R. Schulte-Ladbeck
www.bka.de

Bundeswehr Research Institute for Protective Technologies and CBRN Protection (WIS)
Munster, Germany
Dr. R. Hetzer
www.baainbw.de/portal/poc/baain?uri=ci%3Abw.baain.diensts.wis

Federal Environment Agency Germany (Umweltbundesamt)
Global Atmosphere Watch (GAW) – Globale Überwachung der Atmosphäre
Garmisch-Partenkirchen, Germany
Dr. L. Ries
www.umweltbundesamt.de

Federal Institute for Materials Research and Testing (BAM)
Berlin, Germany
Dr. K. Urban
www.bam.de

Federal Office of Civil Protection and Disaster Assistance (BBK)
Bonn, Germany
M. Drobig
www.bbk.bund.de/

Fire brigade Frankfurt (FF)
Frankfurt, Germany
Dr. U. Annel
www.feuerwehr-frankfurt.de/

Institute for Fire and Disaster Prevention Heyrothsberge (IBK)
Berlin, Germany
Dr. K. Urban
www.inneres.sachsen-anhalt.de/bks-heyrothsberge/bks_neu/

State Office of Criminal Investigations (LKA)
Berlin, Germany
S. Rosenkranz
www.berlin.de/polizei/dienststellen/landeskriminalamt/
Mainz, Germany
Dr. S. Zörntlein
www.polizei.rlp.de/de/startseite/

Funding and Scholarships

List of Funded Third Party Projects of the JMSC (April 2015 – December 2017)

Funding Institution	Grant period	Title	Total HMGU / UR €
Bundesministerium für Wirtschaft und Energie (ZIM-Kooperationsprojekte)	01.06.16-31.05.19	Entwicklung eines Screeningverfahrens für fossile und biogene Schwerflüchter	186.577 € (HMGU)
Helmholtz-Gemeinschaft	01.03.15-31.12.16	SO-084 Helmholtz-Stadtforschungs-Initiative (Phase I)	10.000 € (HMGU)
Bundeskriminalamt	31.12.14-28.02.15	Profiling von Heroin und Grundstoffen mittels zweidimensionaler Gaschromatographie (GcxGC-TOFMS)	18.692 € (HMGU)
Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF)	01.01.14-31.05.17	Untersuchung der Einflussgrößen auf die Messung der Partikelemission von Kleinfeuerungsanlagen	204.150 € (HMGU)
Deutsche Gesetzliche Unfallversicherung e.V.	01.09.14-31.03.18	Dynamisches Verhalten von semi-volatilen Mehrkomponenten-Gefahrstoff-Aerosolen bei der Probenahme am Arbeitsplatz (SEVOMEGA, Messfehler Aerosole II)	696.269 € (HMGU)
Helmholtz Gemeinschaft, Health and Environment Funding	01.07.13-31.08.16	E&H-Projekt „Nanoparticles and health“	151.925 € (HMGU)
Impuls- und Vernetzungsfonds der Helmholtz-Gemeinschaft (IVF) – VH-VI-418	01.01.12-30.06.17	Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE)	1.000.000 € (HMGU) 500.000 € (UR)
Bayerische Forschungsstiftung/ Netzsch-Gerätebau GmbH	01.10.11-31.03.15	Mehrdimensionale Analyse thermischer Prozesse	658.600 € (HMGU)
Bayerisches Landesamt für Umwelt (LfU)	01.08.12-30.06.15	Stickstoffeinträge als Mitverursacher von Diversitätsänderungen im alpinen Raum (N-Alp)	184.720 € (HMGU)
Bundesministerium für Bildung und Forschung (BMBF)	01.05.17-30.04.21	MTSD – Neuartige Monitoring Technologien für eine nachhaltige Entwicklung	66.634 € (HMGU)
Bundesministerium für Bildung und Forschung (BMBF)	01.04.17-31.03.20	Verbundprojekt SmartAQnet	226.143 € (HMGU)
Life Science-Stiftung	01.07.17-30.06.18	Übertragung des HICE-Konzepts auf krankheitsspezifische Modelle	221.648 € (HMGU)
Sasol Technology (Pty) Ltd.	01.09.11-31.10.16	Comprehensive analysis in Fischer-Tropsch related systems	233.240 € (UR)
Deutsche Forschungsgemeinschaft (DFG)	01.01.13-31.08.16	ATOF-PIMS Verbesserung der on-line Charakterisierung von Aerosolpartikeln durch laserbasierte Ionisierungstechniken in einem Flugzeitmassenspektrometer	117.300 € (UR)

Funding Institution	Grant period	Title	Total HMGU / UR €
Deutsche Forschungsgemeinschaft (DFG)	01.04.13-31.03.16	Primary aerosol emissions from wood combustion and shipping engines and their potentials for formation of secondary aerosols	323.250 € (UR)
Deutsche Forschungsgemeinschaft (DFG)	01.11.14-31.10.17	Chemische Zusammensetzung und Herkunft von atmosphärischem Brown Carbon Aerosol	184.600 € (UR)
Bundesamt für Bevölkerungsschutz und Katastrophenhilfe (BBK)	01.01.15-31.12.17	Szenarien, Evaluation und Messtechnik bei Freisetzung chemischer und explosionsgefährlicher Stoffe – SEMFres	142.750 € (UR)
Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF) / Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V. (DGMK)	01.04.15-30.09.17	Einfluss des Verdunstungsverhaltens auf die Verkokungsneigung von flüssigen Brennstoffen auf benetzten Oberflächen	206.900 € (UR)
Deutsche Forschungsgemeinschaft (DFG)	01.11.15-31.10.16	Deutsch-Russischer Workshop und Forschungsinitiative über schädliche Umwelt- und Gesundheitseinflüsse von Aerosol Emissionen von Wald- und Torf- und Kohleflözbränden	8.600 € (UR)
Bundesministerium für Bildung und Forschung (BMBF)	01.12.15-01.03.18	C3-Consortium: Health Entwicklung und Anwendung von analytischen Methoden zur chemischen Charakterisierung von Partikeln und zur biochemischen Untersuchung von Zellkulturen	599.973,60 € (UR)
Deutsche Forschungsgemeinschaft (DFG)	01.05.16-30.04.19	Entwicklung und Optimierung eines Membraneinlasses – Photoionisierungsmassen-spektrometers für die Echtzeitanalytik (poly)aromatischer und halogenierter Kohlenwasserstoff	203.072 € (UR)
Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AIF)	01.03.17-31.08.19	Entwicklung eines alltagstauglichen und mobilen Messgerätes zur Echtzeit-Untersuchung von einzelnen Nanopartikeln (Feinstäuben) hinsichtlich ihrer detaillierten chemischen Zusammensetzung und ihrer Partikelgröße	106.470 € (UR)
Sabic Global Technologies BV	01.06.17-31.05.19	Quantification of Diels-Alder fouling vs. Radical fouling using TGA/DSC/PI-MS	60.000 € (UR)
Bundesministerium für Bildung und Forschung (BMBF)	01.07.17-31.08.19	Prozessanalyse und – steuerung der industriellen Röstung von Lebens- und Genussmitteln mittels Photoionisationsmassen-spektrometrie am Beispiel von Kaffee (PPK), TP Bestimmung der chemischen Indikatoren und Nachweisparameter zur Charakterisierung des Röstprozesses	209.405,94 € (UR)
Deutsche Forschungsgemeinschaft (DFG)	01.10.17-30.09.20	Kopplung von schneller Gaschromatographie an Photoionisierungsmassen-spektrometrie	313.500 € (UR)
EU	01.01.18-31.12.21	European Network of Fourier-Transform Ion-Cyclotron-Resonance MassSpectrometry Centers	410.284,75 € (UR)

List of Funded Scholarships of the JMSC (April 2015 – December 2017)

Name of beneficiary	Funding institution	Title
Xiansheng Liu	Nanjing Normal University, China; Chinese Scholarship Council (CSC)	Spatial variability of ambient particulate matter – composition, source contributions and influencing factors
Xin Cao	Beijing Forestry University, China; Chinese Scholarship Council (CSC)	Development and application of LC-MS methods for the investigation of the metabolom of different cell lines
Hendryk Czech	Landesgraduiertenförderung des Europäischen Sozialfonds (ESF)	Charakterisierung von Aerosolen aus Holzverbrennung und Schiffsmotoren sowie deren Alterungsprodukte mit thermo/optischer Kohlenstoffanalyse gekoppelt mit Flugzeitmassenspektrometrie unter Verwendung von verschiedenen Photoionisierungstechniken
Yuting Huang	Chinese Scholarship Council (CSC)	Investigation of secondary organic aerosol formation from combustion aerosols
Fengxia Li	Peking University, China; Chinese Scholarship Council (CSC)	Long term sampling of environmental nanoparticles in Augsburg and special-temporal variation characterization based on chemical composition measurements
Dac-Loc Nguyen	Deutscher Akademischer Austauschdienst (DAAD)	Characterization of wildfire aerosols
Ahmed Reda	Al-Nahrain University Baghdad, Iraq; Deutscher Akademischer Austauschdienst (DAAD)	Development and application of methods for sampling and characterization of volatile oxygen containing compounds in emission aerosols
Christopher P. Rüger	Landesgraduiertenförderung des Europäischen Sozialfonds (ESF)	Entwicklung und Anwendung von laserdesorptionsbasierten Verfahren zur schnellen molekularen Charakterisierung komplexer petrochemischer Produkte, gesundheitsgefährdender Stoffe und anderer relevanter Proben mit hochauflösender Massenspektrometrie
Aimée Sutherland	Stellenbosch University, South Africa; Sasol Limited, South Africa	Untersuchung von Fischer-Tropsch und anderen petrochemischen Produkten mit chromatographisch-massenspektrometrischen Methoden
Janos Varga	Budapest University of Technology and Economics, Hungary; Bayerische Forschungsstiftung	Anwendung mehrdimensionaler thermischer und chemischer Analyse zur Charakterisierung von Materialien und chemischen Prozessen
Xiao Wu	Shandong University, China; Chinese Scholarship Council (CSC)	Development and application of HPLC and LC-MS methods for the determination of markers of oxidative stress in biological samples

International Conferences and Workshops

2017

Seminar at Louisiana State University (LSU), Baton Rouge, LS, USA, December 14th 2017 (Funded invited seminar lecture)
- Zimmermann et al., *Anthropogenic aerosols: Analysis as well as biological and health effects.*

AGU Fall Meeting 2017, New Orleans, LS, USA, December 11th-15th 2017
- Zimmermann et al., Evaluation of the health impact of aerosols emitted from different combustion sources: Comprehensive characterization of the aerosol physicochemical properties as well as the molecular biological and toxicological effects of the aerosols on human lung cells and macrophages.

LECO – Seperation Science user meeting (workshop), Berlin, 2nd December 2017
- Käfer, et al., The Usage of Direct Inlet Probe in combination with High Resolution Mass Spectrometry for the Characterization of Heavy Petroleum Products.

PEFTEC (Petroleum,Refining,Environmental Monitoring Technologies Conference), Antwerp, Belgium, November 29th-30th 2017
- Zimmermann et al., Profiling of Petrochemical Samples by Thermal Analysis with mass spectrometric detection: Evolved gas analysis using photoionsation-mass spectrometry, high resolution mass spectrometry and ultra-fast gas chromatography-MS. (Fully funded invited lecture)
- Gröger et al., The application of GC and GC×GC in combination with state-of-the-art and novel detection systems for the analysis of petroleum matrices.
- Gröger et al., VUV Applications in Petroleum Analysis: The application of ASTM D8071 for Oxyblends and non-specified matrices.

LECO European SepSci Workshop „Environmental Analysis by TOF-MS“, Berlin, November 2017
- Orasche et al., IDTD (GCx)GC-ToFMS for wood smoke analysis – Analysis of VOCs and SVOCs with in-situ-derivatization thermal desorption gas chromatography and time-of-flight mass spectrometry.

DGMK – Deutsche Gesellschaft für Mineralöl und Kraftstoffe – Jahrestagung der Anlytiker, Hamburg, 24th November, 2017
- Käfer et al., Untersuchungen von Bitumen: Vergleich zu Anwendungstechnischen Analysen.

GDCh-Fresenius Lecture at the Univerität Tübingen, November 23rd 2017 (Fully funded invited GDCh-Fresenius lecture)
- Zimmermann et al., Analytik und Gesundheitsgefahren atmosphärischer Feinstäube.

Deutsche Umwelthilfe (DUH) Fachkonferenz: “Gesundheitswirkungen von Luftschadstoffen”, Berlin, Germany November 22nd 2017 (Invited seminat lecture, fully funded)
- Zimmermann et al., Gesundheitseffekte von Feinstäuben und Gasen: Biologische Wirkung von Abgasen aus Verbrennungsprozessen auf Lungenzellen und Tiere.

International Science conference, Baku, Azerbaijan, November 15th 2017 (Invited plenary lecture, fully funded)
- Zimmermann et al., Air pollution and health: New methods for characterisation of composition and biological effects of antropogenic emissions.

ASIAN EMISSIONS TECHNOLOGY CONFERENCE (EGCSA) Singapore, November 6th-7th 2017 (Invited plenary lecture, fully funded)
- Zimmermann et al., Health effects of Shipping emissions: Will IMO’s revision of Regulation 14 in MARPOL Annex VI really improve human health?

Advances in Gas Chromatography VI, ChromSoc, Runcorn, UK, October 18th 2017
- Gröger et al., Vacuum ultraviolet absorption spectroscopy as a selective and sensitive detection system for one- and comprehensive two-dimensional gas chromatography

GDCh-Fresenius Lecture at the Univerität Münster, October 25st 2017 (Fully funded invited GDCh-Fresenius lecture)
- Zimmermann et al., Air pollution and health: Chemical composition of atmospheric and combustion aerosols and biological effects of combustion onto lung cells and animals.

36th Annual AAAR Conference (American Association of Aerosol Researchers), Raleigh, NC, USA, October 17th–20th 2017

- Zimmermann et al., Investigation of Combustion Aerosol Toxicity within the HICE-Project: Chemical Composition of Different Combustion-Emissions and Their Molecular Biological Effects on Air/Liquid-Interface Exposed Lung Cells (in-Vitro) as well as on Aerosle Exposed Mice (in-Vivo).

36th Annual AAAR Conference (American Association of Aerosol Researchers), Raleigh, NC, USA, October 17th–20th 2017

- J. Passig, J. Schade, M. Sklorz, M. Fuchs, M. Oster, R. Zimmermann, A New Single Particle Aerosol Mass Spectrometer: Multiple-Analyses of the Same Individual Airborne Aerosol Particle for Determination of Particle Size, Polycyclic Aromatic Hydrocarbon-Content and the Elemental Composition.

VII Russian National Mass Spectroemrty Conference, Moscow, Russia October 9th – 13th 2017 (Invited plenary lecture, fully funded)

- Zimmermann et al., Innovative mass spectrometric concepts for analysis of evolved gases form combustion and pyrolysis processes as well as petrochemical samples.

Seminar at Waters Inc., Manchester, UK, September 29th 2017 (Fully funded invited seminar lecture)

- Zimmermann et al., MR-HRTOF technological concepts and applications.

LECO – Seperation Science user meeting (workshop), Berlin, September 27th 2017

- Käfer et al., Pegasus HRT – Mehr als ein Detektor für Gaschromatographie.
- Orasche et al., IDTD (GCx)GC-ToFMS for wood smoke analyses.

Workshop of the EU Life consortium at EAC 2017, Zürich, Switzerland, August 27th–September 1st 2017

- Zimmermann et al., Air-liquid interface lung cell exposure and comprehensive aerosol characterisation for investigation of biological effects of combustion emission aerosols.

European Aerosol Conference (EAC 2017), Zürich, Switzerland, August 27th–September 1st 2017

- Zimmermann et al., Molecular biological effects and toxicity of combustion aerosol emissions on air/liquid-interface exposed human and murine lung cells.
- J. Passig, J. Schade, M. Sklorz, M. Fuchs, M. Oster, R. Zimmermann, A new on-line single particle laser mass spectrometer for detection of both, polyaromatic hydrocarbons and inorganic constituents from the same individual particles.
- Czech et al., A chemometric approach to predict the contribution of ships to air pollution.
- Xiao Wu et al., Detection of air pollution-related biomarkers of exposure and oxidative stress in urine from\u000Btravellers between Germany and China.

UNAM, Mexico-City, Mexico, August 18th 2017 (Invited plenary lecture, fully funded)

- R.Zimmermann et al., New methods to analyse aerosols and fine dust for chemical composition as well as biological and health effects, Lecture within “Panorama Actual de las Ciencias Atmósféricas”.

NATAS Annual Meeting, Newark, DW, USA, August 8th – 10th 2017

- Ralf Zimmermannet al., Fast Thermoanalytical Profiling of Petrochemical Samples by Evolved Gas Analysis using Photoionsation-MS and Ultra-Fast Gas Chromatography.
- C. Rüger, A. Neumann, T. Schwemer, S, Dörk, M. Sklorz, R. Zimmermann, Thermal Analysis coupled to ultra-high resolution FTICR mass spectrometry: Comprehensive molecular profiling in Evolved Gas Analysis.

NASA Goddard Space Flight Center, Greenbelt, MD, USA; August 8th 2017 (Invited seminar lecture)

- Zimmermann et al., Application of photo ionization mass spectrometry (PIMS) for characterisation of organic compounds.

10th Asian Aerosol Conference (AAC), Jeju Island, South Korea, July 2nd-6th 2017

- Zimmermann et al., Human Lung Cells Exposed to Various Combustion Aerosols at the Air-Liquid Interface: Cytotoxic and Molecular Biological Effects.
- J. Passig, J. Schade, M. Sklorz, M. Fuchs, M. Oster, R. Zimmermann, Multiple On-Line Analyses of Individual Airborne Aerosol Particles by Laser Mass Spectrometry: Detection of Polyaromatic Organics from the Particle-Surface and Inorganic Constituents from the Particle-Core.

9th International Symposium on Modern Principles of Air Monitoring and Biomonitoring – AIRMON, June 2017

• Kohlmeier et al., NovaCarb™-Denuders as a Vapour-Particle Partitioning Tool for the Occupational Sampling of Aerosols from Semi-Volatile Organic Compounds.

15th Int. Congress on Combustion By-products and their Health Effects, Seoul, South Korea, June 27th-30th 2017

- J. Passig, J. Schade, M. Sklorz, M. Fuchs, M. Oster, R. Zimmermann, Multiple on-line analyses of the same individual airborne aerosol particles by laser mass spectrometry: Sequential detection of polycyclic aromatic hydrocarbons from the particle-surface as well as inorganic constituents from the particle-core.
- Zimmermann et al., Biological and chemical characterization of ship diesel engine, car engine and wood combustion aerosol emissions: Multi-omics characterization of air-liquid interface aerosol-exposed lung cells and comprehensive chemical profiling of the emissions, (Invited plenary lecture).

21st ETH-Conference on Combustion Generated Nanoparticles, Zürich, Switzerland, June 19th to 22nd 2017 (Invited plenary lecture, fully funded)

- Zimmermann et al., Biological effects of emissions from ship diesel- and gasoline car-engines as well as from wood combustion compliances: Multi-omics characterization of aerosol-exposed lung cells and chemical profiles of the emissions.

GDCh-Fresenius Lecture at the Univerität Essen/Duisburg, June 21st 2017 (Fully funded invited GDCh-Fresenius lecture)

- Zimmermann et al., Combustion, crude oil, coffee roasting and aerosols: Analysis of complex materials and thermal processes by photo ionsation mass spectrometry (PIMS).

65th Annual Meeting of the American Society for Mass Spectrometry (ASMS), Indianapolis, IN, USA, June 4th-8th 2017

- Gröger, U. Käfer, M. Jennerwein, M. Eschner, T. Wilharm, J. Wendt, M. Sarji and R. Zimmermann, High-temperature GC×GC with EI and SPI for nominal and high-resolution TOFMS for the characterization of heavy petroleum matrice.
- J. Passig, J. Schade, M. Sklorz, M. Fuchs, M. Oster, R. Zimmermann, A new on-line single-particle laser mass spectrometer for detection of PAHs and inorganic, constituents from the same individual particles.
- E. Riches, R. Zimmermann, Photoionization (APPI/PI): Applications,Developments and Discussions Organisation of Photoionisation MS, workshop.

GDCh-Fresenius Lecture at the Univerität Paderborn, May 29th 2017 (Fully funded invited GDCh-Fresenius lecture)

Zimmermann et al., Air pollution and health: Chemical composition of atmospheric aerosols and effects onto human lung cells.

Analytical Seminar, Merck, Darmstadt, May 22nd 2017

- Gröger et al., VUV Spectroscopy

Impala Inc., Rustenburg, South Africa, Gauteng; May 18th 2017

- P. Forbes, R. Zimmermann, Novel Monitoring Technologies for Sustainable Development (MTSD) Project: Background in Aerosol Research, Air Quality Monitoring and Aerosol Related Health Effect Research.

SASRI Inc., Durban, South Africa, Kwa-Zulu Natal May 15th 2017

- P. Forbes, R. Zimmermann, Novel Monitoring Technologies for Sustainable Development (MTSD) Project: Background in Aerosol Research, Air Quality Monitoring and Aerosol Related Health Effect Research.

42rd International Symposium on Capillary Chromatography & the 16th GCxGC Syposium, Fort Worth, Tx, USA, May 14th – 19th 2017

- Gröger et al., The application of high temperature GC×GC with nominal and high-resolution TOFMS for the investigation of light crude oil and high boilers.
- Gröger et al., More Selectivity for Complex Samples: Comprehensive Two-dimensional Gas Chromatography – VUV ABSORBANCE Spectroscopy.

SASOL Inc., Sasolburg, South Africa, Free State; May 12th 2017

- Zimmermann et al., New analytical concepts to characterize complex petrochemical samples.

6th Int. Symposium on Ultrafine Particles – Air Quality and Climate, Brussels, Belgium, May 20th-21st (Invited plenary lecture, fully funded)

- Zimmermann et al., Investigation of the toxicity of combustion aerosols within the HICE-project: Chemical composition of ship-, car- and wood combustion-emissions and their molecular biological effects on air/liquid-interface exposed lung cells.

ANAKON 2017, Tübingen, Germany, 3rd – 6th April 2017

- Zimmermann et al., Comprehensive characterization of chemical composition and biological effects of emissions from ship diesel-engines as well as from wood combustion compliances: Multi-omics characterization of aerosol-exposed lung cells and chemical profile of the emissions.
- Rüger et al., Characterisation of heavy crude oils and asphaltene fractions via thermal analysis coupled to ultra-high resolution mass spectrometry equipped with atmospheric pressure ionization.

DGMS – Deutsche Gesellschaft für Massenspektrometrie – 50. Jahrestagung, Kiel, 8th March 2017
- Käfer et al., The Usage of Direct Inlet Probe in combination with High Resolution Mass Spectrometry for the Characterization of Heavy Petroleum Products.
- Czech et al., Direct resonance-enhanced multi-photon ionisation (REMPI) of complex liquid samples under vacuum conditions.
- Rüger et al., Evolved gas analysis ultra-high resolution mass spectrometry – Insights into heavy petroleum fractions and combustion aerosol.

Pittcon 2017, Chicago, IL, USA, March 5th-9th 2017
- Zimmermann et al., Thermal Analysis Coupled to On-Line Ultrafast-Cycling Gas Chromatography-Photo Ionization Mass Spectrometry to Study the Flavor Formation During the Roasting Process of Coffee Beans and Nuts.
- Zimmermann et al., Comprehensive 2D-Gas Chromatography-TOFMS and Direct-Insertion Probe-Multi-Reflection – High Resolution Time-of-Flight Mass Spectrometry for Characterization of Heavy Petrochemical Fractions.

Jinan-University, Guangzhou, China, Februrar 16th, 2017 (Invited Lecture, funded)
- Zimmermann et al., Chemical and biological characterization of aerosols and applications of photo ionization mass spectrometry.

ANAKON 2017, Zurich, Switzerland
- Streibel et al., Charakterisierung gasförmiger und partikulärer Emissionen eines Benzinmotors bei Betrieb mit Superbenzin und Ethanol.

Hexin Inc., Guangzhou, China, Februrar 15th 2017
- Zimmermann et al., Doing it twice in single particle aerosol mass spectrometry: Probing the same individual particle by both, LDI for metals/soot and LD/REMPI for polycyclic aromatic hydrocarbons.

Seminar Lecture at the Institut für Troposphärenforschung, Leipzig, Germany, Februrar 3rd, 2017 (invited lecture)
- Zimmermann et al., Aerosole und Gesundheit am Joint Mass Spectrometry Centre des Helmholtz Zentrum München und der Universität Rostock.

GDCh-Fresenius Lecture at the Univerität Siegen, January 31st 2017 (Fully funded invited GDCh-Fresenius lecture)
- Zimmermann et al., Air pollution and health: Chemical composition of atmospheric aerosols and effects onto human lung cells.

GDCh-Fresenius Lecture at the Univerity of Gießen, Germany, January 24th 2017 (Fully funded invited GDCh-Fresenius lecture)
- Zimmermann et al., Anthropogenic aerosols and dusts: Chemical composition, physical properties and biological effects.

GDCh-Fresenius Lecture at the ETH-Zürich, Zürich, January 12th 2017 (Fully funded invited GDCh-Fresenius lecture)
- Zimmermann et al., Anthropogenic aerosols and dusts: Chemical composition, physical properties and biological effects.

2016

Aerosol Workshop/Seminar at the Desert Research Institute (DRI), Reno, NV/ USA, December 15th 2016
- Zimmermann et al., Thermal/optical carbon analysis combined with photoionization time-of-flight mass spectrometry (TOCA-PI-TOFMS): A powerful tool to identify the molecular composition behind organic carbon.

ZTRI-Zhengzhou Tobacco Research Institute, Zhengzhou, China, November 18th 2016
- Zimmermann et al., On-line quantification, compound mapping and fast puff-resolved GC-MS by photoionisation-mass spectrometry: Previous studies, current state and next steps.

26th ASIC-Conference on Coffee Scienc, Kunming, China, November 14th-17th 2016
- Zimmermann et al., Thermal Analysis coupled to fast cycling on-line Gas Chromatography-Mass Spectrometry: A new laboratory tool for easy simulation of coffee roasting & studying the flavour formation processes on a single bean basis.

Seminar at Jinan University, Guangzhou, China, November 11th 2016 (Invited Lecture)
- Zimmermann, et al., Biological effects of human and murine lung cells exposed to combustion aerosols at the air/liquid-interface: Investigation of ship engine and wood combustion-emissions.

Seminar at Hong Kong Polytechnical University, Hong Kong, China, November 10th 2016 (Invited Lecture)
- Zimmermann et al., Biological effects of human and murine lung cells exposed to combustion aerosols at the air/liquid-interface using a mobile exposure station: Investigation of wood combustion- as well as ship- and car engine-emissions.

35th Annual AAAR Conference (American Association of Aerosol Researchers), Portland, OR, USA, October 18th-21st 2016
- Zimmermann et al., On-line and hyphenated Photoionization Mass Spectrometric Techniques for Gas and Particulate Phase Analysis: Investigation of Wood Combustion-, Ship- and Car Engine-Emissions.
- Zimmermann et al., Biological effects of human and murine lung cells exposed to combustion aerosols at the air/liquid-interface: Investigation of wood combustion-, ship- and car engine-emissions.

Seminar at University of Pretoria, South Africa, Gauteng, September 15th 2016 (Invited Lecture)
- Zimmermann et al., Comprehensive characterization of petrochemical fractions: High temperature GCxGC with TOF&HR-TOF detection and thermal analysis-soft ionisation mass spectrometry.

ChromSAAMS 2016, Vanderbijlpark, Gauteng, South Africa, September 11th-14th 2016 (Invited Lecture, fully funded
- Zimmermann et al., Aerosol and Health: Chemical composition and biological effects of wood combustion-, ship- and car engine-emissions.
- Zimmermann et al., Fast profiling of (petrochemical and) food samples by Thermal Analysis-Photoionization Mass spectrometry (TA-PIMS): Enhanced selectivity due to photo ionisation and ultrafast fast gas chromatography.

EAC 2016, Tours, France, 4th-9th September 2016
- Zimmermann et al., Studying the biological effects of combustion aerosols on air/liquid-interface exposed human and murine lung cells within the HICE-project: Composition and molecular biological effects of emissions from wood combustion, ship emissions and car engines.

21st International Mass Spectromerty Conference (IMSC), Toronto, Canda, August 20th-26th 2016
- Zimmermann, et al., New mass spectrometric tools to study the flavor formation during the roasting process of coffee beans and nuts.
- Zimmermann et al., Characterization of heavy petrochemical fractions: High temperature GCxGC with TOF & HR-TOFMS detection and thermal analysis-photo ionization TOFMS (TA-PIMS).

16th Intenational Conference on Thermal Analysis and Calorimetry (ICTAC) 2016, Orlando, FL, USA, August 14th–18th 2016
- Zimmermann et al., Thermal Analysis coupled to fast cycling on-line Gas Chromatography-Photo Ionization Mass Spectrometry to study the flavor formation during the roasting process of coffee beans, cacao beans and nuts.
- Zimmermann et al., Fast profiling of petrochemical samples and simulation of processes by Thermal Analysis-Photoionization Mass Spectrometry (TA-PIMS).

GDCh-Fresenius Lecture, TU-Kaiserslautern, Germany 7th July 2016 (Fully funded invited Fresenius lecture)
- Zimmermann et al., Kaffeeröstung, Nüsse, Tabakrauch und Erdöl: Neue analytische Methoden zum Verständnis komplexer Prozesse und Stoffsysteme.

Petrophase 2016, Marienlyst, DK June 19th-23rd 2016
- Zimmermann et al., Fast profiling of petrochemical samples by Thermal Analysis (TA) coupled to Photoionization Mass spectrometry (TA-PIMS) or high resolution Mass Spectrometry (TA-FTICRMS).

Dust 2016, 2nd Int. Conf. on Atmospheric Dust, Castellaneta Marina, Italy 12th-17th June 2016 (Invited Lecture)
- Zimmermann et al., Composition and biological effects of ship diesel engine aerosol emissions: Joint analysis of aerosol properties and the molecular biological effects on human lung cells.

64th Annual Meeting of the American Society for Mass Spectrometry (ASMS), San Antonio, TX, USA, June 5th-9th 2016
- J. Syage, R. Zimmermann: New Developments in Photoionization (APPI/PI) Organisation of Photoionisation MS workshop.
- Zimmermann et al., Multidimensional comprehensive gas chromatography with high resolution-TOFMS/photo ionization-TOF-MS: Combining ultra-high chromatographic resolution, accurate mass-information and soft photoionisation for petrochemical samples.
- Zimmermann et al., Multiple novel techniques for petrochemical analyses...require multiple data analysis approaches, Workshop MS in Petrochemistry (Invited Lecture).

40th ISCC – Int. Symposium of Capillary Chromatography, Riva del Garda, Italy, May 30th-June 3rd 2016 (Invited Lecture, fully funded)
- Zimmermann et al., Photoionisation-TOF mass spectromertry as detector for Thermogravimetry coupled to fast optically heated gas chromatography: Investigation of flavour formation in roasting of foodstuffs and anaylsis of petrochemical fractions.

PM2016 – VII Convegno Nazionale sul Particolato Atmosferico, Roma, Italy 17th-20th May 2016 (Invited Lecture, fully funded)
- Zimmermann et al., Why are aerosols so toxic: Lung cell-based approaches for identifying the adverse agents in emissions aerosols.

Semainar at Institute of chemicalkinetics and combustion SB RAS, Novosibirsk, Russia, March 17th 2016
- Zimmermann et al., The HICE Project: Composition and biological effects of ship diesel engine, wood combustion and car engine emission aerosols.

Russian-German DFG workshop, Tomsk, Russia, March 14th-16th 2016 (DFG-funded)
- Zimmermann et al., Wildfires and Health – Composition and health-effects of fresh and atmospherically aged particles emitted by forest and peat fires as well as durning coal seams.

Pittcon 2016, Atlanta, GA, USA, March 6th-19th 2016
- Zimmermann et al., Multidimensional comprehensive gas chromatography multi-reflection high resolution time-of-flight mass spectrometry: Combining accurate mass information with ultra-high chromatographic resolution.
- Zimmermann et al., Fast profiling of petrochemical samples by Thermal Analysis-soft ionization Mass Spectrometry: From source rock via crude oil to petrochemical products.

XX SASP, Davos Switzerland, 7th – 12th February 2016 (Invited Lecture)
- Zimmermann et al., New analytical and statistical tools to study the flavor formation during the roasting process of coffee beans, cacao beans and nuts.

HTC-2016, Ghent, Belgium 27th – 29th January 2016 (Invited Lecture, fully funded)
- Zimmermann et al., Novel gas chromatography based concepts for revealing the chemical signature of complex petrochemical mixtures.

14th International Symposium on Hyphenated Techniques in Chromatography and Separation Technology Ghent, Belgium:
- Gröger et al., Vacuum Ultraviolet Spectroscopy as a Complementary Detection System to Mass Spectrometry for One- and Comprehensive Two-Dimensional Gas Chromatography.

6th TRC – JCCP / Idemitsu International Symposium, Abu Dhabi, UAE:
- Gröger et al., The application of comprehensive two-dimensional gas chromatography for the qualitative and quantitative Analysis of modern and complex petrochemical matrices.

Analytica Conference 2016, Munich, Germany:
- Gröger et al., The application of multidimensional chromatographic techniques with different detection systems for a detailed qualitative and quantitative analysis of medium and high boiling petrochemical matrices from fuel processing.
- Streibel et al., Characterization of crude oils and asphaltenes by pyrolysis GC/MS and thermal analysis coupled to photo ionization mass spectrometry.

40th International Symposium on Capillary Chromatography, 13th GCxGC Symposium, Riva del Garda, Italy:
- Gröger et al., Quantification based on Vacuum Ultraviolet Absorption Spectroscopy (VUV): The Application of Comprehensive Two-Dimensional Gas Chromatography – VUV towards Middle Distillates.

The 17th International Conference on Petroleum Phase Behavior and Fouling, Elsinore, Denmark:
- Gröger et al., The investigation of intermediates and higher boiling point cuts/ residuals with multi-dimensional chromatographic techniques: The advantage of state-of-the art detection systems.

LCxGC User Meeting (Axel Semrau), Berlin, Germany:
- Gröger et al., Enabling technologies for the chemical analysis of petroleum, petroleum products and related matrices.

DGMK Jahrestreffen der Analytiker, Hamburg, Germany:
- Gröger et al., The application of vacuum ultraviolet radiation for absorption spectroscopy and mass spectrometry – new tools for the petrochemical analysis.
- Rüger et al., Heavy petroleum characterization via thermal analysis ultra-high resolution mass spectrometry.

10. Rostocker Bioenergieforum, 2016, Rostock, Germany:
- Ulbrich et al., Online Gasphasenanlyse der Verbrennungsemissionen eines EURO-5-Motors für zwei Kraftstoffe mit unterschiedlichem biogenem Anteil mithilfe von Photoionisierungs-Flugzeit Massenspektrometrie.

49. Jahrestagung der DGMS, 2016, Hamburg, Germany:
- Ulbrich et al., Volatile organic emissions from a spark ignition engine during NEDC and High Speed analysed by on-line Photoionisation-Time-Of-Flight-Mass-Spectrometry (PI-TOFMS).

12th European FT-MS Workshop and school. 2016, Matera, Italy:
- Rüger et al., Advanced automatized processing of gas chromatographic high resolution data for petroleum derived samples.

Jahrestreffen der Analytiker der Deutschen Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V. (DGMK), 2016, Hamburg, Germany:
- Rüger et al., Charakterisierung von schweren Petroleumfraktionen mittels thermischer Analyse ultra-hochauflösender Massenspektrometrie.

2nd International Conference on Innovations in Mass Spectrometry: Instrumentation and Methods (INNMS), 2016, Moscow, Russia:
- Rüger et al., Characterisation of heavy petroleum and combustion aerosol via thermal analysis atmospheric pressure ionisation ultra-high resolution mass spectrometry.

The International Congress on Electronic Nicotine Delivery Systems and Smoking Cessation, 2016, La Rochelle, France:
- Heide et al., On-line analysis of e-cigarette and heat-not-burn (HnB) tobacco product vapours using soft ionisation mass spectrometry.

Jahrestagung der Deutschen Gesellschaft für Massenspektrometrie (DGMS), 2016, Hamburg, Germany:
- Czech et al., Photoionisation Time-of-Flight Mass Spectrometry (PI-TOFMS) at Different Wavelengths of Coffee Roasting Off-Gas to Trace Roasting Phases.

European Aerosol Conference (EAC), 2016, Tours, France:
- Czech et al., Primary Volatile Emissions and Secondary Organic Aerosol Formation Potential from a 25 kW Pellet Boiler
- Schnelle-Kreis et al., Seasonal and spatial variation of organic composition and source contributions of ambient particulate matter in the ultrafine and accumulation mode size range.

35th Annual Conference of the American Association of Aerosol Research (AAAR), 2016, Portland, Oregon, United States:
- Czech et al., On-line and hyphenated Photoionization Mass Spectrometric Techniques for Gas and Particulate Phase Analysis: Investigation of Wood Combustion-, Ship- and Car Engine-Emissions.

Pyrolysis 2016, Nancy, France
- Streibel et al.: Characterization of crude oils and asphaltenes by pyrolysis GC/MS and thermal analysis coupled to photo ionization mass spectrometry.

2015

Pacifichem, Honolulu, HI, USA, December 14th-18th 2015
- •Zimmermann et al., Two-dimensional comprehensive gas chromatography multi-reflection high resolution time-of-flight mass spectrometry: A unique tool to merge accurate mass information with high chromatographic resolution.
- Zimmermann et al., Combustion, crude oil, coffee roasting and industrial processes: Analysis of complex materials and thermal processes by Photo-Ionisation Mass Spectrometry (PIMS), (Invited Lecture).
- Zimmermann et al., Detection of gaseous compounds by needle trap sampling (TTD) and direct thermal-desorption photoionization mass spectrometry: Concept and demonstrative application to breath gas analysis and ship exhaust (Invited Lecture).

XXII Workshop „Siberian Aerosols", Tomsk, Russia, November 26th 2015 (Invited Lecture, funded)
- Zimmermann et al., Environmental aerosols: Source apportionment and health effects and Study on composition of particles emitted from combustion of Pine wood and debris under flaming and smoldering conditions in the LAC.

A.V.Topchiev Institute of Petrochemical Synthesis, Moscow, Russia 25th November 2015 (Invited Lecture, funded)
- Zimmermann et al., New techniques for comprehensive analysis of complex petrochemical matrices: Multidimensional gas chromatography, high resolution mass spectrometry and soft photo ionization mass spectrometry.

PEFTEC 2015, Antwerp, Belgium, November 19th 2015 (Invited Lecture, fully funded)
- Zimmermann et al., Comprehensive analysis of the chemical signature of complex petrochemical mixtures: Thermal analysis coupled to soft photo ionization MS or gas chromatography or high resolution-MS.

BASF AG, Reserch Seminar, Competence Center Analytics, Ludwigshafen, 6th November 2015 (Invited Lecture, fully funded)
- Zimmermann et al., On-line real-time process monitoring as well as analysis of materials and products by Photo-Ionisation Mass Spectrometry (PIMS).

Complex matrix analysis discussion meeting, Topsoe Inc., Copenhagen, DK, October 29th 2015 (Invited Lecture)
- Zimmermann et al., Photo ionization mass spectrometry: Application for characterization of petrochemical fractions and process analysis.

CORESTA meeting (SSPT) 2015, Jeju Isalnd, South Korea, October 4th-8th 2015
- Zimmermann et al., On-line puff resolved analysis of e-cigarette vapours and heat-not-burn tobacco products.

HEXIN Inc., Guangzhou, China, October 2nd 2015 (Invited Lecture, funded)
- Zimmermann et al., Two-Step Single Particle Mass Spectrometry for On-line Monitoring of Particle-Bound Polycyclic Aromatic Hydrocarbons.

TSCR Conference, Naples, Florida/USA, September 20th- 23rd 2015
- Zimmermann et al., On-line real-time analysis of e-cigarette vapors and heat-not-burn tobacco products by photo-ionization mass spectrometry.

European Aerosole Conference, EAC 2015, Milan, Italy,September 6th-11th 2015
- Zimmermann et al., Biological effects of combustion aerosols on human lung cells exposed at the air liquid interface: Comparison of the molecular biological effects of log wood and pellet combustion aerosols with the effects of ship engine emissions.

GOLDSCHMIDT Conference 2015, Prague, Czech Republic, August 16th-21st 2015
- Zimmermann et al., Molecular composition and biological effects of aerosols from ship diesel engines and wood combustion.

NATAS 2015, Montreal, Canada, August 10th-14th 2015
- Zimmermann et al., On-line characterization of the organic chemical signature of thermal processes in Evolved Gas Analysis: Thermogravimetry hyphenated to Photo-Ionization Mass Spectrometry or fast Gas Chromatography-Photo-Ionization Mass Spectrometry.

Aerosols and Health, Russian-German Worksshop, IAO, Tomsk, Russia, 29th-31st July 2015
- Zimmermann and the HICE consortium, Research initative on wildfire aerosolemisions and dangereous imacts on environment and health – Introduction on the HICE concept.

Skolkovo Oil Center at Moscow State University, Moscow, Russia, July 27th 2015 (Invited Lecture, funded)
- Zimmermann et al., New approaches for analysis of petrochemical matrices.

Seminar lectire, SABIC Inc., Geelen, NL, July 24th 2015 (Invited Lecture)
- Zimmermann et al., New techniques for analysis of petrochemical matrices.

HICE Summer School: Data Structure & Data Integration Cardiff, UK July 2nd-4th, 2015
- Zimmermann and the HICE consortium: Combustion-derived aerosols and their health effects: Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) –the ship emission study.

HICE Summer School: Data Structure & Data Integration, Cardiff, UK July 2nd-4th, 2015
- Zimmermann, Introdutionary remarks and overview on the HICE-project

16th Petrophase, Playa del Carmen, Yucatan, Mexico, June 7 th-11th 2015
- Gröger et al., State-of-the-art technologies for chemical characterization of medium and high boiling downstream matrices.

63rd Annual Meeting of the American Society for Mass Spectrometry (ASMS), St. Louis, MO, USA, May 31st-June 4th, 2015
- R.Zimmermann, J.Syage, Workshop "Photoionisation Mass Spectrometry", Introductionary presentation and workshop co-chair.
- Zimmermann et al., GCxGC-TOFMS and GCxGC-high resolution TOFMS for analysis of petrochemical matrices LECO-Seminar.

39th International Symposium on Capillary Chromatography, Fort Worth, TX, USA, May 17th – 21st 2015 (Invited Keynote Lecture, fully funded)
- Zimmermann et al., GCxGC-multi-reflection high resolution time-of-flight mass spectrometry: Integration of isomeric-composition information and HRMS-mass defect data for petrochemical matrices.

Selber Kopplungstage 2015, Selb , Germany April 16th 2015 (Invited Plenary Lecture, fully funded)
- Zimmermann et al., Thermal Analysis and Soft Ionization Mass Spectrometry: A Perfect Marriage.

Anakon 2015, Graz, Austria, March 23th – 26th 2015
- Zimmermann et al., Biological effect-study of aerosols from ship diesel engine: Joint analysis ofaerosol properties and the molecular-biological effects on human lung cells.
- Streibel et al., Pyrolyse-GC/MS mit zwei Ionisationsmethoden zur Chraketrisierung von Rohöl.
- Rüger et al., Hyphenation of evolved gas analysis (EGA) to ultra-high resolution mass spectrometry using atmospheric pressure chemical ionisation (APCI) for studying lignocellulosic biomass pyrolysis, PIC

International Workshop of Helmholtz Zentrum München and US-EPA: "Comprehensive Evaluation of Acute and Chronic Environmental Factors and Their Interaction with Genetic, Epigenetic and Social Factors in Germany and the U.S.", München and Chiemsee, Germany, March 17th-19th 2015
- Zimmermann, Aerosol analysis within the HICE framework.

NOSA Annual meeting 2015, Kuopio, Finland, March 12th – 13th 2015
- Zimmermann et al., Composition and biological effects of aerosols from ship diesel engine and wood combustion compliances: Joint analysis of aerosol properties and the molecular biological effects on human lung cells.

48. Tagung der Deutschen Gesellschaft für Massenspektrometrie, Wuppertal, 1-4. März 2015
- Zimmermann et al., Dynamic two-dimensional mapping of combustion product concentrations in solid fuel combustion: Looking into a burning cigarette during puffing.

Pittcon 2015, New Orleans, LS, USA; March 9th-12th 2015
- Zimmermann et al., Highly time-resolved two-dimensional mass spectrometric imaging of molecular combustion and pyrolysis product concentrations in a burning cigarette.

CNR-HMGU Meeting, Rome, Italy, February 23rd – 24th 2015
- Zimmermann et al., Anthropogenic aerosol emissions: Characterisation and health effects.

TU-Dresden, 21.01.2015 (proposal granted)
- Zimmermann, Porpoael defence BMBF 2020: C3-Carbon concret composite V1.3 – Health aspects: Carbonfaser-Material Stäube: Untersuchung der Zusammensetzung und biologischen Wirkung auf humane Lungenzellen sowie arbeitsmedizinische Aspekte.

Sino-German Symposium, Essen:
- Lintelmann et al., Determination of hydroxyl-PAH in biological and aerosol samples: LC-MS or HPLC-FLD?

European Academy of Allergy and Clinical Immunlogy Congress 2015, Barcelona, Spain:
- Öder et al., Immunological effects of particles and gasses from ship diesel emissions in human bronchial epithelial cells

Asian Aerosol Conference 2015, Kanazawa, Japan:
- Öder et al., Composition and biological effects of aerosols from ship diesel engine and wood combustion compliances: Joint analysis of aerosol properties and the molecular biological effects on human lung cells

26. Doktorandenseminar des AK Separation Science, Hohenroda, Germany:
- Gruber, B. et al.: Vacuum ultra violet spectroscopy as a complementary detection system to mass spectrometry for one- and comprehensive two-dimensional gas chromatography.

48. Jahrestagung der Deutschen Gesellschaft für Massenspektrometrie (DGMS), Wuppertal, Germany:
- Gröger et al., Chromatographic resolved mass defect plots: A new analytical tool for the interpretation of high-resolution MS data

LECO User Meeting, Aachen, Germany:
- Gröger et al., LECO PEG4D and LECO ChromaTOF: Very versatile tools for the analysis of complex samples in the field of petrochemical, metabolomic and forensic applications

Catalysis – Novel Aspects in Petrochemistry and Refining, Berlin, Germany:
- Gröger et al., State of the Art Technologies for a Comprehensive Chemical Characterization of Syncrude and Downstream Matrices

Gulf Coast Conference, Houston, USA
- Gröger et al., Novel and State-of-the art Detection Systems for Two-dimensional Gas Chromatography and their Application to Petrochemical Matrices.

- Gröger et al., Next Generation Hyphenations for Simultaneous Thermal Analysis (STA) in combination with Soft Ionization Time of Flight Mass Spectrometry and its Application to Complex Petrochemical Matrices

Jahrestagung der Deutschen Gesellschaft für Massenspektrometrie (DGMS), 2015, Wuppertal, Germany:
- Rüger et al., Analysis of polar trace components in middle distillate fuel by ultra-high resolution mass spectrometry using ESI and GC-APCI

ANAKON Conference, 2015, Graz, Austria:
- Rüger et al., Novel hyphenation of evolved gas analysis (EGA) to ultra-high resolution mass spectrometry using atmospheric pressure chemical ionisation (APCI) for studying ligno-cellulosic biomass pyrolysis
- Gröger et al., Vacuum Ultraviolet Spectroscopy as Complementary Detection Method for Comprehensive Two-Dimensional Gas Chromatography Time-of-Flight Mass Spectrometry

PIC – Products of Incomplete Combustion – Conference, 2015, Umea, Sweden:
- Rüger et al., Hyphenation of evolved gas analysis (EGA) to ultra-high resolution mass spectrometry using atmospheric pressure chemical ionisation (APCI) for studying lignocellulosic biomass pyrolysis

Jahrestagung der Fachgruppe FT-MS der Deutschen Gesellschaft für Massenspektrometrie (DGMS), 2015, Bonn, Germany:
- Rüger et al., Improved processing of gas chromatography atmospheric pressure chemical ionisation ultra-high resolution mass spectrometric data for complex mixtures

Jahrestagung der Deutschen Gesellschaft für Massenspektrometrie (DGMS), 2015, Wuppertal, Germany:
- Czech et al., On-line Analysis of Organic Emissions from Residential Wood Combustion with Single-Photon Ionization Time-of-Flight Mass Spectrometry (SPI-TOFMS)

14th International Congress on Combustion By-Products and Their Health Effects (PIC), 2015, Umeå, Sweden:
- Czech et al., On-line Analysis of Organic Emissions from Residential Wood Combustion with Single-Photon Ionization Time-of-Flight Mass Spectrometry (SPI-TOFMS)

European Aerosol Conference (EAC), 2015, Milano, Italy:
- Czech et al., Carbonaceous particulate emissions from small-scale wood-burning appliances

Gefahrstoffe am Arbeitzplatz, Heidelberg, Germany:
- Dragan, G.-C.: SVOC Aerosole: Verhalten von mittelflüchtigen Stoffen.

43rd Annual Conference of NATAS, Montreal, Canada:
- Varga, J. et al.: Investigation of sulfur and selenium vapors with thermal analysis – single photon ionization mass spectrometry.

Pittsburgh Conference on Analytical, Chemistry and Applied Spectroscopy PITTCON 2015, New Orleans, LA USA:
- Wohlfahrt, S. et al., Evolved gas analysis for petrochemical products using a newly developed TG–Fast-GC–SPI/EI–HRTOFMS system.

HPLC 2015, Ghent, Belgium:
- GhentWu et al., Determination of potentially air pollution related biomarkers of oxidative stress in urine of travelers between Germany and China using LC and LC-MS methods.

Colloquium Spectroscopicum International 2015, Figueira da Foz, Portugal
- Streibel et al., Characterization of crude oil by pyrolysis-GC/MS applying two ionization methods in parallel.

→ All contributions to conferences and workshops can be found here: www.helmholtz-muenchen.de/cma

Publications

2017

1. Alosmanov, R.* et al.: Effect of functional groups on the thermal degradation of phosphorus- and phosphorus/nitrogen-containing functional polymers. J. Therm. Anal. Calorim. 130, 799–812 (2017)
2. Czech, H.* et al.: A chemometric investigation of aromatic emission profiles from a marine engine in comparison with residential wood combustion and road traffic: Implications for source apportionment inside and outside sulphur emission control areas. Atmos. Environ. 167, 212-222 (2017)
3. Czech, H. et al.: Time-resolved analysis of primary volatile emissions and secondary aerosol formation potential from a small-scale pellet boiler. Atm. Environ., 158:236–45 (2017)
4. Czech, H.*, Schnelle-Kreis, J., Streibel, T.* & Zimmermann, R.: New directions: Beyond sulphur, vanadium and nickel – About source apportionment of ship emissions in emission control areas. Atmos. Environ. 163, 190-191 (2017)
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Seminars

Seminar of the Joint Mass Spectrometry Centre and the Helmholtz Virtual Institute HICE

The seminar takes place at the Institute of Chemistry, Albert Einstein Str. 3a, 18059 Rostock, once a week. These lectures are transmitted to the Helmholtz Zentrum München as well as to the partners of the Helmholtz Virtual Institute HICE via video conferencing.

Winter term 2017 / 2018

#	Date / Time	Speaker	Title
1	24.10.17	**Dr. Heinz Renner** Linseis GmbH Selb, Germany	Thermogravimetry under extreme conditions-measurements at high pressures and high temperatures
2	14.11.17	**Prof. Dr. Mikhail Yavor** Institute for analytical instrumentation of the Russian Academy of Sciences St. Petersburg, Russia	Multi-pass time-of-flight mass analyzers: advances in iončoptical design
3	21.11.17	**Dr. Jonathan Symonds** Cambustion Ltd., Cambridge, GB	Novel methods of aerosol particle classification by size and mass
4	05.12.17	**Prof. Dr. Joakim Pagels** Lund University Lund, Sweden	Black Carbon Research at Lund University – From Formation and Oxidation in the Cylinder to Atmospheric Aging and Health Effects

Summer term 2017

#	Date/ Time	Speaker	Title
1	05.04.17	**Dr. HJ Jost** Kärsa Ltd., Helsinki, Finland	Demonstration of touchčless molecular explosives detection on checked passenger luggage at Helsinki-Vantaa Airport
2	11.04.17	**Prof. Dr. Dietmar Breuer** Inst. für Arbeitsschutz der DGUV, Sankt Augustin, Germany	Chemical hazards at workplaces – two examples Passive smoke at workplace – a retrospective assessment Measurement of chemical hazards which are not clearly identifiable
3	25.04.17	**Dr. Torben Gentz** Alfred-Wegener-Institut Bremerhaven, Germany	Distribution and fate of methane released from submarine sources – Challenges and results of measurements by using an improved in situ mass spectrometer
4	02.05.17	**Dr. Lei Li** Hexin Instrument Co. Ltd., Guangzhou, China	tba
5	08.05.17	**Dr. Jan-Christoph Wolf** Plasmion GmbH, München, Germany	SICRIT Mass Spectrometry: A Powerful and Versatile Ionization Source
6	23.05.17	**Dr. Klaus-Peter Hinz** Justus-Liebig-Universität Giessen, Giessen, Germany	Single particle analysis byončline laser mass spectrometry with mobile LAMPAS instrumentation

Summer term 2017			
#	**Date/ Time**	**Speaker**	**Title**
7	30.05.17	**Prof. Dr. Astrid Kiendler** Scharr Forschungszentrum Jülich, Jülich, Germany	Atmospheric aerosol: how to understand sources and chemical aging from composition measurements based on mass spectrometry
8	12.06.17	**Prof. Dr. Xiangdong Li** Hong Kong Polytechnic University, Hong Kong, China	Airborne particulate matter pollution in urban China: a chemical mixture perspective from sources to impacts
9	20.06.17	**Prof. Dr. Jan Andersson** University of Münster, Münster, Germany	Supercomplex mixtures cannot be analyzed – or?
10	26.06.17	**Dr. Xiang Shawn Li** University of Maryland, Baltimore County, MD, USA	tba

Winter term 2016 / 2017			
#	**Date/ Time**	**Speaker**	**Title**
1	11.10.16	**Prof. Dr. John Dimandja** Georgia Institute of Technology, Atlanta/ GA, USA	GCxGC/MS: From Emerging Technology to Standardized Method Development Tools
2	25.10.16	**Dr. Arnd Ingendoh** Bruker Daltonics GmbH, Bremen, Germany	Next Generation FTMS: Pushing novel applications by mass spectrometry innovations
3	01.11.16	**Dr. Thomas Moehring** Thermo Fisher Scientific GmbH, Bremen, Germany	Orbitrap Technology for Enhanced Mass Spec Performance
4	07.11.16	**Dr. Brian Goolsby** Hitachi, Dallas/ TX, USA	Improving thermal analysis measurements through imaging and highčsensitivity instrumentation
5	22.11.16	**Ph.D. Eleanor Riches** Waters Corporation, Wilmslow, UK	Addressing Chemical Diversity with Complementary Ionisation Techniques Coupled to Ion Mobility-Mass Spectrometry
6	29.11.16	**Dr. Bill Morrow** Resonance Ltd., Barrie/ON, Canada	VUV Light Sources for Photočionization and a UV Gas Camera for Plume Studies
7	06.12.16	**Prof. Dr. Jef Focant** University Liège, Belgium	GCxGCč(HR) TOFMS: Why we love it!
8	10.01.17	**Dr.Yury Tsybin** Spectroswiss, Lausanne, Switzerland	Asking more from FTMS
9	17.01.17	**Prof. Elke Richling** TU Kaiserslautern	Coffee consumption – studies investigating biological effects and bioavailability of major coffee constituents
10	23.01.17	**Dr. Thomas Denner** Netzsch GmbH, Selb, Germany	Advanced Methods for Chemists in Thermal Analysis

Summer term 2016			
#	**Date/ Time**	**Speaker**	**Title**
1	19.04.16	**Prof. Dr. M. Przybylski** Universität Konstanz	Analysis of biomolecular interactions using ESI-and MALDI-mass spectrometry
2	26.04.16	**Dr. Dimitris Papanastasiou** Fasmatech Inc., Greece	New tools and methods for ion trapping, activation and transport in mass spectrometry
3	02.05.16	**Dr. Yves Gamache** Analytical Flow Products Inc., Quebec, Canada	The Optical emission and physical Chemistry of a dielectric barrier discharge as the basis for a gas chromatographic detector system
4	03.05.16	**Prof. Dr. Stefan Zimmermann** Leibniz University Hannover,	Hochenergie-Ionenmobilitätsspektrometrie (HiKE-IMS) zur schnellen Spurengasdetektion in Luft
	11/12.05.16 Munich	One day session on Crude Oil and Fuel Analysis at “Analytica Munich” conference with invited speakers and workshop at Helmholtz Zentrum München	
5	24.05.16	**Prof. Dr. Gerd- Uwe Flechsig** University of Albany, NY, USA	Mass spectrometric studies of electrochemical systems
6	06.06.16	**Prof. Totaro Imasaka** Kyushu University, JPN	Femtosecond laser ionization in mass spectrometry and its application to trace analysis of allergy substances in fragrances
7	14. 06.16	**Prof. Dr. Klaus Müller-Dethlefs** University of Manchester, UK	Non-covalent interactions, a challenge to experiment and theory: Determination of dissociation energies of molecular clusters by ZEKE/MATI Spectroscopy
8	05.07.16	**PD Dr. Thomas F. Mentel** Forschungszentrum Jülich	Highly oxidized multifunctional molecules: A New Class of Intermediates in Gas-Phase Chemistry and Particle Formation
9	12.07.16	**Prof. Dr. Gesine Witt** University of Applied Sciences (HAW) Hamburg	Festphasenmikroextraktion von organischen Schadstoffen in marinen Systemen

Winter term 2015/2016			
#	**Date/ Time**	**Speaker**	**Title**
1	20.10.15	**Prof. Dr. Frank Dorman** Pen State College, USA	Using Multidimensional Gas Chromatography Coupled to Time of Flight Mass Spectrometry for Investigation of Environmental Impact from Shale Gas Operations
2	27.10.15	**Dr. Slava Artaev** LECO Inc, St. Joseph, USA	Gas Chromatography-High resolution TOFMS (HRT): Past, Present and Future
3	03.11.15	**Dr. Simon Andersen** Schlumberger, Denmark/Canada	Petroleum heavy end analysis – how far should we go?
4	10.11.15	**PD Dr. Thomas Kuhlbusch** IUTA, Duisburg	Differentiating BC/EC/OC: Measurement methods, source apportionment and correlations to other particle metrics
5	17.11.15	**Prof. Dr. Luke Hanley** University of Chicago, USA	Mass Spectrometry Imaging using Femtosecond Lasers and Postionization

Winter term 2015/2016			
#	**Date/Time**	**Speaker**	**Title**
6	01.12.15	**Prof. Dr. Klaus Dreisewerd** Universität Münster	MALDI-2: Sensitive MS Imaging through Laser-induced Generation of Secondary MALDI-like Ionization Processes
7	08.12.15	GDCh Fresenius Lecture: **Prof. Dr. Jürgen Einax** Friedrich-Schiller-Universität Jena	Chemometrik – Werkzeug für die Analytik
8	05.01.16	**Prof. Dr. Tina Kasper** Universität Duisburg-Essen	Combustion Chemistry: Mass spectrometry in reacting systems
9	12.01.16	**Prof. Dr. Thorsten Schmidt** Uni Duisburg Essen	What stable isotopes can tell us about the world: From prehistoric times to current doping scandals
10	19.01.16	**Dr. Pierre Giusti** TOTAL, Harfleur, France	Recent advances in molecular characterization of complex industrial matrices such as oils and polymers

Summer term 2015			
#	**Date/Time**	**Speaker**	**Title**
1	21.04.2015	**Dr. Pieter Joos** Water-link, Antwerp, Belgium	The use of screening techniques in a drinking water company
2	28.04.2015	**Dr. Horner** Five Technologies GmbH, München	Select-eV – Novel GC-MS electron gun for variable ionisation energies between 10 und 70 eV
3	30.04.2015 at Helmholtz Zentrum München	**1. Dr. Mikko Happo, PhD.** **2. Dr. Pasi Jalava, PhD.** University of Eastern Finland, Kuopio, Finland	1. Multidisciplinary aerosol research unit ILMARI – results from pilot studies 2. Results from combustion aerosol toxicity studies at UEF
4	05.05.2015	**Prof. Dr. M. Lalk** Institut für Biochemie, Universität Greifswald	Microbial Metabolomics – Insights into physiological process through bioanalytics
5	12.05.2015	**Prof. Dr. O. Popovicheva** Moscow State University, Moscow, Russia,	Micromarkers of combustion aerosols
6	26.05.2015	**Prof. Dr. W. Rogge** University of California, Merced, USA	PAHs and other Organic Compounds in Smoke from the Combustion of Individual Wood Biopolymers
7	23.06.2015	**Dr. Dale Harrison** VUV Analytics, Austin, Texas, USA	GC-VUV – A Simple and Robust Approach to Automated Class Determination
8	30.06.2015	**Dr. Rainer Wolf** BASF AG, Ludwigshafen	Hyphenated mass spectrometry in industrial chemical analysis
9	09.07.2015	Institute of Chemistry/GDCh – Colloquium: **Prof. Dr. P. O'Connor** University of Warwick, UK United	Pushing the Limits with High Performance Mass Spectrometry

HICE

Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – Aerosol and Health

The Helmholtz Virtual Institute HICE: Short Description and Overview for 2012-2017

Adverse health effects caused by air pollution represent a serious worldwide public health problem. Based on current knowledge, particulate matter (PM), organic and inorganic or reactive organic compounds on the particles are suspected to be health relevant factors (WHO). Furthermore, gas phase components such as nitric oxides and ozone are relevant. Although the health effects of aerosols are well documented, little is known about the exact mechanisms of health effects induction and the bioactive chemical species or factors. The objective of the "Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health– Aerosol and Health" (HICE) which was funded by the Helmholtz association from 2012-2017 is the establishment of a long-term, multi-disciplinary scientific research initiative for the investigation of the causes and mechanisms of health effects and diseases caused by air pollution.

The multi-disciplinary consortium of the virtual institute HICE is based on the core cooperation (Joint Mass Spectrometry Centre) of the Helmholtz Zentrum München (HMGU) and the University of Rostock (UR), established in 2008. The consortium is augmented by the incorporation of further Helmholtz partners (Max Delbrück Centre, MDC and Karlsruhe Institute of Technology, KIT) and University partners (Technical University Munich) as well as by excellent foreign institutions (University of Luxemburg, ULUX, University of Eastern Finland, UEF and University of Cardiff, UCA). Small and medium enterprises (SME) such as the Vitrocell GmbH and Photonion GmbH (the latter being a spin-off of the JMSC) are represented in HICE as non-funded partners. Analytical-, environmental-, and technical-chemists, engineers, aerosol scientists, physicists, molecular biologists, medical scientists, biologists and toxicologists are working together in HICE.

The scientific concept of HICE is based on a consequent multidisciplinary analysis of combustion aerosols to better understand the reason for the strong observed health effects.

Thus, comprehensive research on the properties of different combustion aerosols (e.g. chemical composition and physical properties etc.) is performed and put into context to the molecular-biological responses of combustion aerosol exposed lung cells. Human lung cell cultures/tissue models are exposed to diluted combustion aerosols directly at the emission source, using a unique, mobile air-liquid interface (ALI) exposure unit (HICE-ALI exposure station, developed with KIT and Vitrocell GmbH in conjunction with HICE) and a mobile S2-biosafety laboratory (the HICE MobiLab, developed/build by HICE). The composition and physical properties of the aerosol as well as the response of the biological systems are investigated comprehensively by state-of-the art analytical and bio-analytical techniques. Novel state-of-the-art analytical systems, such as photoionisation mass spectro-

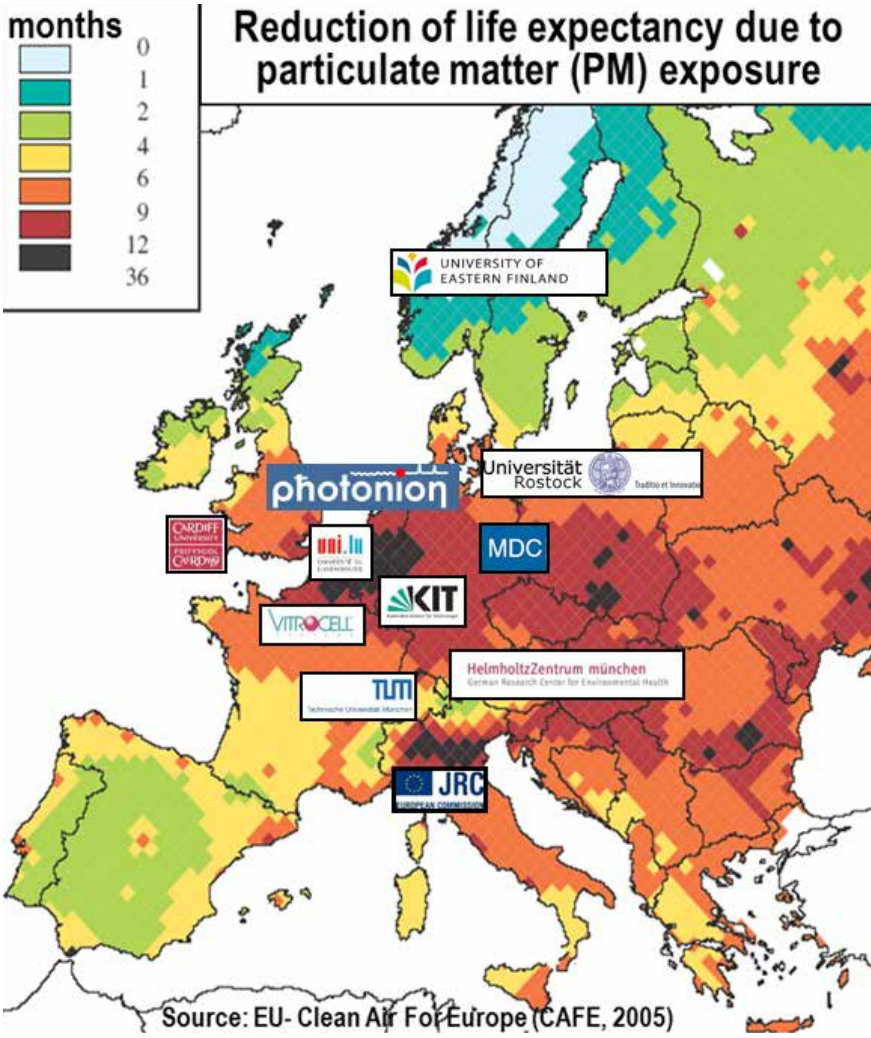

Fig. 1: Logos of then HICE-partners depicted on an air pollution health-risk map of Europe

meters for on-line analysis of gases and particulates were developed by Photonion and in conjunction with HICE. Biological responses and the toxicological effects are detected on different biological levels (transcriptome, proteome, metabolome, cytotoxicological parameters etc.). Subsequently, a joint analysis of biological, chemical and physical data occurs. The technological and scientific results obtained in HICE are very promising and are in part depicted in this progress report. Concerning emissions from diesel ship engines running either on heavy fuel oil (HFO) or diesel fuel (DF), it could be shown by a preliminary HICE-campaign that HFO-emissions contain more particle mass as well as higher concentrations of transition metals and organic chemicals, whereas elemental carbon-dominated particles (soot) prevailed in DF-emissions.

During the first regular consortium-wide HICE-measurement campaign with a ship engine test facility at University of Rostock the HICE-concept of simultaneous on-site ALI-lung cell exposure and comprehensive physical/chemical characterization of the emitted aerosols was applied. Cellular response for HFO-emission particles revealed strong biological effects. Notably, inflammation processes were triggered and oxidative stress was observed. Surprisingly, exposure to DF-emission particles led to similar strong biological responses. In particular, basic cellular metabolism was stronger influenced by DF-emission particles when compared to HFO-emission particles. Acute cytotoxicity is comparable for both particle types, although pollutant concentrations are much higher on HFO-particles. Hence, one can assume that utilization of both fuels leads to very health critical particulate emissions. The results suggest that switching from HFO to Diesel without incorporation of particle filter systems is not sufficient to reduce health issues arising from ship traffic.

A second consortium wide HICE measurement campaign addressed aerosols from wood combustion. Namely emissions of a log wood fired masonry heater and a semi-automatic pellet burner were studied. The effects caused by the emissions of the wood combustion compliances were also compared to diesel exhaust. In general, the biological effects of the wood combustion processes were less pronounced. Furthermore, the log would combustion emissions induced a similar strong overall response as the pellet burner emissions, albeit exhibiting much more toxic compounds such as aldehydes and polycyclic aromatic hydrocarbons. Mitigation of some of the acute biological impacts of wood combustion particles by preventing genotoxic effects is a hypothesis in this respect, motivating further experiments to proof or disproof this, especially the role of phenolic antioxidants.

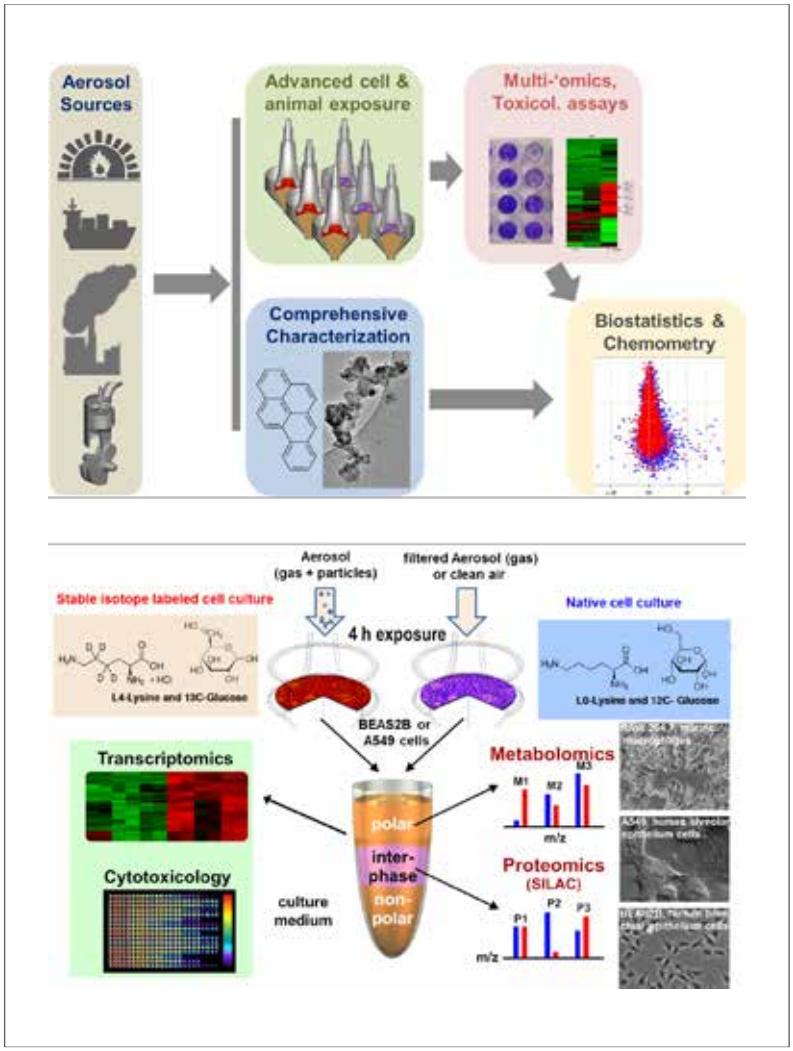

Fig 2: The concept of HICE: Aerosols from different combustion emission sources (grey box) are exposed to lung cells at the ail-liquid-interface (green box) and are comprehensively characterized with respect to their chemical composition and physical properties (blue box). After exposure, the cells are subjected to a comprehensive toxicological and molecular biological characterization (red box). The biological data and physical-chemical information are then jointly analyzed (yellow box) in order to learn more about hazardous components of the aerosol and biological effect/disease induction mechanisms.

Fig. 3: Technical innovation within HICE: A) HICE-ALI, a mobile air-liquid interface (ALI) exposure unit (exposure station, developed with KIT and Vitrocell GmbH in conjunction with HICE. B) HICE MobiLab, a mobile S2-biosafety laboratory (developed/build by HICE). C) Novel photoionisation mass spectrometers for on-line analysis of gases (developed by Photonion and HICE).

The third joint HICE-measurement campaign dealt with the emissions of a passenger car engine, fueled with either gasoline (E10) or ethanol (E85), while driving two cycles, an urban driving and a high-velocity driving cycle. The results indicate that the velocity does not strongly affect the toxicity of car emissions. However, emissions of conventional E10 caused adaptive cell responses, such as inflammatory signaling and modulation of energy metabolism. E85 lead to more severe cell responses, such as DNA damage, apoptosis and the expression of genes that are associated with type 2 diabetes. In general, the biological effects induced by gas phase compounds are relatively strong for the passenger car engine experiments.

The fourth consortium-wide HICE-measurement campaign comprised test experiments concerning aerosol aging and an animal model for validation purposes. In parallel to ALI-cell exposure, mice were exposed to emissions of a diesel engine. Macrophages from the mouse model (alveolar lavage) revealed substantial decrease of viability in lung tissue and severe DNA damage (mutagenity). Thereby, pathway analysis showed similarities to effects observed with murine macrophage cell cultures.

The scientific results obtained in HICE resulted in more than 40 peer-reviewed publications in scientific journals. A large number of further publication manuscripts are still under preparation. Furthermore, the scientific HICE activities resulted in 9 excellent finalized doctoral theses (PhD) as well as in 5 Master theses (MSc), highlighting the educational aspects of the program. This brings us to the additional important focus of HICE, namely the education and training of young scientists from bachelor to post-doc level. The educational measures in HICE include joint workshops, summer schools, joint scientific conferences, a video transmitted seminar series (20 lectures per year), laboratory exchange courses, post-doc- and PhD student- secondments, and – particularly important- the annual large HICE-consortium-wide experimental measurement campaigns (one 4-5 week joint HICE campaign per year, see above). The Ph.D. students have the opportunity to be associated with the graduate program of HMGU (HELENA). A number of young scientists that obtained scientific qualifications during HICE (Ph.D. or post-doc) resumed permanent positions afterwards.

Fig.4: Group photos of the four main HICE campaigns in 2012 (Rostock), 2014 (Kuopio), 2015 (Rostock) and 2016 (Kuopio)

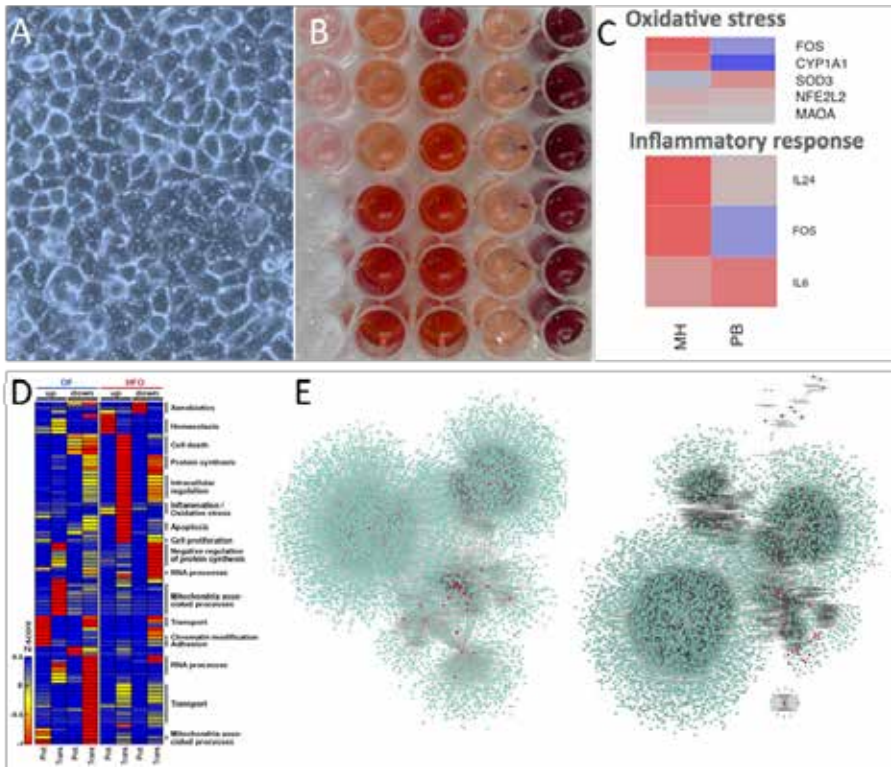

Fig. 5 Levels of biological information obtained in HICE: A) A549 cells (adenocarinogenic human alveolar basal epithelial cells) growing on the membrane in the ALI exposure unit; B) readout of the LDH-cytotoxicity assay for wood-combustion aerosol exposed A549 cells; C) gene expression of the A549 after wood combustion exposure (MH= log wood burner, PB=pellet burner). The different wood combustion sources induce the transcription of different genes, showing that the two aerosol sources have different biological effects on the ALI exposed lung cells. D) Illustrative integration of transcriptomic and proteomic data for human epithelial cells exposed with aerosols from a heavy fuel oil (HFO) & diesel fuel (DF) operated ship engine; E) biological response network for HFO (left) and DF (right) exhaust exposure of Beas2B cells. The networks are generated after merging individual chemical-gene/protein network for the chemicals present in high concentration in one exhaust compared to another one (Chemicals – red nodes, gene/proteins – green nodes).

HICE Highlights

Flexi-fuel Car engine emissions upon operation with gasoline and bio fuel (Ethanol): Physico-Chemical Properties and Biologic Effects in Human Lung Cells after Realistic In Vitro Exposure at the Air-Liquid Interface (ALI)

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The third consortium wide measurement campaign in the framework of HICE took place during April and May 2015 at the University of Rostock. The campaign was targeted at the emissions from a gasoline engine, which could be operated with gasoline as well as with ethanol. This enables the consortium to evaluate the influence of seminal biogenic fuels on the emission characteristics and the health related responses in comparison with commonly used fuels.

A 2.0 litre flexi-fuel engine with 132 kW and a maximum torque of 320 Nm was taken as the aerosol source for the experiments. The engine was operated with either gasoline containing 10 % ethanol (E10) or with a mixture of 85 % ethanol and 15 % gasoline (E85). In addition to the influence of the fuel, a second aim was set for the campaign. In the European Union, fuel consumption and emission factors of regulated pollutants such as CO and NO_x as well as the CO_2-emisisons are determined on dynanometers, utilizing a standardized driving cycle. This cycle is called the "New European Driving Cycle" (NEDC) and consists of two parts, a so-called "Urban Driving Cycle", during which stop-and-go traffic in cities is simulated, followed by an "Extra-urban Driving Cycle", which simulates driving on rural roads including a small section of highway, however not exceeding a speed of 120 km/h.

For the experiments carried out in the framework of the HICE campaign, the known and convenient acceleration, deceleration and velocity pattern from the NEDC cycle was taken as the basis for a cycle reflecting four-hour driving in urban environments. The cycle was continuously repeated with periods of idling in-between to avoid reiterative starting procedures. This driving pattern is referred as "municipal driving cycle" (MDC).

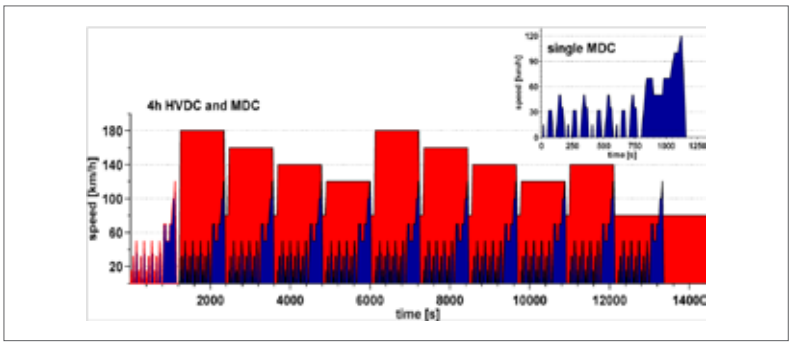

Fig.1 Schemes of the applied Driving Cycles. In red, the High Velocity Driving Cycle (HVDC) is depicted, showing the phases of constant velocities. In blue, the constantly repeated Municipal Driving Cycles (MDC) are shown. The inserted graph in the upper right depicts a single MDC

The usage of the NEDC has been criticized for being unrealistic and not reflecting real driving, leading to lower levels of pollutant concentration compared to real life driving. Therefore a second self-invented driving cycle was introduced for operating the engine during this campaign. The cycle was named "High Velocity Driving Cycle" (HSDC). It starts with one MDC cycle followed by equally long sections of driving with constant velocity. The velocity in these sections was varied between 80 and 180 km/h in a predetermined order. By doing this, a complete travel starting at home, and then driving through the city to the highway followed by a highway drive was simulated, lasting for four hours in total. The schemes of both cycles are depicted in Fig.1.

The sampling setup was kept similar to that of previous campaigns at the ship diesel engine and the wood combustion devices. The exhaust was diluted by a combination of a porous-tube dilutor and an ejector dilutor. Two different dilution ratios, 1:10 and 1:40, were adjusted for the experiments. The diluted aerosol was split into several streams and led to the different analytical systems as well as the cell exposure unit. An aerosol mass spectrometer (AMS), a scanning mobility particle sizer and an aethalometer were applied for real-time characterization of the particles. Sampling of particulate matter was carried out by quartz fibre filters and Teflon filters as well as an Electrical Low Pressure Impactor. Gas phase sampling of carbonyls was also realized. Regulated emissions such as carbon monoxide, hydrocarbons, nitric oxides as well as the particle numbers were monitored by a commerci-

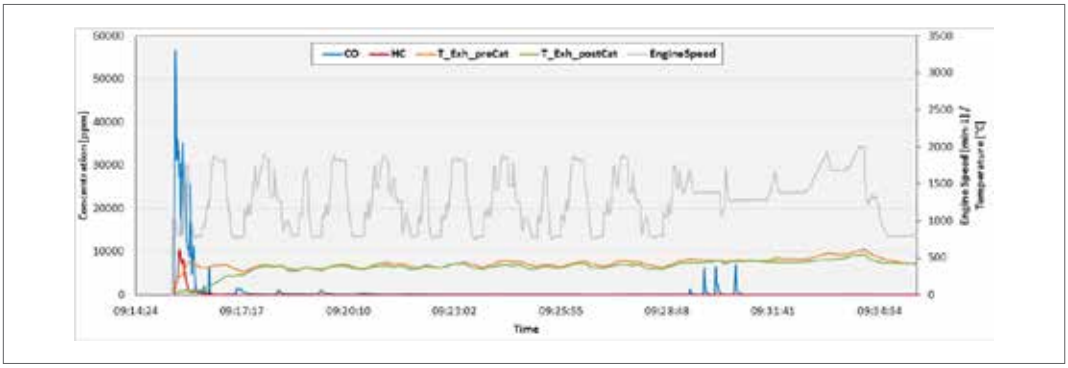

Fig.2 CO and HC exhaust concentrations during a cold start MDC cycle. Temperatures before and after the catalyst as well as the engine speed are also depicted

al measurement system. Additional chemical analysis in real-time was carried out directly in the raw gas by means of Photo-ionization mass spectrometry (PIMS).

For the cell exposure two different cell lines were used during this campaign. On the one hand, A-549, human lung cell cultures were exposed with the car exhaust. Furthermore murine macrophages (RAW 264.7) were inserted. All experiments were duplicated to cover every experimental condition with both cell cultures. With both dilution ratios, E10 fuel as well as E85 fuel was investigated with both driving cycles, yielding a total of sixteen experiments. Exposure time was set to four hours in every case. Since the NEDC lasts only 24 minutes, this afforded a continuous repetition of the cycle to bring the total running time to the appropriate four hours.

One general characteristical property of the car engine emissions is depicted in Fig.2 for the E10 fuel, which displays the temporal trend of CO and HC emissions during a MDC cycle when started with a cold engine. The vast majority of the pollutants are emitted immediately after the start of the engine. After a very short time span of maximal 90 seconds, the emitted concentrations are decreasing drastically, often reaching the limits of detection afterwards. Only when short accelerations happen in the course of the driving cycle, a small temporal increase is observed in CO exhaust concentration, which vanishes rapidly. This behaviour is independent on the fuel and stays roughly the same for all analyzed species.

Results

Particulate matter sampled on quartz fibre filters was investigated by a thermal/optical carbon analyzer to determine the total integral contents of organic carbon (OC) and elemental carbon (EC). The results for both fuels, each operated with both driving cycles are depicted in Table 1 along with the total PM2.5 particle concentration. The exhaust gas was diluted by a factor of 1:10. With the E85 fuel, concentrations are lower in general. This is especially pronounced for elemental carbon, indicating a reduction is soot particles for ethanol fuelled engine operation. The differences in organic carbon are not excessive. Comparing the two driving cycles, a tendency to higher concentrations for the HVDC can be observed, but it is not as distinctive as one may have expected. Here the influence of the cold start shows its effect.

1:10

µg/m³	PM2.5	OC	EC
E10 HVDC	293,2	30,3	268,7
E10 MDC	260,8	23,6	182,0
E85 HVDC	150,3	15,9	10,5
E85 MDC	45,6	14,0	8,2

Table 1 PM2.5, OC and EC concentrations for emitted particulate matter

Emissions of aromatic species are very interesting with respect to health issues, since many aromatic species are considered as toxic, carcinogenic and mutagenic. The application of PIMS with Resonance enhanced multi-photon ionization (REMPI) for gas phase emissions allows a real-time monitoring of such emissions, since the REMPI technique is selective for aromatic compounds. Fig.3 shows two-dimensional contour plots of gaseous aromatic emissions in the engine exhaust for both cycles and both fuels. The aromatic pattern is dominated by monoaromatic compounds (benzene and its alkylated derivatives). In addition naphthalenes and three-ring PAH are observed. Generally the concentration of aromatic species is higher when E10 fuel is used. Especially at the highest speed of 160 and 180 km/h, respectively, a strong increase in concentration is happening independent of the fuel.

The emissions of the car engine were tested for their toxicity in lung cells after direct exposure at the air liquid interface (ALI). A simple lung epit-

helial cell line (A549) was used and compared to a 3D cell culture model of primary human bronchial epithelial cells. Cell responses were assessed by measuring the transcriptome of emission exposed cells compared to clean air exposed cells. Complete aerosols were applied to the cell cultures as well as particle-free gaseous emissions in dilutions 1:10 and 1:40.

The majority of cellular responses were caused by the gas phase of the aerosols. Particles in the complete aerosol did not have a high additional impact on cell responses, but were sufficient to change slightly but reproducibly the quality of the cell response (see exemplary distinct clusters of treatment in Fig.4).

As expected, did high aerosol concentrations in less diluted emissions lead to a higher number of specific cell responses (significantly enriched gene ontology (GO) terms, see Fig. 5). Compared to normal gasoline (E10) the usage of E85 caused a higher number of specific responses. The driving cycle did not change the number of responses significantly.

More informative than the numbers are the qualities of cellular responses. By enrichment analysis from over 1.5 fold regulated genes specific gene ontology terms for molecular functions and biological processes were identified. The summary of those in Table 2 shows that higher aerosol concentrations (1:10 dilution) lead to more severe effects like DNA damage and apoptosis. Interestingly, also low concentrations of E85 emissions are already sufficient to elicit severe cell damage. High speed driving emissions were recognized by the cells as mechanical stimulus and affected specifically responses to unfolded protein and lipid metabolism which are so far unknown effects of gasoline car emissions.

Comparing the results of A549 cells with those of the 3D primary cell cultures, commonly up-regulated genes were found that are independent from the used cell culture model and therefore most reliable. E10 emissions induced gene expression of ABCA7 and D2HGDH. The first being an ABC transporter involved in cellular uptake and export might lead to increased phagocytosis of aerosol particles. The second being an enzyme of the TCA cycle suggests changes in the cellular energy metabolism upon E10 exposure. E85 emissions induced expression of CAPN10, a glucose importer, STRA6, a retinol transmembrane transporter, RUBCN, a negative regulator of endocytosis and the heat shock protein HSPB2. All four genes are associated with an increased risk for type 2 diabetes. Additionally, a marker for ethanol toxicity (ADAL) and an important regulator of apoptosis (TRADD) were upregulated by the biofuel E85.

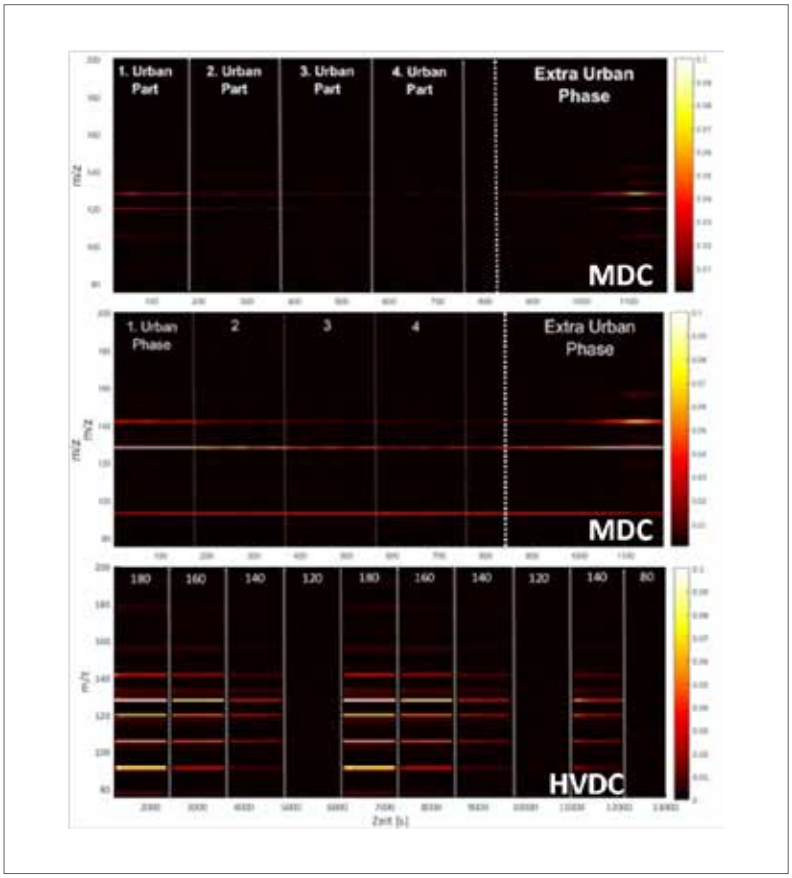

Fig.3 Contour plots depicting the concentration trends with time of aromatic species. The difference between E10 and E85 when driving the MDC cycle as well as the differences between MDC and HVDC cycle when fueld with E10 become obvious

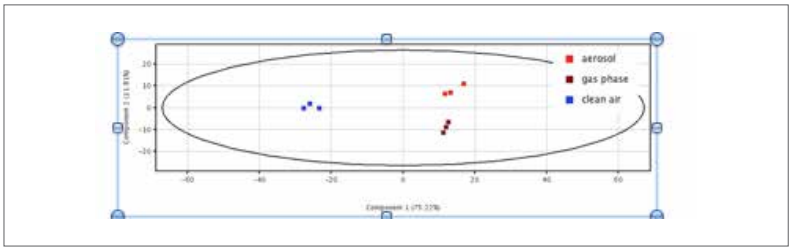

Fig.4 Schemes of the applied Driving Cycles. In red, the High Velocity Driving Cycle (HVDC) is depicted, showing the phases of constant velocities. In blue, the constantly repeated Municipal Driving Cycles (MDC) are shown. The inserted graph in the upper right depicts a single MDC

The results indicate that the speed cycle does not strongly affect the toxicity of car emissions, but the usage of fuel changes strongly the possible health impacts. While emissions of conventional E10 caused adaptive cell responses like inflammatory signaling and modulation of the energy metabolism, E85 lead to severe cell responses like DNA damage and apoptosis and the expression of genes that are associated with type 2 diabetes.

Fig.6 shows the biological results in comparison to the other emission sources investigated in HICE. Generally the effects of car engine aerosols is less pronounced compared to wood combustion or especially ship engine aerosols. Only the overall gene regulation (right column) shows values comparable to wood combustion,

Dilution	1:40			1:10		
Fuel type and driving cycle	E10 NEDC	E85 NEDC	E10 HSDC	E10 NEDC	E85 NEDC	E10 HSDC
Transcription	x	x	x	X	x	x
Intracellular signaling	x	x	x	X	x	x
Wounding	x	x	x	X		
Inflammatory response	x	x	x	X		
DNA damage		x		x	x	x
Apoptosis		x		x	x	x
Response to stress		x		x	x	x
Cell cycle		x		x	x	x
Cell migration				x	x	x
Response to oxygen levels	x			x	x	x
Hormone metabolism	x					
Response to unfolded protein			x			x
Response to mechanical stimulus			x			x
Lipid metabolism						x

Table 2 Cell responses to E10 emissions from NEDC and HSDC and E85 NEDC; Summary of significantly enriched specific cell responses (GO terms, p<0.05), most severe responses marked in grey.

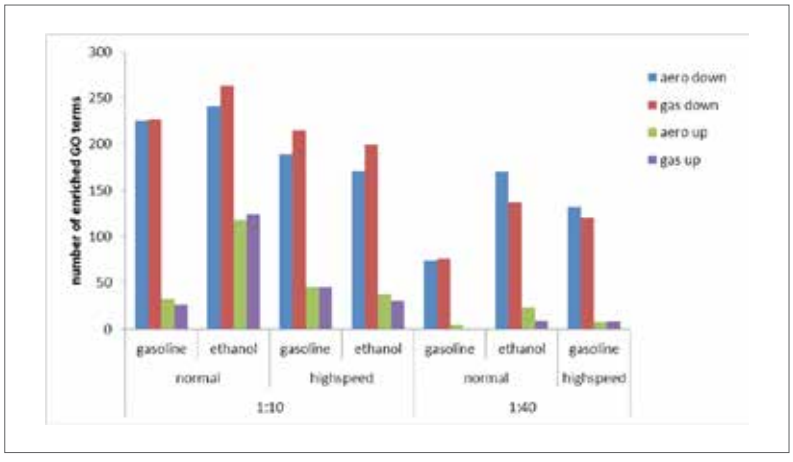

Fig.5: Numbers of specific cell responses (GO terms)

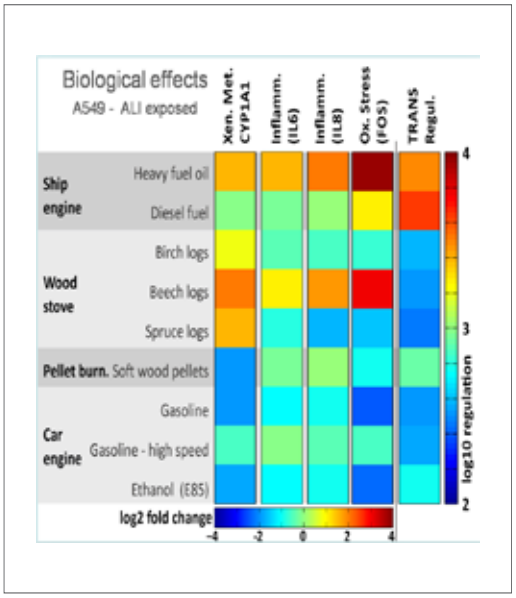

Fig.6 Biological effects of A549 cell cultures exposed with aerosols from various combustion sources. From left to right the columns depict regulation of xenometabolism, two types of inflammation, oxidative stress and overall transcript regulation

but stay much lower than in the case of ship engine emissions. Despite exhibiting lower concentrations of chemical species in the exhaust, E85 aerosol shows relatively equal responses when compared to gasoline. Driving with high speeds on the other hand seems to lead to an increase in gene regulation.

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Emissions of a ship engine operated with heavy fuel oil or distillate diesel fuel: Physico-Chemical Properties and Toxicogenomic Effects in Human Lung Cells and Macrophages after Realistic In Vitro Exposure at the Air-Liquid Interface (ALI)

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Pollution by airborne particulate matter (PM) from fossil fuel combustion is an important cause of morbidity and premature death, as it was proven by several epidemiological studies [1]. Chronic PM exposure can induce short-term effects like cardiovascular diseases or asthma and long-term health effects, e.g. cancer [2]. Epidemiological studies attribute up to 60,000 annual deaths from lung and cardiovascular disease [3] to ship engine PM. Current regulations target HFO use by limiting their sulphur content. To comply with the new sulphur limits, highly refined distillate fuels are necessary (diesel fuel, DF, or marine gas oil, MGO).

Within the Rostock 2012 campaign we operated a four-stroke, one-cylinder common rail research ship diesel engine (80 kW) using either HFO (HFO 180) containing 1.6% sulphur or DF containing less than 0.001% sulphur and 3.2% plant oil methyl ester in compliance with the 2014 IMO-SECA-legislation (DIN EN590), which represents the common dual-fuel use in commercial shipping. The engine was operated according to the test cycle ISO 8178-4 E2 for ship diesel engines with a balance between harbour-manoeuvring and cruising engine-loads (Fig. 2a). The combustion aerosol was cooled and diluted with sterile air. Chemical and physical properties of the HFO and DF aerosol were comprehensively characterised using state-of-the-art, on-line and real-time techniques as well as off-line filter

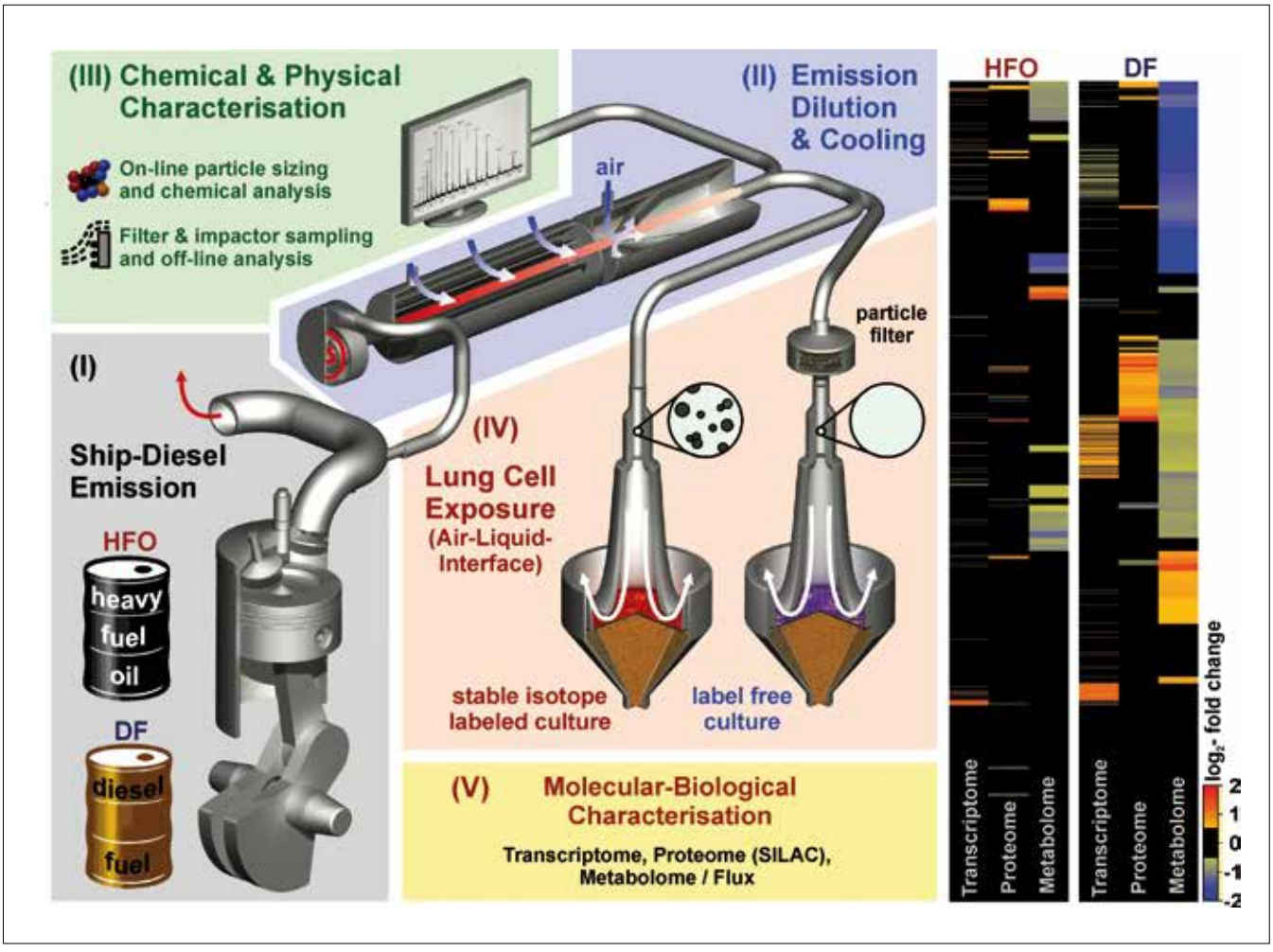

Fig. 1 Experimental set-up (a), omics overview (b)

sample analyses. Results are summarised in Fig 2. In parallel with aerosol characterisation, confluent layers of two human epithelial lung cell lines (the human lung alveolar cancer cell line A549 and human SV40-immortalised bronchial epithelial cells BEAS-2B) were exposed to the diluted engine exhaust for 4 h at the ALI. Epithelial lung cells have direct contact to inhaled aerosol particles and gases and were therefore used as a model of aerosol inhalation. The cell lines A549 and BEAS-2B have been widely used for testing particles and gases at the air-liquid-interface. The BEAS-2B cells are considered to better resemble the situation in human lung tissue while requirements for the cultivation of the cancer derived cell line A549 are better suited for labeling with the L-D4-Lysine isotope maker for the quantitative proteomics. In summary the cells were analysed using transcriptome (BEAS-2B), SILAC-proteome (A549), metabolome and metabolic flux measurements (A549) as well as cytotoxicity tests (A549).

All experiments were performed in 3 independent exposures and referenced to filtered aerosol resulting in an analysis of the particle effects alone. First the optimal dose for cell exposure and omics analyses was tested in decreasing aerosol dilutions. The reaction of the cells was monitored using the LDH release from macrophages and Alamar Blue viability test in A549 cells. LDH release was found to be significantly higher for particle containing aerosol than for gas phase alone and slightly higher with DF than with HFO (Fig. 3a). Due to the higher particle concentration in HFO-exhaust (see below) a dilution of 1:100 was required to achieve a non-impaired cell status while for DF-exhaust a lower dilution of 1:40 was possible without any viability impairment. With these dilution ratios a similar deposition dose was achieved. Based on a gravimetric filter analysis of PM2.5 and assuming a size-independent, constant deposition probability of 1.5% after Comouth et al. [5], the accumulated particle mass deposited on the lung cell monolayer surface area was roughly estimated as 28 ± 1.5

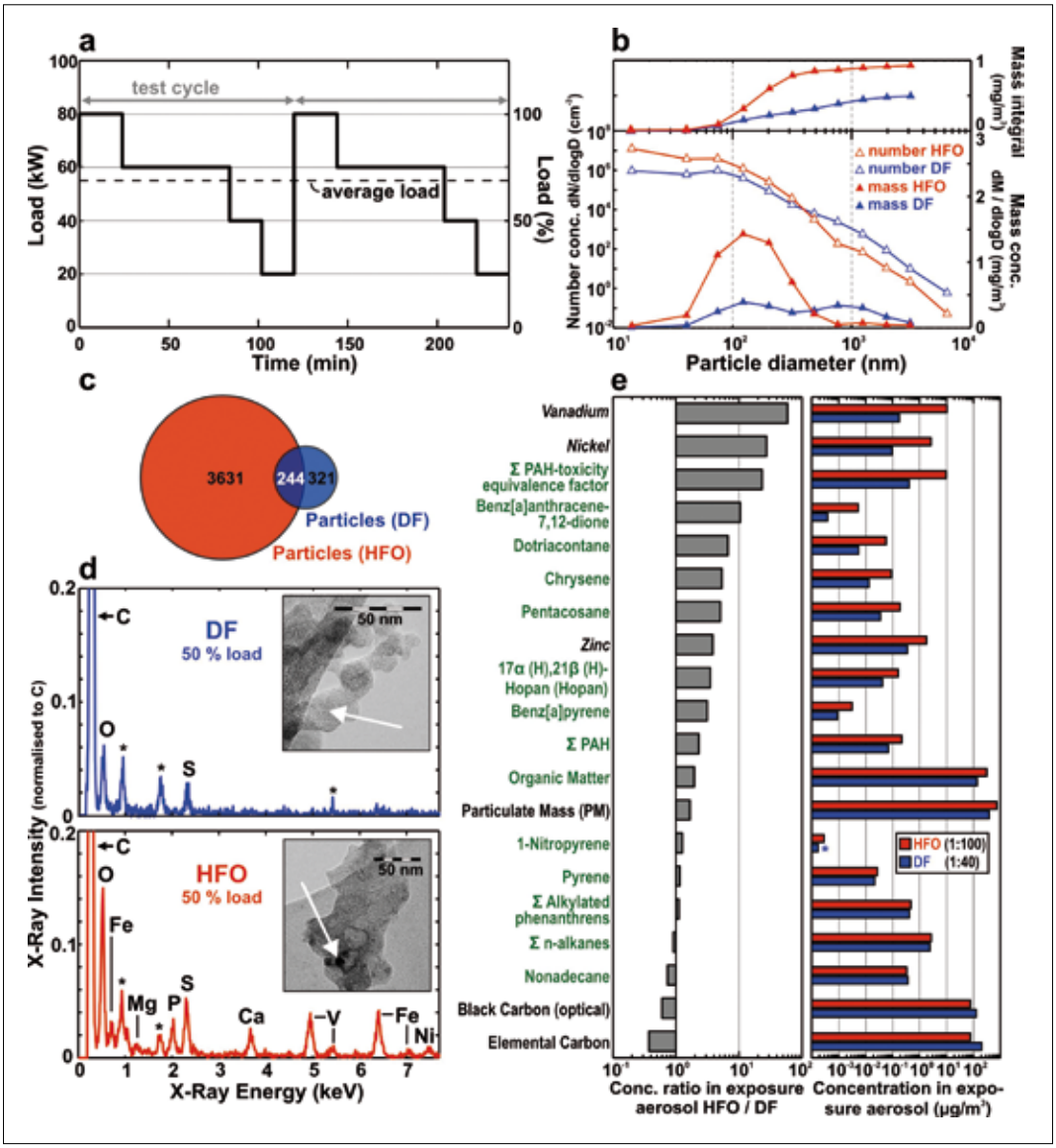

Fig. 2 Engine test cycle (a), physical (b) and chemical (c-e) properties

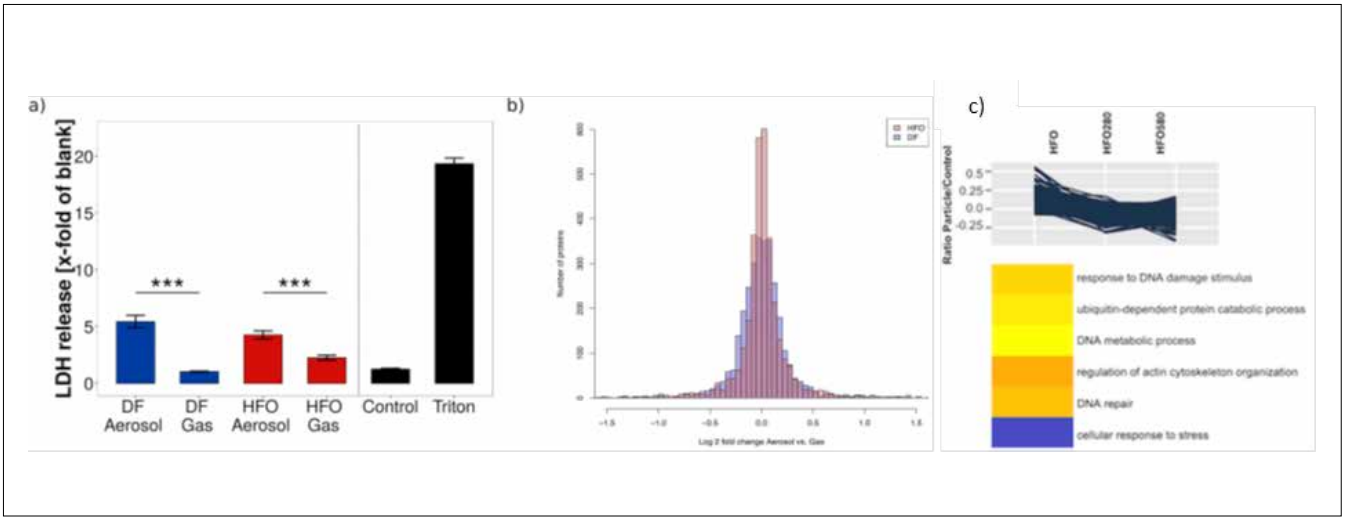

Fig. 3 Macrophage responses: Cytotoxicity measured by LDH release (a), proteome regulation (b) and Gene Ontology analysis after treatment with HFO, 280°C and 580°C heated HFO.

(DF) and 56 ± 0.7 ng/cm2 (HFO) per 4 h exposure duration with the variance of the mass measurement expressed by the standard deviation of the filter samples. A more elaborated model taking into account the particle size distribution from an electric low pressure impactor (ELPI) and a size dependent deposition probability after Comouth et al. [5], which was determined using previous measurements from ALI exposure systems, predicts 15.7 (DF) and 41.5 ng/cm2 (HFO) per 4 h exposure. For the improved deposition approximation model, the estimated uncertainties are about a factor of 2. Therefore the deposition dose in both cases can be considered being approximately equal for DF and HFO. In the following all aerosol parameters are reported considering the specific aerosol dilution factors (i.e. the exposure aerosol, EA, as delivered to the cells).

The concentration of particles with an aerodynamic diameter larger than 200 nm was higher for the DF-EA (particle number and mass concentration), whereas nanoparticles smaller than 50 nm were approximately 100-fold more abundant for the HFO-EA (see the size distributions in Fig. 2b). TEM images of the particles show that the smaller HFO particles (Fig 2d) contained high levels of amorphous organic material around carbonaceous fractal cores with metal inclusions. The DF-EA particle analysis reveals a different picture (Fig 2d), in which the particles appear larger and are mostly composed of pure carbonaceous aggregates with spherical soot cores (Ø ~ 20– 30 nm). Energy-dispersive X-ray spectroscopy (EDX, Fig 2d) on TEM showed large differences between HFO-EA and DF-EA particles with regard to the abundance of heavy elements. High intensities of elements such as vanadium, nickel, sulphur and iron were detected in the HFO particles, whereas the DF particles primarily contained carbon and oxygen in the EDX spectrum. Fig. 2d shows an overview of the differences in the inorganic and organic chemical composition (Fig. 2e) as well as the absolute concentrations of the respective substances in the DF- and HFO-exposure aerosol particles. Almost all of the measured components, except elemental carbon and black carbon, were more abundant in HFO-EA compared with DF-EA, despite a 2.5-fold higher dilution for HFO-EA. On-line aerosol mass spectrometry and off-line analyses showed considerably higher mass concentrations of particle-bound organic material and much more complex organic material in the HFO-EA. High-resolution mass spectrometry (ESI-FTICR-MS) revealed 3631 different polar organic compounds in the HFO particles compared with only 321 in the DF particles (Fig. 2c); 244 compounds were common to both fuel types. The quantification of aromatic and aliphatic compounds revealed that higher molecular weight components were more abundant in the HFO particles (green text in Fig. 2e), such as the higher molecular weight carcinogenic PAH benzo[a]pyrene (Fig. 3e). The sum of PAH toxicity equivalency factors (Fig. 2), which ranks different toxic PAHs weighted by their concentration and relative toxicity, was more than 10-fold higher in HFO-PM compared with DF-PM (Fig. 2e). The only component over-represented in the DF-PM was the elemental carbon fraction (EC) and the corresponding optically measured "black carbon" factor (BC; Fig. 3e). Summarising the chemical and physical characteristics, particles emitted from ship engines differ in concentration, size distribution, morphological appearance and chemical composition depending on whether DF or HFO is used. The DF particles in the inhalable size region were dominated by elemental carbon-rich soot-aggregate particles, whereas the HFO particles were smaller (nanoparticles) and rich in organic material, including known organic air toxicants (PAHs and their derivatives) and reactive transition metals such as V, Ni, Fe and Zn. However, it shall be noted that also DF-PM contains organic compounds in relatively high concentrations. The HFO-PM just contains much higher concentrations (Fig 2).

To relate the extensive chemical and physical characterisation of the exhaust aerosols to bio-

logical effects, the HFO and DF emission particles were directly deposited on human lung cells using ALI exposure technology. Transcriptome, proteome, metabolome and metabolic flux analyses were performed, which yielded parallel and relative quantification of 42205 different transcripts, 6192 proteins and 400 metabolic molecules. Proteins and metabolites were extracted from the same cell material (A549) that was previously metabolically labelled using D_4-lysine (SILAC proteomics) and $^{13}C_6$-glucose. Ribonucleic acid (RNA) was isolated from BEAS-2B cells and was used for the transcriptome analyses. The transcriptome, proteome and metabolome analyses revealed widespread changes in the cellular system upon exposure to both HFO and DF aerosol particles. Surprisingly, regulation of gene expression, proteins and metabolites was higher in the DF-particle-exposed cells compared to the HFO-particle-treated cells ($p<0.001$, Fig. 4a,b,c). The same effect was observed in the proteome data of RAW-macrophages (Fig. 3b).

A higher regulation alone only proofs a stronger biological reaction onto the deposited PM at the given exposure conditions (i.e. 4 h exposure at a deposition dose below measurable cytotoxicity) and does not necessarily indicate a higher toxicity or risk of disease. Further conclusions can be drawn from a specific biological pathway analysis. Pro-inflammatory signaling, xenobiotic metabolism and oxidative stress pathways were indicated by the regulated genes (Fig. 4d) [4]. The HFO particles specifically induced the transcription of primary and secondary inflammation markers (IL-8, IL-6 and IL-1), and both fuel types affected the cytokines CSF3, CXCL1, and CXCL2 (Fig. 4f). Considering xenobiotic metabolism, CYP1A1 (PAH metabolism) was induced by exposure to HFO particles which corresponds to the higher PAH concentrations in HFO PM, whereas the DF particles affected other cytochromes (CYP3A4 and CYP17A1) and the carbosulphotransferase CHST6 (Fig. 4e). In addition to these, in the context of aerosol exposure well-known pathways [4], we searched for other cellular responses

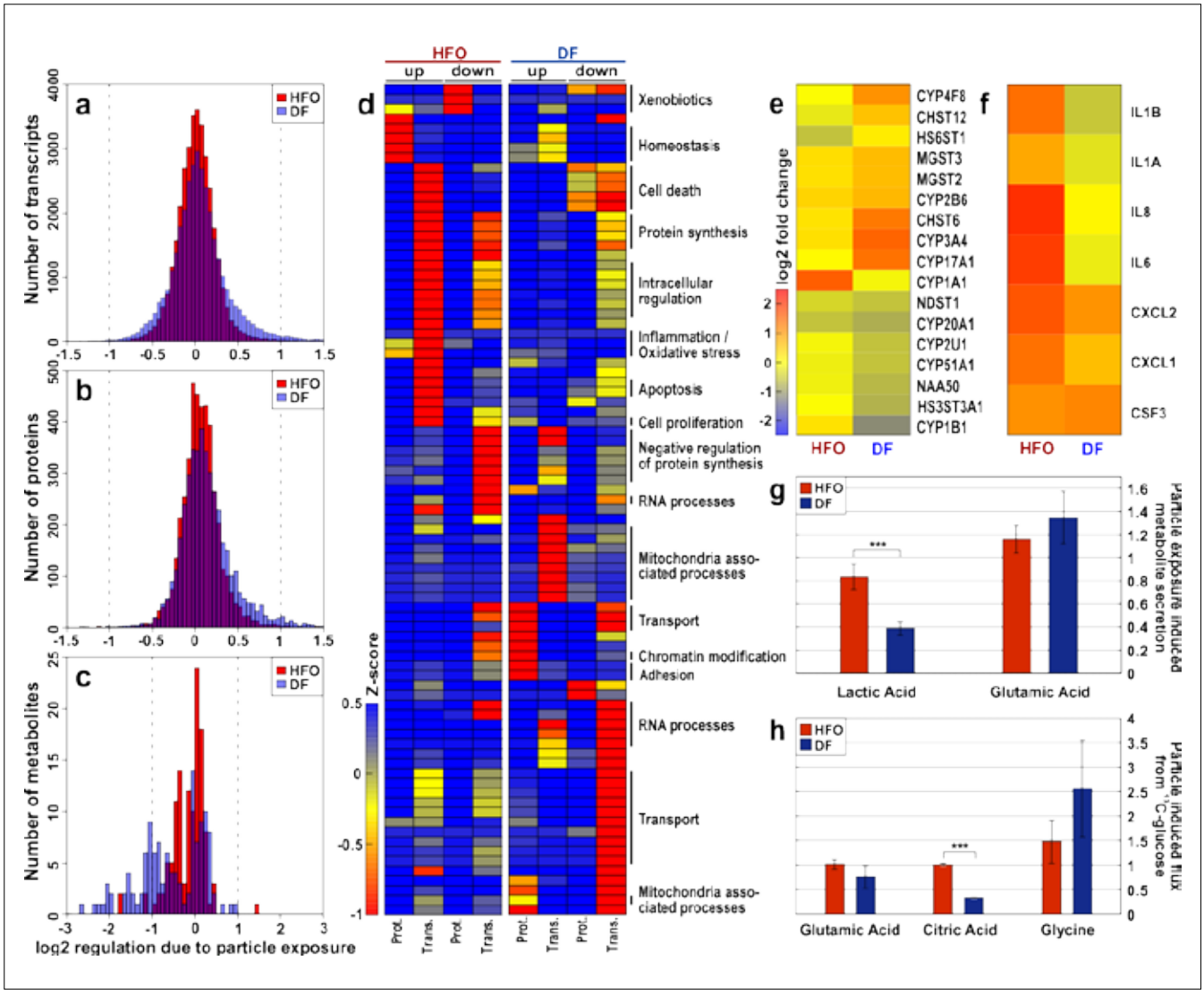

Fig. 4 Omics regulation (a-c), combined proteome-transcriptome GO-term analysis (d), genes of xenobiotic metabolism (e) and pro-inflammatory effects (f), most regulated metabolites (g,h)

Table 1. Summary of the main HFO- and DF-particle exposure effects.

Effect	HFO	DF
Pro-inflammatory signaling	↑	-
Oxidative stress	↑	-
Cell homeostasis	↑	-
Response to chemicals	↑	↓↑
Cellular stress response	↑	↑
Motility	↑	↑
Endocytosis	↑	↑
Cellular signalling	MAPK, TGF beta, PDGF, EGF, GPCR	ID, kinase cascade
Energy metabolism	-	↓↑[x]
Protein synthesis	-	↓
Protein degradation	-	↑
RNA metabolism	-	↓
Chromatin modifications	-	↑
Cell junction and adhesion	-	↓↑*

The arrows indicate the direction of regulation for cellular functions derived from the most statistically significant enriched Gene Ontology terms from the transcriptome, proteome, and metabolome (details in S2 Table).

[x] BEAS-2B up, A549 down

* BEAS-2B down, A549 up

undergoing modulation. A meta-analysis combining the proteome and transcriptome data was performed to examine the significant enrichment of gene ontology (GO) terms. The results indicate that the HFO and DF particle effects were distinct (Fig. 4d). Particles from both fuels induced effects on cell motility, the cellular stress response, the response to organic chemicals, proliferation and cell death (Fig. 4d). Genes and proteins associated with vesicle transport pathways were enriched, which might be connected to the endocytosis of diesel particulate matter. The pathways specifically regulated by DF particle exposure included the general translation pathway (Fig. 4d). The translational elongation, RNA-processing and ribosome translation pathways were down-regulated, whereas the pathways that affect chromatin organisation and modification were up-regulated. The down-regulated pathways included histone acetylation, which may result in DF particle-induced epigenetic changes. Other pathways modulated by DF particles were involved in processes such as cell junction organization and cell adhesion. Pathways such as the energy metabolism, cell junction and cell adhesion were clearly affected in both cell lines when assessed using transcriptomics and proteomics but differed in the direction of regulation (Table 1 and Fig. 4), which indicates a time-delayed reaction in the cell. Exposure to DF particles induced mitochondria-associated genes and proteins, which indicates that mitochondrial stress was induced, whereas the HFO particles did not yield this response. Pathways specifically regulated by the HFO particles include the homeostasis, oxidative stress and inflammatory response pathways, whereas the metabolic and biosynthetic processes were slightly down-regulated (Fig. 4). In RAW macrophages HFO additionally provoked a DNA-damage response that was found to depend on the organic load of the HFO particles, as it disappeared by heating the particles to 580°C (Fig. 3c).

The metabolome analyses supported the finding that biosynthetic and protein synthesis processes were down-regulated in the DF particle-treated cells. ATP-binding cassette transporters, which are involved in actively transporting biomolecules across membranes, were also affected. Further information supporting the inhibition of biosynthetic activities includes the negatively affected metabolites secreted by the cells (Fig. 4). The pathways affected by HFO particle exposure include glycolysis and pyrimidine metabolism. Glycolysis is a pathway that is typically altered during inflammation and is generally increased in cells under inflammatory conditions [6]. Glucose flux into lactic acid through glycolysis was significantly reduced ($p<0.05$) in cells treated with DF particles (Fig. 4). Mammalian cells oxidise glucose and glutamine in the TCA cycle to produce NADH/H+, which is re-oxidised in the respiratory chain to produce ATP. DF exposure strongly decreases the levels of relative glucose oxidation in the TCA cycle compared with HFO, as reflected by the significantly lower levels of labelled citric acid ($p<0.001$; ratio data: Fig 4). Simultaneously, we observed an increase in glucose-derived carbon flux into glycine (Fig

4); enhanced glycine metabolism has previously been associated with tumourigenesis in lung cancer [7]. These observations suggest a lower ATP production and, hence, lower available energy compared with HFO. Increased carbon flux into glycine is directly linked to the increased transformation of hydroxymethyl groups through one-carbon metabolism. The latter is essential for DNA synthesis and repair.

We assessed human lung cell responses to ship exhaust particles. A unique combination of extensive chemical and physical aerosol characterization and multiple omics analysis was used to generate a broad overview on cellular mechanisms affected by shipping particles and to identify possibly harmful constituents of two types of ship exhaust aerosols. While not providing a classical toxicological risk assessment, which would require the testing of multiple doses and points of time, this study rather gives a comprehensive picture on the cellular responses to ship exhaust particles after short-term exposure, which should be used as starting point for more mechanistic studies. Although the HFO particles deposited in the ALI system were about equal in mass, higher in number and contained a large excess of toxic compounds, DF particle exposure induced a broader biological reaction in the human lung cells (BEAS-2B and A549) on all investigated „omic" levels. As discussed, a stronger affected cell metabolism is not an adverse effect per se, but it holds a higher risk of disturbance of normal cell functions. Within known pathways, such as pro-inflammatory signaling, oxidative stress and xenobiotic metabolism, the levels of certain well-known indicators (e.g., IL-1/6/8 and CYP1A1) surged following HFO particle exposure. In contrast, DF particles strongly affected basic cellular functions (energy and protein metabolism) and mechanisms little yet known to be affected by aerosol treatment, such as mRNA processing and chromatin modification. The large EC fraction in DF exhaust is one of the prominent differences between the two particle types. The chemical and physical surface properties of freshly formed EC fractions might be of relevance here. Experiments using combustion aerosol standard generator (CAST), which allows generating fresh combustion particles with adjustable EC/OC ratios, are currently performed. There is no doubt that the carcinogenic emissions from HFO-operated vessels need to be minimized. HFO emissions contain among other constituents high concentrations of toxic metals (V, Ni etc.) and polycyclic aromatic hydrocarbons. However, also emission of diesel engines operated with refined DF, are known to be toxic and carcinogenic, although the toxicant concentrations are much lower [3] than in HFO emissions. Consequently the implementation of emission reduction measures for land-based diesel engines started decades ago. Due to the substantial contribution of ship emissions to global pollution, ship emissions are the next logical target for improving air quality worldwide, particularly in coastal regions and harbour cities. In this context our findings on the biological effects of HFO and DF ship diesel emissions can contribute to the current debate about the reduction measures to be implemented for shipping. The results from this study provide the information that at comparable lung deposition doses the acute biological activity of particles of ship emissions from DF fueled ships is not less relevant than the activity of HFO emission particles. This supports the suggestion that a general reduction of the PM emissions from shipping in harbours and the vicinity of the coast should be implemented for both, HFO- and DF-operated ships. The presented results were published by Oeder et al. 2015 [8], Kanashova et al. 2015 [9] and Sapcariu et al. 2016 [10]

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Emissions from a modern log wood masonry heater and wood pellet burner: Composition and biological impact on air-liquid interface exposed human lung cells

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The study is motivated by the increased use of wood as renewable, carbon- and climate- neutral fuel in the industrialized countries. Known cellular responses to wood smoke include inflammatory response oxidative stress and DNA damage. To provide a link between the chemical and physical characteristics of emissions from a modern log wood masonry heater and wood pellet burner and the cellular responses they elicit and sequentially to identify potentially harmful fractions in wood combustion aerosols the human lung epithelium cells (A549) were exposed to pellet and beech log wood combustion aerosols using an Air Liquid Interphase cell exposure system. Comprehensive chemical characterization of the aerosols, transcriptomic and proteomic changes of the A549 cells were monitored to compare the cellular responses to the combustion aerosols and particles. The findings are discussed in conjunction with recently obtained results on ship diesel engine emissions. Despite the highest particle deposition dose, a high dose of PAH, Oxy-PAH and the high gas phase concentration of organic compounds the biological regulation on proteome and transcriptome level in response to the beech combustion aerosols was the lowest compared to the Pellet and DF. The exposure of A549 cells to 1:40 diluted beech combustion aerosols mostly induced regulation of RNA metabolic processes as well as immune responses. Furthermore, cytochrome P450 1A1 (CYP1A1), which is considered to be a key metabolic enzyme in Bena[a]pyrene metabolism, was induced by exposure to the beech combustion aerosols. Treatment with the pellet combustion aerosols at dilution ratio 1:40 influenced signal transduction, endosome transport, cell cycle and tight junctions related processes.

Exposure of the lung cells at the same dilution ratio of 1:40 and approximately equal particle deposition dose for DF and pellet and the 2.5 times higher deposition dose for the beech combustion particles caused only mild biological response to the wood burning aerosols compared to exposure to DF ship emission particles, which influenced several essential pathways of lung cell metabolism. Regarding the fact that in DF combustion experiments only particle effect was considered [Oeder et al. 2015] the additional effect of the gas phase could lead to a much stronger biological impact. Pellets are currently found to be the most efficient and cleanest way by far to use wood as renewable energy source. Our study proved that compared to log wood combustion there were significant lower emissions of PM and hazardous organic substances [Boman et al. 2011, Orasche et al. 2011, Ozgen et al. 2014]. Interestingly, despite the highest particle deposition dose, a high dose of PAH, Oxy-PAH and the high gas phase concentration of organic compounds the biological regulation on proteome and transcriptome level in response to the beech log wood combustion aerosols was the lowest. From another hand the inflammation marker IL8 as well as CYP1A1, which corresponds to high content of PAHs, were induced after beech log wood combustion exposure. Synergistic and antagonistic effects could play a major role explaining

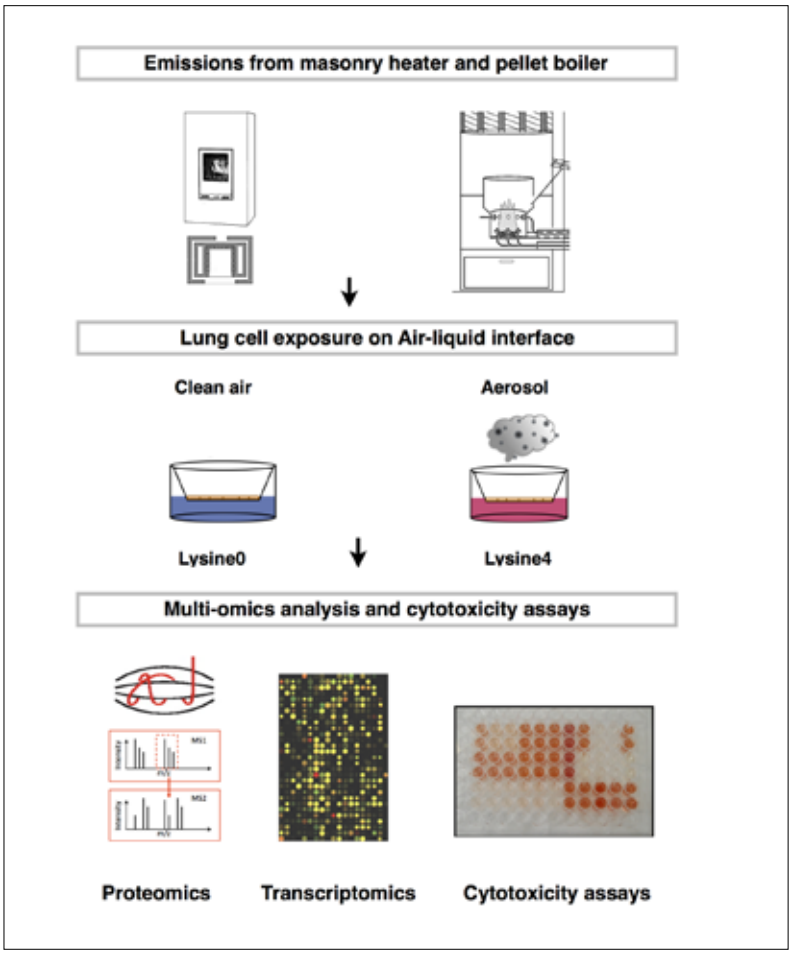

Fig 1 Experimental set-up and global omics analyses

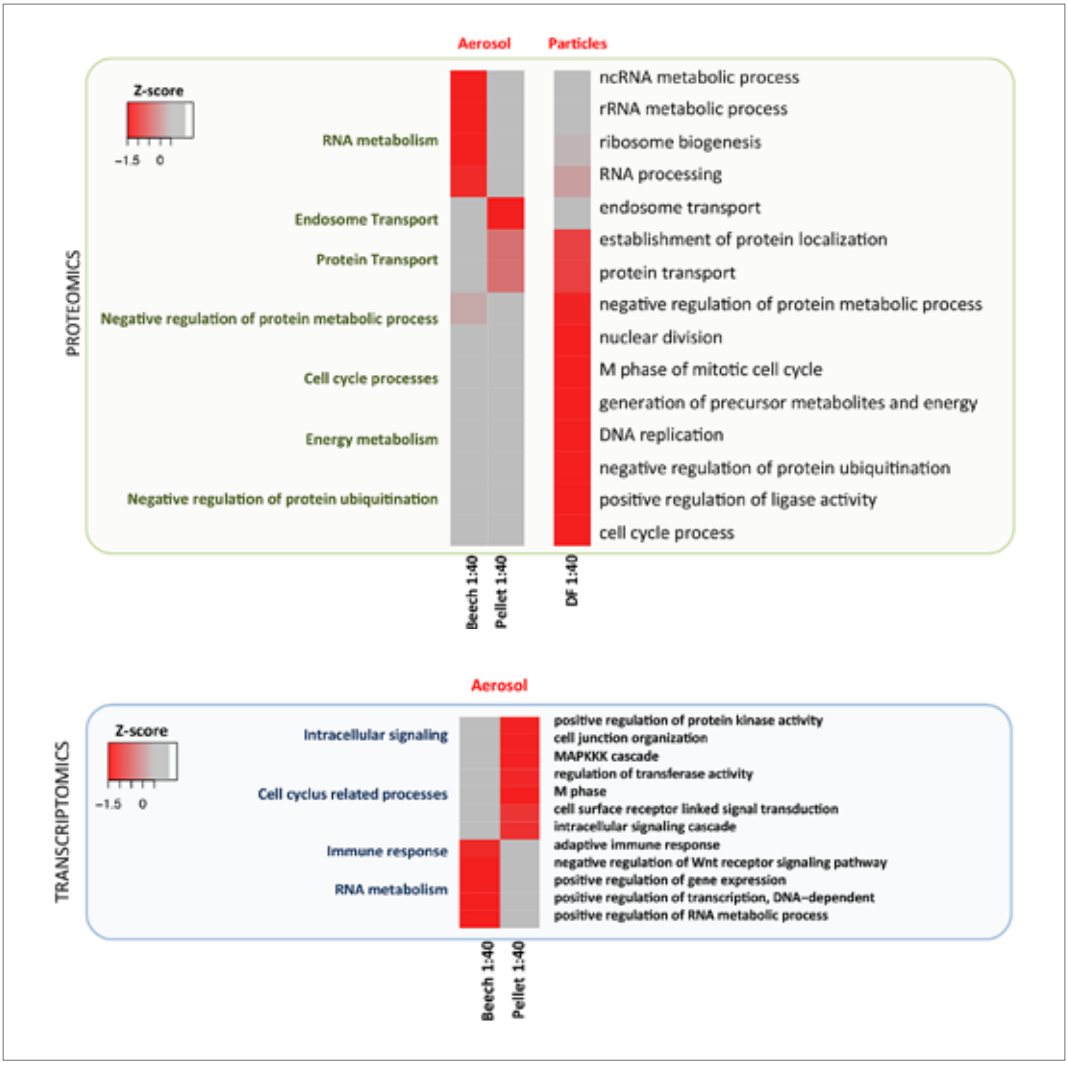

Fig 2. Meta-analyses for the proteome and transcriptome using the combined Gene Ontology (GO) term analysis of the 10% most regulated proteins and transcripts v

these mechanisms. The mitigation of the biological impact of the wood combustion particles compared to the particles from the ship diesel fuel combustion could be related to the phenolic antioxidant properties in the wood smoke. In addition to their antioxidative effect, phenols are also potential trapping agents for electrophilic geneotoxic compounds that are regarded to be carcinogenic [Newmark et al. 1996]. To predict the harmful effects of combustion particles it is not enough only to measure the composition of PM2.5 combustion particles. Instead, a complex source mix must be investigated in detail. Moreover aging processes in the atmosphere could play a major role in changing of the toxic effects of the combustion aerosols.

The obtained results suggest formulating specific hypotheses about the mitigation of the biological impact of the wood combustion particles compared to the particles from the ship diesel fuel by preventing geneotoxic effects [Newmark et al. 1996] and are motivating further experiments to proof or disproof those. In this context the role of phenolic antioxidants, which appear condensed on particles [Hawthorne et al. 1989], and their influence on the biological activity should be investigated.

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Development of air liquid interface (ALI) exposure system for the purpose of multi-omics effects analysis of combustion emissions in the framework of the HICE Project

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In HICE, one of the main objectives is the investigation of biological effects of freshly generated combustion aerosols on human lung cell models. Therefore, OMICs-analyses are applied at cell cultures, exposed at air liquid interface. The combination of both techniques applied in four large measurement campaigns, are unique in these dimensions. To fulfil the high requirements in sample number and reproducibility for OMICs-analysis within HICE the "Karlsruhe Expositionssystem" was further developed.

For the reproducible air-liquid-interface (ALI) exposure of the bioassays the ALI Exposure System was set up based on the prototype of the Karlsruhe Exposure System (Paur et al. 2011). In this fully automatic system cell cultures grown on porous membrane inserts, which are in contact with nutrient medium, are exposed directly to diluted aerosol from combustion sources. Two pre-test measurement campaigns were performed at KIT with the established Karlsruhe Exposure System (Mülhopt et al., 2008) to investigate the off gases of a log wood burner. Within these campaigns the biological systems were tested and final configurations for the setup of the new exposure system were defined: it was agreed to use modules for 18 positions to expose membrane inserts of 24 mm in diameter.

The ALI system was assembled and intensively validated using the prevoiusly developed fluorescein sodium dosimetry (Mülhopt, et al., 2009). During independent experiments the variability in between the 18 exposure chambers was measured. With a series of biological validation experiments, the compatibility of the materials with the biological exposure procedure was verified. The addition of facultative positions for negative controls by exposure to clean air distinguishes our ALI exposure system from other solutions and is importantant for testing combustion derived aerosols: off-gases in the gasous phase of the combustion aerosol render the common practice of filtering the aerosol for negative controls unsuitable. Cells exposed at the air-liquid interface are very susceptible to being damaged by insufficient humidification. The humidification of the newly developed positions for negative controls were compared with the aerosol humidification by using filtered ambient air instead of an aerosol source. No difference in cell vitality was observed for cells exposed to humidified air via either of the different gas streams. With the same experimental setup the next technical improvement, the use of an electrostatic field to increase the deposited particle dose, was tested for influences on cells. A549 cells exposed to clean air in a field caused by a potention of – 1000V between the electrodes showed no difference in cell vitality compared to cells in the absence of an electrostatic field. A detailed description of the HICE Exposure System with the reasults of validation are reported by Mülhopt et al. (Mülhopt et al. 2016a)

The new ALI exposure system was then used to test the effects of a beech combustion aerosol on A549 lung epithelial cells. The cells were exposed for 4h to the 1:10 diluted aerosol. LDH release shows no acute toxicity of the complete or filtered aerosol compared to cells that were exposed to air. However, when particle dose was increased by applying an electrostatic field, a clear increase of released LDH, i.e. cell death, was observed. Two marker genes, representing inflammatory (IL-8) and PAH-mediated (CYP1A1) cell responses, were analyzed by quantitative PCR. Expression of IL-8 was not significantly affected after 4h of exposure, while CYP1A1 is clearly induced by the particulate fraction of the aerosol.

On the basis of this project KIT and VITROCELL developed the automated exposure station for commercial application. Customized solutions now allow the use of different cell types, aerosols and well sizes and shapes. An overview of previously established cultures and aerosols is given by Mülhopt et al. (Mülhopt et al. 2015, 2016b). The gained experience during HICE- campaigns added a significant contribution to development of the system regarding automatization and usability. The ALI exposure systems were successfully used in several campaigns with different combustion derived aerosols. A detailed investigation of aerosol composition is described by Reda et al (Reda et al. 2014). The effects to cell cultures is described by Oeder et al. (Oeder et al. 2015) and Sapcariu et al. (Sapcariu et al. 2016).

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Photochemical emission aging tube reactor (PEAR) method for simulation of the atmospheric aging of combustion emissions

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One of the main challenges for the assessment of the health and environmental effects of combustion emissions is their constant transformation in the atmosphere due to photochemical aging reactions. Traditionally atmospheric reactions of various biogenic and anthropogenic emissions have been studied in laboratory chamber setups. More recently different flow tube reactors have been developed to achieve a wider degree of oxidant exposure times and a continuous aging process. In this work, we designed, constructed and utilized a novel photo-oxidation flow tube reactor to simulate photochemical aging of combustion emissions. The reactor is designed for relatively high flow rates (up to 200 lpm) and high oxidant concentrations in order to provide sufficient flow rates and concentrations for toxicological air-liquid cell exposure studies, as well as for collecting offline PM samples for comprehensive chemical and toxicological analyses. The system was used to study photochemical aging of exhausts from a passenger car engine and various wood combustion sources. Finally, the system was also utilized in connection with toxicological exposure systems to investigate the effect of photochemical aging on the toxicological properties of emissions.

The reactor is constructed from stainless steel tube which has four 254 nm UV lamps assembled at the inner walls (Fig.1). The lamps are surrounded by quartz glass tubes, which are flushed with cooling air. The reactor volume is 150 dm3. Ozone and water vapor are added into the reactor to produce OH radicals via photolytical decomposition of 03. The inlet part of the reactor consists of flow diffuser, which is designed to achieve a nearly optimal laminar flow profile in the reactor. Furthermore, the reactor is assembled vertically, to reduce flow disturbation by buoyancy forces. Similar to the PAM-tube (Kang et al., 2007), at the outlet the flow is divided into a ring flow, taken from the perimeter of the tube, and to a center flow. Only the center flow is used for analysis, in order to reduce possible wall effects.

The flow dynamics of the reactor were simulated with the aid of computational fluid dynamics software (ANSYS 15.0, Fluent) to optimize the reactor dimensions and other boundary conditions (Fig.2). Furthermore, the residence times in the reactor were measured with CO_2 marker gas from the center flow at the outlet. These results indicate that at 100 lpm the flow is almost fully developed laminar flow and that decreasing of the flow rate broadens the residence time distribution indicating less ideal flow pattern (Fig.2).

The engine applied for the experiments was turbo charged flexi fuel engine which was operated with two different gasoline-ethanol fuel mixes (E5 and E85). Both the New European Driving Cycle (NEDC) and selected steady state conditions were used. The wood stoves were representing modern technology of both heat storing and non-heat storing appliances. The stoves were operated with spruce and beech logs. The combustion emissions were first diluted and then introduced to the tube reactor. The emission OH exposure times were estimated by measuring D9-butanol gas decay with proton transfer reaction mass spectrometry (PTR) during the experiments. Downstream the tube reactor the aerosols were sampled to the aerosol measurement instruments, including AMS (Aerodyne), SMPS (TSI) and Aethalometer (Magee Scientific).

With all the studied emissions the photochemical aging clearly increased organic aerosol concentrations. In gasoline engine experiments (Fig.3), it was observed that the carbon oxidation state of the aerosols, estimated according to Kroll et al. (2011), increased with OH-exposure in E5 fuel case, while there was no clear effect for the E85 fuel case. Wood combustion primary emissions

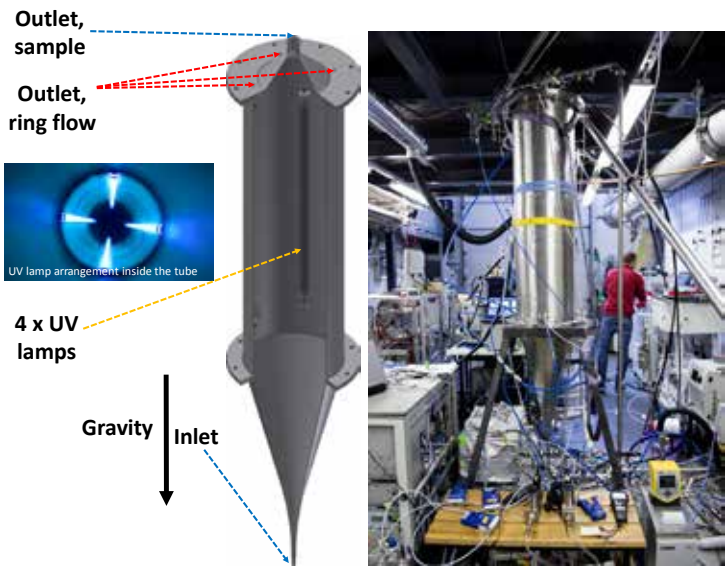

Fig.1 Scheme and photograph of the PEAR flow reactor

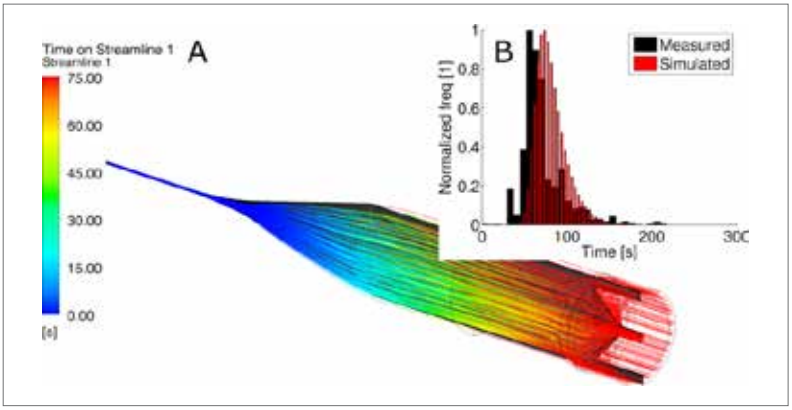

Fig.2 Simulated (A & B) and measured (B) residence time distribution in the flow tube reactor at 100 lpm flow rate

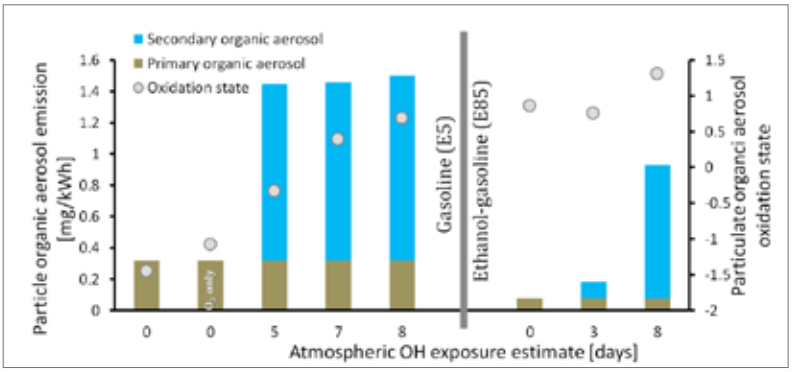

Fig.3 Primary and secondary organic aerosol emissions and the organic carbon oxidation state in the exhaust emitted a gasoline engine operated with two different fuel blends. The secondary organic aerosol formation is simulated using the PEAR reactor and measured with AMS-ToF.

exhibited relatively high oxidation states which were further increased during the aging process up to a value of 1.5. The SOA emission factors were highly dependent on the wood fuel moisture content since increasing moisture increases the emission of volatile organic compounds serving as precursors of SOA formation.

In conclusion, a novel online method to study the effect of photochemical aging on combustion emission properties was developed and successfully utilized. Photochemical aging of gasoline engine and small scale wood combustion emissions, with atmospherically relevant OH radical exposures, caused a significant increase in particulate matter concentrations as well as transformation of the chemical characteristics of the emissions.

Acknowledgements

Support by the Academy of Finland (Grants: 304459 & 258315) and the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) is gratefully acknowledged.

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Development of a Mobile Laboratory of Biosafety 2 security level for at-site human lung cell exposure experiments in the framework of the HICE Project

S. Öder, R. Zimmermann, T. Gröger (UR/HMGU), Jeroen Buters (TUM)

In HICE measurement campaigns cell cultures are exposed to freshly emitted combustion aerosols directly at the sites of aerosol generation. At these places the conditions are not suited to work with cells under sterile conditions and in agreement with rules for biosafety. Therefore, a possibility to bring sterile cell culture conditions to the site of aerosol generation and to work in an environment that fulfills the biosafety requirements was needed and was accomplished by building a unique biosafety level 2 cell culture lab within a mobile maritime container. The idea, it's planning, construction, and regulatory approval was mainly done by the HICE partner Center of Allergy and Environment (ZAUM).

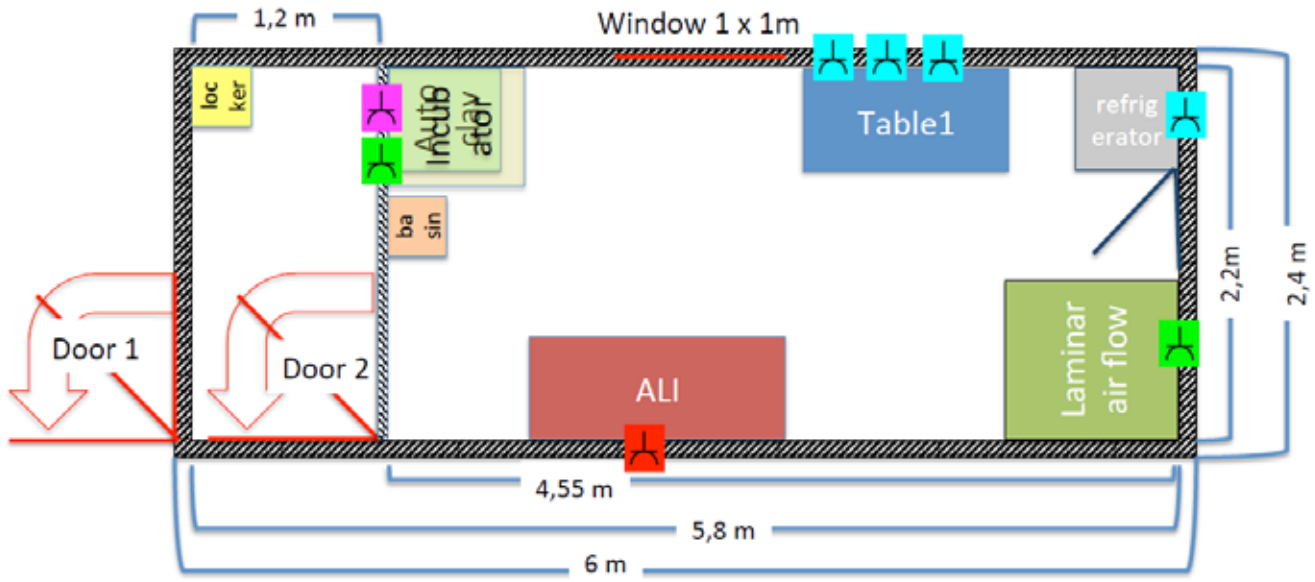
The HICE mobile lab is based on the structure of standard size a 20 ft. shipping container which can easily be transported by a truck and is equipped with four wheels making it even more flexible for short distance movements.

It contains two sequential doors to avoid a complete opening of the biosafety room. Behind the 2nd door there is a biosafety level 2 lab. The space in between the doors is used to change from jacket to lab coat and for the well ventilated storage of a CO_2 bottle needed for the cell culture incubator. The interior of the lab complies with biosafety 2 standards and was authorized by the District Government of Upper Bavaria for operations with organisms of the biosafety level 2 (§50 IfSG).

The ventilation system provides a high air renewal rate and can optionally be connected to a fume hood if necessary. Water supply can be connected and allows the usage of a safety shower, eye shower and a small basin. Waste-water removal is accomplished by active pumping the water out of the mobile lab. Electricity is provided via one or two high-voltage current plugs and enables air conditioning, heating and the operation of cell culture instruments like laminar air flow, cell incubator, autoclave, microscope, water bath, fridge, and the cell exposure system (ALI). For the connection of the ALI to the aerosol source there is an aperture on the mobile lab´s roof where the aerosol tubes can be fed through. After cell exposure the exhaust gas is led outside the mobile lab again to avoid contamination of the lab air.

The HICE mobile lab with its clean bench with laminar air flow and its HICE exposure system allows working with cell cultures under sterile conditions providing high quality cell models for air-liquid-interface cell exposure directly at the site of aerosol generation and subsequent sensitive and comprehensive analyses of cell metabolism and signaling using for example multiple omics techniques.

Besides its home base at the HMGU campus the mobile lab container was so far stationed for measurement campaigns at the ZAUM in Munich, at the University of Rostock (UR), and at the University of Eastern Finland (UEF) in Kuopio, Finland.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5,8 m
6 m

Validation of aging equipment and testing of an animal model for cell culture experiment evaluation

S. Kasurinen, R. Zimmermann (UR/HMGU), M. Happo, O. Sippula, P. Jalava, M.-R. Hirvonen (UEF)

A point of discussion in using lung cell cultures for the evaluation of health effects is the comparability to more established systems such as animal experiments. Therefore, for validation of the lung cell exposure experiments an animal model was tested with a diesel engine as combustion source. The engine was a water-cooled non-road diesel engine (Kubota D1105-T, 24.5 kW), which represents diesel engines used e.g. in power generation or excavators.

Experiment

Pathogen free male C57BL/6J mice 8-9 weeks old (weight 23.9 ± 1.6 g, S.E. 0.17 g) were used in the studies. Each exposure group had 12 mice that were used in two different study set-ups. The mice were exposed for four hours daily to DEE at three consecutive days. For the exposure, mice were placed into a monitored inhalation exposure unit and the diluted emission aerosol was led into the whole body exposure chamber. Untreated animals that were kept in a room conditions behind laminar airflow in animal transfer station were used as negative control. Immediately after the third exposure, mice were euthanised and after surgical anesthesia was received, the animals were exsanguinated by cardiac puncture. The collected blood was placed into serum separation tubes and kept on ice. The first group of mice (n = 6) were cannulated with polyethylene tubing and lungs were perfused with 0.9 % sterile saline, followed by collection of bronchoalveolar lavage fluid (BALF). After the lavage, lungs were removed and left lung was used in preparation of single cell suspension and right lung was divided into three parts and shock frozen in liquid nitrogen. The second group of mice (n = 6) was used to collect tissue and serum samples. The left lung of these mice were removed and filled with 10% phosphate buffered formalin that was also used as a preservative of the lung tissue samples.

Cells were separated from the BALF and the supernatant was removed for separate analyses. One half of the BALF cells was used to determine the type and number of cells, the second half of BALF cells was used to assess genotoxicity by single-cell gel electrophoresis (SCGE) assay. The total protein concentration in the BALF supernatant was analysed using a modified Lowry assay following the manufacturer's instructions. To assess cell viability and genotoxicity of the cells in the lung tissue, a single cell suspension was obtained following the protocol described previously5. All tissue samples were filtered before other analyses for removing larger particles from the single-cell suspensions. We assessed cell viability using acridine orange and (4',6-diamino-2-phenolindole (DAPI) staining. Ten cytokines were measured from the BALF supernatant and the serum: interferon gamma (IFNγ), interleukin 10 (IL-10), interleukin 12p70 (IL-12p70), interleukin 1 beta (IL-1b), interleukin 2 (IL-2), interleukin 4 (IL-4), interleukin 5 (IL-5), interleukin 6 (IL-6), tumor necrosis factor alpha (TNFα) and keratinocyte derived chemokine (KC). The formalin-fixed left lung was embedded into paraffin, cut into 3 µm thick slices and stained for histological analysis of hematoxylin-eosin (HE) and immunohistochemistry of matrix metalloprotease 12 (MMP12).

Results

Inflammatory responses in mice were studied by measuring number of inflammatory cells in BALF and the concentrations of 10 different cytokines in BALF and serum. The exposure to DEE caused only a slight increase in the total number of cells in mice lungs, which was mostly due to the higher number of macrophages in the BALF of DEE exposed mice. No signs of neutrophilic inflammation were measured. Low inflammatory activity was also observed in the cytokine concentrations both in mice BALF and serum (Table 1). In BALF, no significant increases or decreases in cytokine production was measured after DEE exposure. However, in serum, DEE exposure caused a decrease of TNFČ (p=0.000) and an increa-

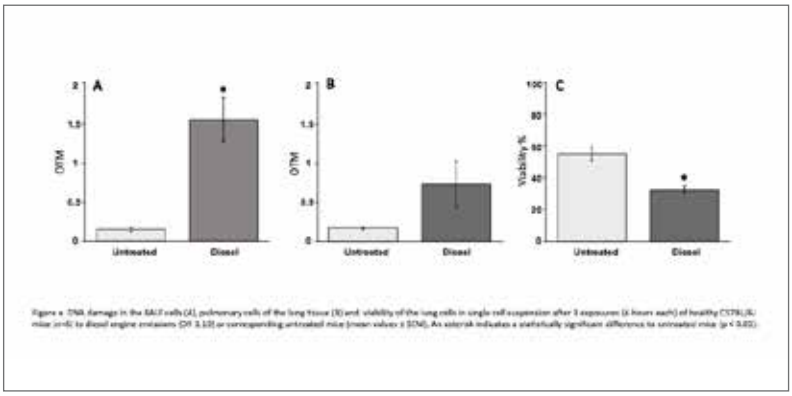

Fig.1 DNA damage in the BALF cells (A), pulmonary cells of the lung tissue (B) and viability of the lung cells in single cell suspension after 3 exposures (4 hours each) of healthy C57BL/6J mice (n=6) to diesel engine emissions (DR 1:10) or corresponding untreated mice (mean values ± SEM). An asterisk indicates a statistically significant difference to untreated mice (p < 0.05).

		BALF				Serum			
Parameter	Unit	Untreated		DEE		Untreated		DEE	
IFN-γ	pg/ml	0.03	± 0.01	0.02	± 0.01	1.02	± 0.24	0.38	± 0.06
IL-10	pg/ml	0.22	± 0.03	0.29	± 0.04	18.47	± 0.97	13.97	± 0.76
IL-12p70	pg/ml	1.16	± 0.62	1.37	± 0.49	15.33	± 4.26	11.92	± 2.42
IL-1b	pg/ml	0.08	± 0.01	0.07	± 0.01	2.02	± 0.15	2.19	± 0.18
IL-2	pg/ml	0.19	± 0.03	0.14	± 0.03	2.42	± 0.32	2.30	± 0.35
IL-4	pg/ml	0.08	± 0.02	0.13	± 0.01	0.39	± 0.06	0.36	± 0.07
IL-5	pg/ml	0.15	± 0.05	0.07	± 0.00	3.54	± 1.48	1.27	± 0.16
IL-6	pg/ml	0.73	± 0.07	0.77	± 0.12	6.22	± 0.80	5.21	± 0.89
TNFα	pg/ml	0.41	± 0.04	0.38	± 0.01	14.56	± 0.96	**9.08**	± **0.63**
KC	pg/ml	1.34	± 0.13	1.57	± 0.15	63.91	± 4.18	**81.10**	± **6.88**

Table 1 Inflammatory parameters measured from BALF and serum in DEE exposed and untreated mice

se of (p=0.046). The cytotoxicity of DEE in mice lung was assessed using DAPI-based staining method, which separates dead and living cells of the lung tissue. Microvascular leakage of blood proteins (e.g. albumin) was detected measuring total protein concentration in BALF. Tissue damage was analysed using histopathological analyses of lung tissue samples. The DAPI analysis required a preparation of single cell suspension from the lung tissue, which also decreased the viability of the cells. However, exposure to diesel emission decreased viability of lung tissue cells significantly more (p=0.000) than those of untreated animals. Diesel engine emission increased significantly total protein concentration in mice lungs (p=0.041).

The DNA-damage in BALF cells and in lung single cell suspension is shown in Fig.1. DEE exposure caused a significant increase of DNA-damage in pulmonary cells both in BALF (p=0.000) and homogenized lung tissue (p=0.000), as measured by SCGE assay. The measured response was about two-fold higher in the BALF cells, consisting mostly from macrophages.

We observed significantly increased numbers of MMP12-stained macrophages on airways and vessels in the lung tissue of DEE-exposed wild type animals. Filtered air exposed mice on the other hand showed no staining for MMP12, which is consistent with the observation obtained from Galectin-3-stained macrophages. Interestingly, we observed enhanced number of Galectin-3-stained macrophages in diesel exposed mice.

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Submerged exposure to particulate matter derived from log wood and pellet combustion

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Experiment

We burned logs of birch, beech and spruce, which are used commonly as firewood in Central and Northern Europe in a modern masonry heater, and compared them to the particulate emissions from an automated pellet boiler fired with softwood pellets. Particles were collected using a Dekati® gravimetric impactor (DGI), which separates particulate matter (PM) according to its aerodynamic diameter (d_a) into five stages: (1) $PM_{0.2}$ (d_a< 0.2 µm), (2) $PM_{0.2-0.5}$ (d_a = 0.2–0.5 µm), (3) $PM_{0.5-1}$ (d_a = 0.5–1.0 µm), (4) $PM_{1-2.5}$ (d_a = 1.0–2.5 µm), (5) $PM_{>2.5}$ (d_a> 2.5 µm). Because over 90 % of the primary emissions from heating appliances like the ones we used are smaller than 1 µm, we combined fractions (1), (2) and (3) to obtain the PM_1 size fraction of the emissions. We determined the chemical composition of the PM samples (elements, ions, and carbonaceous compounds) and then assessed inflammation by enzyme-linked immunosorbent assay (ELISA), oxidative stress by 2‘,7‘-dichlorodihydrofluorescein diacetate (H_2DCF-DA) assay. We furthermore determined the cytotoxic effects of the PM samples by various assays, as well as genotoxicity by single-cell gel electrophoresis (SCGE) assay. All of the PM1 samples were tested in three different cell culture setups to emulate mitigating or aggravating effects of cell/cell interactions on PM toxicity. We used two monocultures of either human macrophage-like cells (THP-1) or human alveolar epithelial cells (A549), and a co-culture of these two cell lines. THP-1 cells are immune cells, which can mimic the immune response caused by exposure to PM. A549 cells resemble type II pulmonary epithelial cells and thus are a suitable model to investigate the effects of PM exposure on the alveoli. The adverse effects of the PM samples were compared between these setups and the observed adverse effects were correlated with the chemical composition of the PM samples.

Results and Discussion

The chemical composition of the samples differed significantly, especially with regard to the carbonaceous and metal contents. Also the toxic effects in our tested endpoints varied considerably between each of the three log wood combustion samples, as well as between the log wood combustion samples and the pellet combustion sample. We detected clear differences in the endpoints between the mono- and co-cultures. In A549 cells we found only an increase in the production of IL-8[2] while the other measured cytokines were below detection level.

The absolute concentration of IL-8 by THP-1 cells after exposure to the PM1 samples was approximately the same as that of the A549 cells, but the basal level of IL-8 in THP-1 cells was lower, thus the relative increase by THP-1 cells was higher than that of the A549 cells. Contrastingly, in the co-cultured-cells, the basal level of IL-8 was already approximately 47 ng/ml, compared to 100 pg/ml in THP-1 cells and 230 pg/ml for A549 cells. The relative increase in the production of IL-8 however, was smaller in the co-cultured cells than in either monoculture. Correlation analysis showed that mostly ions (Na, K, and Cl) and metals (Cr, Cu, and Pb) were associated with an increase in inflammatory parameters. This further strengthens previous findings that mainly the metals in PM emissions cause inflammatory reactions [3].

The PM1 sample from the pellet combustion had the least effects on cell viability in all three cell culture setups; all of the log wood combustion samples induced a far greater reduction cell viability. This pellet combustion PM_1 sample is composed mainly of inorganic components, such as sodium, potassium and sulfate[2], all of which have been shown to cause very little toxicity in previous studies [4,5]. Correlation analysis revealed that carbonaceous components, especially OC and EC,had the highest positive associations with a reduction of the CMA in all three cell culture setups. These compounds were found in significantly higher concentration on the PM1 samples from the log wood combustion.

The production of reactive oxygen species was the highest in epithelial cells. Macrophages seemed to have protective effects against oxidative stress from the PM samples. A previous study6 found that alveolar macrophages protected A549 cells from oxidative damage and attributed this to the macrophages’ ability to effectively sequester Fe-ions from the medium and thus minimize Fe-driven (Fenton-type) oxidative reactions.

All samples caused DNA damage in macrophages, whereas only beech and spruce log combustion samples caused DNA damage in epithelial cells. Correlation analysis showed that in A549 cells Fe, Ca and NO_3- and PAH compounds had strong positive associations with an increase of

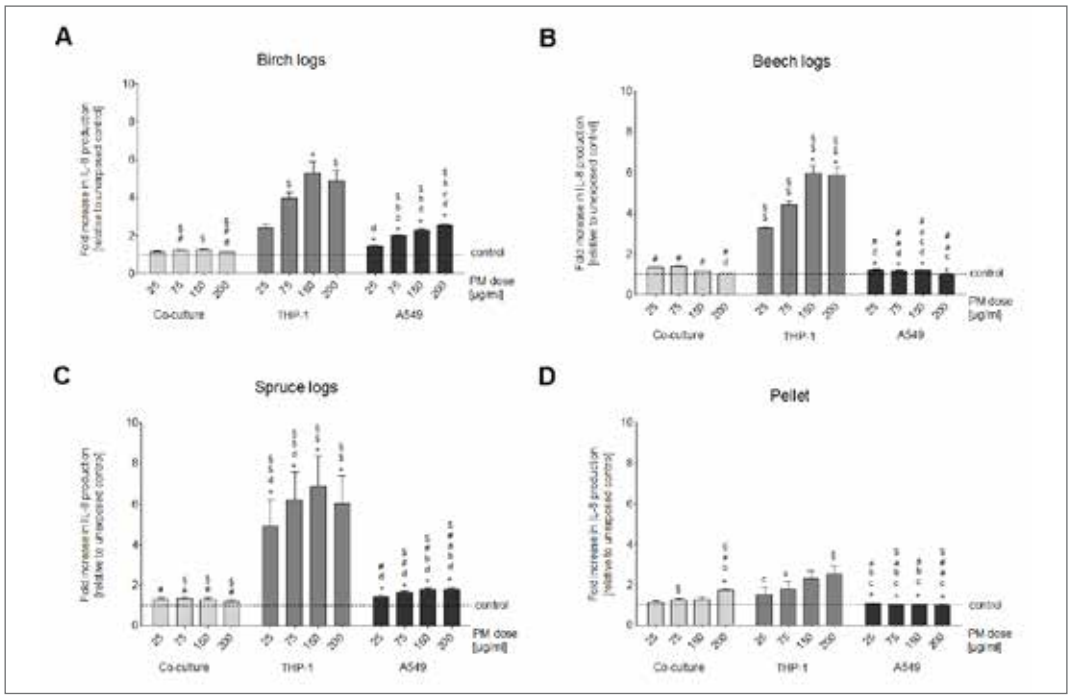

Fig.1 IL-8 production. Production of the pro-inflammatory marker IL-8 after a 24 h exposure of three different cell culture setups (A549 and THP-1 monocultures and A549/THP-1 co-culture) to four doses (25, 75, 150 and 200 µg/ml) of PM1 samples from the combustion of three different wood logs and wood pellets. Bars represent the increase in IL8 secretion by the cells in comparison to unexposed control cells + SEM of the experimental averages. Asterisks indicate significance from blank control. a indicates significance from the birch log PM1 sample, b indicates significance from the beech log PM1 sample, c indicates significance from the spruce log PM1 sample, d indicates significance from the pellet combustion PM1 sample; § indicates significance from the A549 monoculture, # indicates significance from the THP-1 monoculture, $ indicates significance from the A549/THP-1 co-culture.

the percentage of DNA in the tail, in addition to PAH compounds2. Contrastingly, for THP-1 cells we did not find the same correlation between the Fe and Ca content of the samples and DNA damage. Rather, EC and OC had high positive correlations in addition to the PAH compounds.

Conclusion

The difference in the toxicological potential of the samples in the various endpoints indicates the involvement of different pathways of toxicity depending on the chemical composition. All three emission samples from the log wood combustions were considerably more toxic in all endpoints than the emissions from the pellet combustion. In vitro testing of the toxicity of combustion-derived PM in monocultures of one cell line, however, is inadequate to account for all the possible pathways of toxicity. Conclusively, our results support that OC, EC and PAH compounds are associated with the observed cytotoxicity in all three experimental setups, while the metal content correlates with the inflammatory potential of the samples. Furthermore, our results suggest that the content of PAH compounds in the PM samples is the main cause of DNA-damage. Thus, the physicochemical composition of the sample determines which pathway of toxicity is induced. Finally, it is clear that all of the tested wood combustion-derived PM samples induce adverse effects and that rather than preferring one type of fuel or combustion appliance over the other, the main effort should be put into minimizing PM emissions overall. The results obtained from these in vitro experiments will need to be evaluated against results from in vivo studies to find the most suitable in vitro setups and endpoints and to use in vitro toxicity screening in favor of in vivo screening where applicable.

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Carbonyl compounds in the gas phase are critical determinants of wood smoke toxicity

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Experiment

In order to identify the toxic constituents of wood smoke aerosol, we exposed human A549 and BEAS-2B cells to 1:10 diluted wood smoke using a recently developed air-liquid-interface exposure system (Mülhopt2016) (Fig1A). We first characterized the effects of wood smoke by transcriptional profiling using mRNA-sequencing. The disturbance of affected cellular pathways identified by bioinformatic analyses was verified by targeted analysis of selective markers by established assays. To determine the responsible aerosol constituents initiating the molecular actions of wood smoke, we hypothesized that the transcriptional signatures can be used to query toxicogenomic databases and discover compounds triggering similar gene expression profiles thus providing potential lead candidates.

Regulation of global gene expression is dominated by gaseous components in wood smoke

In order to characterize the effects of wood combustion aerosols on lung cells in an unbiased manner, we evaluated global changes in gene expression by next generation sequencing. The transcriptome of A549 and BEAS-2B cells was analyzed after ALI exposure to clean air, complete aerosol and particle-filtered aerosol (combustion gases). In striking contrast to expectations, gene regulation after treatment with complete aerosol is very similar to the one observed upon exposure to the gas phase only (Fig1B). As the complete aerosol is the composite of particulate and gaseous phase, this result indicates that gaseous combustion products are the dominant drivers of changes in gene regulation by wood combustion emissions. As the biological response to wood smoke is correlates fairly well between the alveolar transformed A549 and bronchial non-transformed BEAS-2B cells the underlying adverse events and mechanisms seems to be conserved across cell types of different origin. Pathway enrichment analysis revealed perturbations in various DNA damage recognition and repair pathways (Fig 1C). In addition, MAP kinase signaling and energy metabolism was affected. As systems biology approaches such as pathway enrichment analyses only provide a first clue on the disturbance of critical biological networks, we further verified these predictions by more directly assessing the impact of wood smoke on selected and toxicological relevant processes.

Verification of pathway perturbations and identification of carbonyls as main drivers of toxicity

As predicted by the GO term analysis, wood smoke induced DNA damage evidenced by strand breaks, independent of the particulate phase (Fig 2A). Gaseous combustion products also trigger MAPK activation (Fig 2B) and disturb metabolic fluxes of TCA intermediates (Metallo2011) (Fig 2C). As the transcriptional profile induced by filtered wood smoke partially resembles the pattern provoked by protein-crosslinking compounds (PCC) (Lamb2006), we reasoned that carbonyls, which also act as PCC (Montaner2007), could be the causative agents in wood smoke responsible for toxicity. Indeed, the gas phase promoted protein-protein (Fig 2D) as well as DNA-protein (Fig 2G)

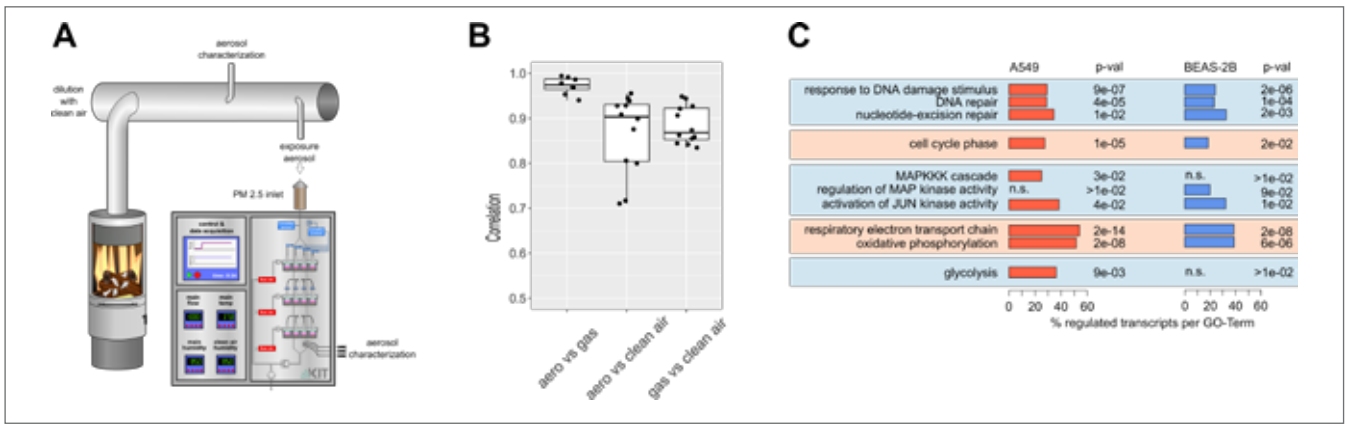

Fig.1 (A) The exhaust from a log wood stove was diluted 1:10 with filtered ambient air in a dilution tunnel used for cell exposure in the exposure system. (B) Pearson correlation values of sequenced sample replicates, each bar represents the combined values of A549 and BEAS-2B comparisons (n ≥ 8 from at least 2 independent experiments per cell line). (C) GO-Term enrichment analysis of differentially regulated transcripts of cells exposed to the gas phase compared to clean air.

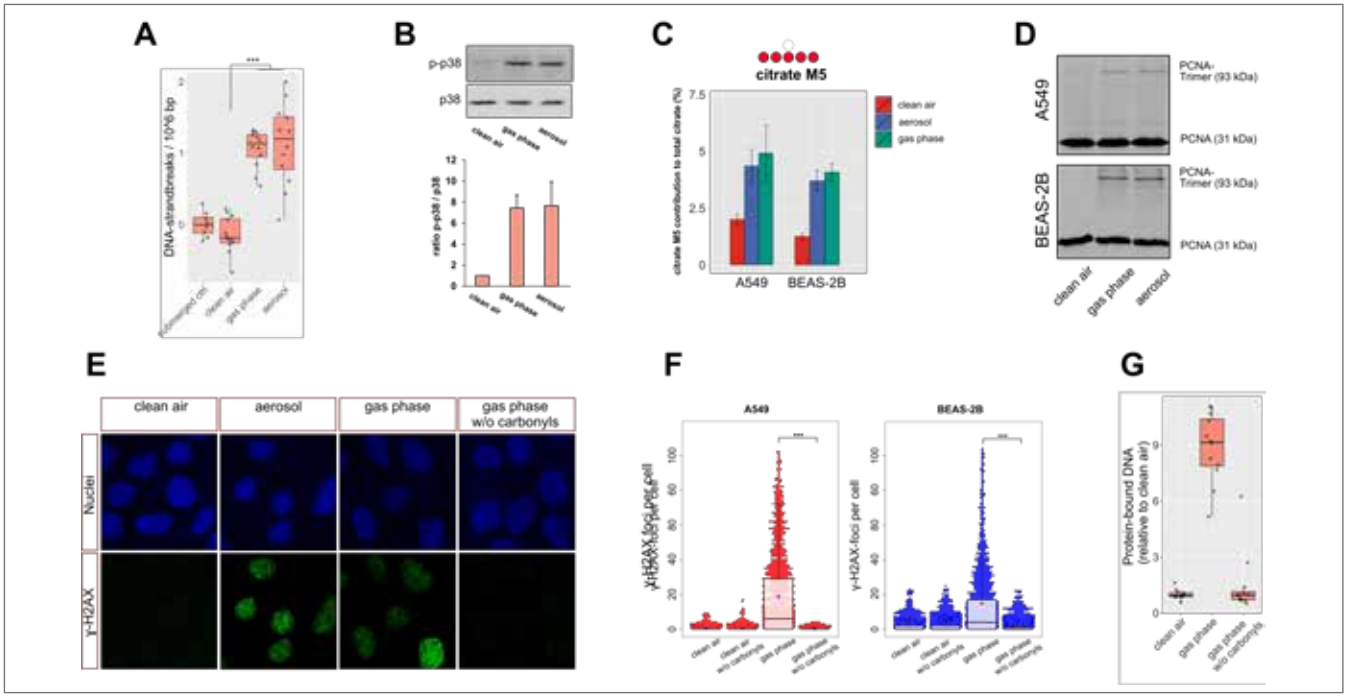

Fig.2 (A) Quantification of DNA-strand breaks by alkaline unwinding. Plotted are individual samples from 3 experiments with A549 cells. (B) Activation of the MAPK p38 determined by immunoblotting. Calculated ratios of p-p38 relative to p38 are based on samples from 3 independent experiments with pooled replicates. (C) Increased reductive glutamine metabolism in response to combustion gases. Data are means ± SEM of 9 samples originating from 3 independent experiments. (D) PCNA trimer formation in A549 and BEAS-2B cells. (E) gamma-H2AX immunostaining of A549 cells exposed to clean air, complete aerosol and particle-free gas phase both with and without carbonyl-stripping and quantification (F). (G) DNA-protein-crosslinking in cells exposed to the gas phase and the carbonyl-stripped gas phase.

cross-links, as well as subsequent DNA damage (Fig.2 E). Removal of carbonyls from the gas phase abrogated all of these toxic effects (Fig. 2 E-G).

In conclusion, we could show that ALI exposure in combination with systems toxicology approaches is a successful strategy to identify drivers of toxicity in complex heterogeneous mixtures like combustion derived aerosols. The dominating effect of volatile compounds on all identified changes of cellular processes is striking. This result is highly relevant for the risk assessment of aerosols, as so far gas phase constituents are hardly considered as potential hazards and are often not accounted for in experimental designs. In the case of beech log wood combustion, the effects of the gas phase seem to be dependent on carbonyls like FA and acetaldehyde. As highly soluble carbonyls are usually absorbed already in the upper respiratory tract they can lead to tumorigenesis e.g. nasopharyngeal cancer (Baan2009). Whether carbonyls present in wood smoke would also affect the lung needs to be addressed by appropriate in vivo studies. In this context, it is of particular interest to investigate whether hygroscopic particles may adsorb carbonyls and thus act as vectors to deliver carbonyls to regions in the lung that are usually not targeted by water soluble compounds. Regardless of the impact of carbonyls on the deeper lung regions under physiological conditions, their genotoxic actions are still of high concern regarding health effects in the upper respiratory tract. Our results indicate that advanced and physiologically more relevant ALI systems enable the investigation of noxious gases in complex aerosols. Furthermore, this work sheds light on the hitherto unknown complexity of systems perturbations by wood smoke which, for the first time, provides a basis to understand mechanisms of toxicity and allows identifying critical constituents. As worldwide millions are exposed daily to wood smoke and the health of many is affected, future research needs to build on these initial findings with the aim of mitigating the negative impact of one of the most abundant aerosols.

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The Carbon Concrete Composite project (C3): Investigation of the Potential health risks caused by use and processing of carbon concrete materials

T. Streibel, C. Knizia, T. Kanashova, S. Öder, R. Zimmermann (UR/HMGU), L.Hillemann (TU Dresden), M. Saraji-Bozorgzad, A. Walte, S. Ehlert (Photonion), M. Berger, T. Krebs (Vitrocell), D. Konczack, S. Grosse, A. Rudolph (TOPAS)

Carbon concrete is a novel building material currently under intensive investigation concerning its applicability to replace ferroconcrete in the construction of bridges and buildings. The introduction of carbon concrete is supposed to bring about several advantages such as exhibiting less corrosion and thus much longer endurance as well as being much lighter than ferroconcrete.

However, when researching the structural engineering and materials scientific properties of carbon concrete, one must not neglect aspects of safety and health risks. During the life cycle of carbon concrete there is the possibility of releasing particulate matter, which may partially constitute out of airborne respirable fibres or respirable dust. In the here delineated project the potential exposure of humans will be evaluated and health hazards will be determined.

For this, laboratory test benches have to be developed and constructed for simulation of a defined and reproducible release of particulate matter by mechanical treatment of carbon concrete, in this case friction sawing. The evolving aerosol is characterized extensively for its chemical, physical, and morphological properties. Furthermore, the Air-Liquid –Interface technique for exposure of lung cell cultures has to be enhanced to serve as a platform for direct investigation of dust and aerosol released by the cutting of carbon concrete. Biological effects are subsequently analyzed by various omics-methods (e.g. Transcriptomics and Proteomics).

Fig.1 shows a photograph of the laboratory test bench for friction sawing. The cutting apparatus is connected to a heating box, which serves as an interface to the mobile photo-ionization mass spectrometer. Gaseous compounds that are formed during the sawing process are sucked through the box to the ion source of the mass spectrometer. In parallel, particles are sampled on filters with added sizing filters, allowing the sampling of coarse dust, PM10, and PM2.5, respectively.

Table 1 depicts concentration values of gaseous compounds that have been released during the cutting process. Besides carbon concrete, common concrete and the carbon fibres that are incorporated into the concrete to produce carbon concrete are investigated. With concrete, almost no organic material is released. Carbon concrete releases especially 1,3-butadienen and styrene besides acetaldehyde and toluene. These organic species are clearly derived for the carbon fibre material. The concentrations are however very low when compared to the MAK-values, which represent the maximum allowed concentrations at working places.

The sampled particles were analyzed for their content of organic compounds with a thermal analytical device coupled to photo-ionization mass spectrometry, which detects the evolved gas. The results are identical to the gas phase analysis.

Fig.1 Photograph of the best bench for friction sawing

Preliminary experiments concerning cell toxicity have been conducted applying the so-called submerse method, where sampled particles are directly put on a cultured cell medium for 48 hours in defined concentrations. Fig.2 shows the cell toxicity, when the cells are subjected to dust from the cutting of concrete and carbon concrete, respectively. Several standard particles such as hydrophilic pyrogenic silica, quartz, and Printex 90, a sooty material, are depicted in comparison. Two important conclusions can be drawn from these first toxicity tests. First, there are no significant differences between concrete and carbon concrete. Second, the reference material exhibits higher toxicities than the concrete dust. These results however have to be more thoroughly investigated with the Air-Liquid-Interface, which allows more realistic exposure conditions. This system is currently under construction.

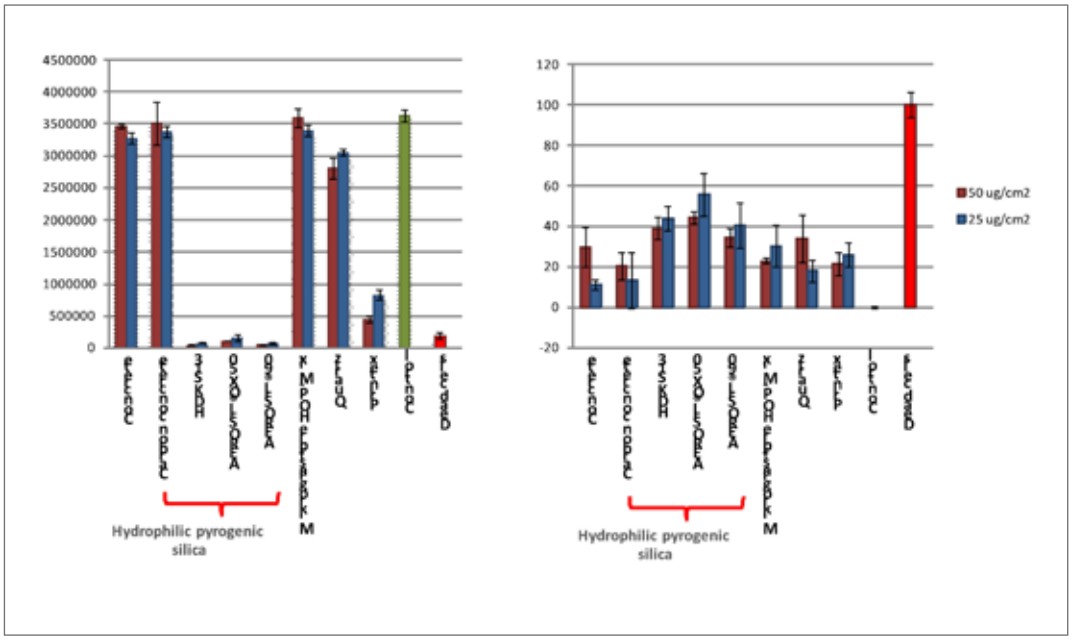


Fig.2 Cell toxicity tests (submerse configuration) using the ATP –(left) and LDH-assay (right)

Sample		Concrete		Carbon concrete		Carbon fibres with SB-polymer		MAK-value
Compound	m/z	$C_{(SPI)}$ [µg/m³]	$C_{(REMPI)}$ [µg/m³]	$C_{(SPI)}$ [µg/m³]	$C_{(REMPI)}$ [µg/m³]	$C_{(SPI)}$ [µg/m³]	$C_{(REMPI)}$ [µg/m³]	c [mg/m³]
Acetaldehyde	44	1.3	N/A	3.3	N/A	5.8	N/A	91
1,3-Butadien e	54	0.03	N/A	4.7	N/A	3.9	N/A	11[2*]
Toluene	92	0.02	0.005	0.2	0.2	0.3	0.3	190[1]
Styrene	104	0.04	N/A	2.1	N/A	5.0	N/A	86[1]

Table 1 Gas phase concentrations of organic trace gases evolving from friction sawing

Data Integration – Constructing Chemical-Gene Regulatory Networks

S. Smita, O. Wolkenhauer (UR/LSB), T. Streibel, J. Orasche, T. Kanashova, S. Öder, R. Zimmermann (UR/HMGU)

The described advancement in instrumentation techniques made it possible to identify the compositions and concentrations of various chemicals and metals in combustion aerosols as well as to elucidate the biological impacts on cell cultures However, the prediction of combustion aerosols induced toxicity end points is difficult due to the large number of non-linear chemical-biological interactions. It is evident that some chemicals present in the combustion aerosols up-regulate certain genes/ proteins, while other chemicals down-regulate them, making the prediction of toxicity of a mixture of chemicals a challenging task. Moreover, the presence of a large number of feedback and feedforward regulatory loops makes the entire prediction process highly dynamic.

In HICE a regulatory network has been developed to identify molecular level events that contribute toward the understanding of adverse outcomes due to the exposure of combustion aerosols. For this, information about chemical-gene/protein interaction was collected from Comprehensive toxicogenomics database (CTD) (http://ctdbase.org); chEMBL (https://www.ebi.ac.uk/chembl); STITCH (http://stitch.embl.de), AOP KB (http://aopkb.org); ToxCast from US EPA (https://www.epa.gov/chemical-research/toxicity-forecaster-toxcasttm-data). Chemicals present in wood combustion aerosols were screened for which interacting partners (genes/ proteins) in humans are available in the above mentioned resources. For all those chemicals then initial interaction networks were generated using the basic expression e.g. “chemical X interact with gene/protein Y”. The framework was evaluated using the exposure of lung epithelial cell line A549 to the combustion aerosols generated by burning of beech, birch and spruce wood.

In total 51 chemicals were identified, for which the biological interacting partners are available in chemical gene interaction databases. 13 of them revealing the highest concentration were labeled as “priority chemicals”. These are predominantly PAH or oxy-PAH such as chrysene and benzopyrenes and one phenolic species (acetovanillone). Fig.1 depicts the wood type specific networks. An interesting fact from these networks is the somewhat unique role of the phenolic compounds acetovanillone. It is inhibiting the activity of several genes that are activated by PAH. Despite the fact that acetovanillone is regulating other genes (such as genes associated with atherosclerosis), this could be a valuable contribution to the discussion about the potential mitigating role of phenolic species with respect to acute PM-induced health effects.

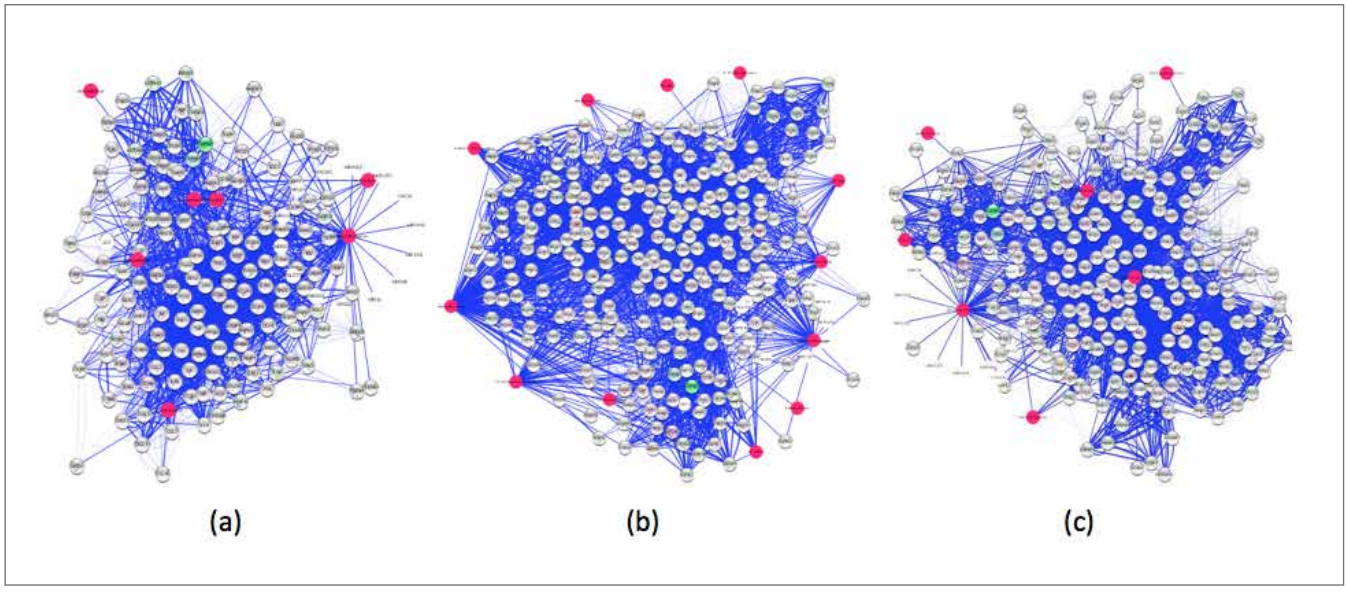


Fig.1 Wood type-specific combustion aerosol network for a) beech, b) birch, and c) spruce. These networks are generated by merging interaction networks of priority chemicals present in each of the combustion aerosols. Chemicals are shown as red colour nodes.

Education

Experimental learning: you can do it!

The HICE PhD students had several opportunities of working together during the 5 years research project. The four measurement campaigns at the University of Rostock, Germany, and the University of Eastern Finland, Kuopio, gave them the exceptional possibility for training during experiments. The PhD students were involved in the preparation of the campaigns and independently conducted their measurements during the four weeks experiment rounds. The supervisors gave them a helping hand and were on demand when questions and problems arose. Biologists, chemists, physicists and engineers collaborated on the common goal to find out about the health effects and chemical characterization of emissions from ships, cars and wood stoves. Around 40 people were involved in the preparation, organisation, logistics, scientific conduct and research. Huge data has been gathered, measured and analyzed. The results have been published 40 publications.

Show your work to international fellows

The students presented their works in front of an international audience and of their project partners during three summer schools and workshops that took place in Prague 2013, Munich 2014 and Cardiff 2015. The topics ranged from analytical methods, challenges of health and aerosol research to data structure and statistical data integration. Also HICE organized together with the German Association for Aerosol Research a Workshop on "Aerosol Emissions from Fossil Fuel and Biomass Combustion" as part of the European Aerosol Conference (EAC) 2013. A HICE session on "Aerosol and Health: A challenge for chemical and biological analysis" took place at the Analytica Conference 2014, the world's biggest fair on laboratory technology, analytics and bio tech. Leading experts from the fields of aerosol chemistry and physics, toxicology, and cell biology gave lectures and discussed their research with the young students at the HICE Summer School 2014.

Get to know other labs and workflows

The partners from the University of Eastern Finland tested their cell exposure devices in the laboratory of the Helmholtz Zentrum München. They aimed to test new approaches for enhancement of particle deposition by exposure with defined aerosol sources such as the CAST device. The group at the Karlsruhe Institute for Technology (KIT) invited the HICE students to learn about the handling of the air-liquid interface system for the exposure of human lung cell cultures to aerosols. They got to know the basic operation principles and the preparation of the cells before being implemented into the interface system. After the experiments, that ran with wood smoke the students learned about the extraction procedures of the cells.

The Metabolomics Group of the Luxembourg Centre for Systems Biomedicine (LCSB) organised a lab training course on profiling cellular metabolism. During the one week course the HICE students analyzed metabolic effects on human lung cancer cells caused by wood combustion-derived nanoparticles. To measure intracellular metabolic flux changes, the scientists applied stable-isotope tracers. After the cultivation of the cells, they extracted intracellular metabolites and prepared them for chromatographic and mass spectrometric measurement. Finally, they analyzed the data and detected particle-induced changes in metabolite amounts and intracellular fluxes.

It's science, virtually!

The students followed weekly lectures on science and technology such mass spectrometry and its applications. International experts presented the newest developments in research and industry and invited to open discussions. The lectures were hold at the University of Rostock and transmitted via video conferencing to all HICE Partners.

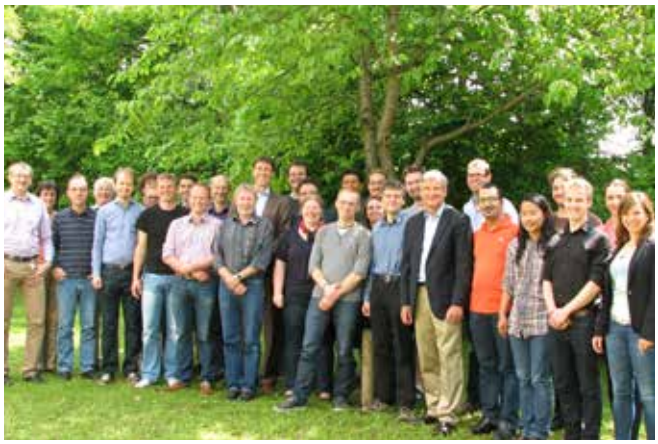
HELENA – Helmholtz Graduate School of Environmental health

All HICE PhD students and young scientists were embedded in the graduate and mentoring program of their host universities. Furthermore they had the opportunity to participate in the Helmholtz Graduate School of Environmental Health – HELENA which is established together with the LMU Munich and the Technical University of Munich (TUM). HELENA offers courses to foster independent scientific working as well as training such as self-management, scientific writing and presentations. PhD students are assigned a personal thesis committee for intensive guidance and mentoring. They can earn a certificate in environmental health research as an extra qualification. Post docs are advised and supported in their career-planning. HELENA promotes international networks by financially supporting the attendance at conferences and research stays at other consortium organizations.

Consortium Meetings

From 2012 to 2016 the HICE partners regularly met as a consortium as well as in smaller groups to discuss the results and proceedings of the project. Biostatistics experts from HICE as well as from the Institute for Computational Biology at the Helmholtz Zentrum München and the Faculty of Biology at the University of Mainz came together in January 2016 to discuss the statistical data integration which is incorporated in one main work package of HICE. Theory and practice seminars concerning the air liquid interface system that HICE worked with in its several measurement campaigns were hold at the Karlsruhe Institute of Technology. In January 2015 the HICE biologists hold a meeting about the different omics analyses that are the core of the biological work in the project at the Environmental Research Station on the Zugspitze.

The HICE Consortium Meetings took place at the University of Rostock and at the Helmholtz Zentrum München once per year. The Scientific Advisory Board of HICE also participated in the meetings and consulted the scientists on the proceedings of the project.



Group Photo taken at one of the HICE consortium meetings

Scientific Advisory Board

Advisory board member Per E. Schwarze, NIPH, Oslo, Norway

At the HICE consortium meeting results from the project and plans for the remainder of the project were presented. An impressive online and offline chemical characterization was shown of the particle fraction from diesel fuel and ship heavy fuel oil burned in a ship diesel engine. Of notice, the heavy fuel oil exhaust (HFO) contained more organic material and more nanoparticles than the diesel fuel exhaust. This is of particular interest since some research indicates that certain classes of chemical compounds are especially important for health effects. In addition smaller particles are regarded as potentially more hazardous than larger particles of the same composition.

In the cytotoxicity tests the exhausts at the concentration chosen did not seem to be toxic. Both exhausts at this subtoxic concentration have strong effects in lung cells that were exposed in an air liquid interface direct exposure system. Analysis included different omics systems such as transcriptomics and proteomics. Whereas the HFO exhibited strong effects on proinflammatory responses and oxidative stress, DE affected fundamental cellular systems such as protein degradation and synthesis to a greater extent. The exposure lasted only for a few hours. In another set of experiments Ship diesel fuel exhaust was compared to wood smoke from a small scale combustion unit.

The wood smoke experiments revealed differences in emissions between different wood types. Aging resulted in a substantial increase in organic matter in PM.

Gasoline car emission varies with fuel composition (ethanol content) and speed. The cellular responses differ somewhat between the different fuels and how diluted the exhaust is when the cells are exposed.

The project brought new insights into the composition and effects of emission from different transport and heating sources. The project provides important information that feeds into the database that can be used to determine how to reduce exposure and health impact. Overall the system proved to be a valuable research tool that can be developed further. Of major interest would be to monitor longer lasting exposures, possibly at lower concentrations, and investigation of biomarkers and mechanisms, relevant to disease development.

Dissemination

Selected presentation of HICE projects on national and international conferences

2017

36th Annual AAAR Conference (American Association of Aerosol Researchers), Raleigh, NC, USA, October 17th–20th 2017
- Zimmermann et al., *Investigation of Combustion Aerosol Toxicity within the HICE-Project: Chemical Composition of Different Combustion-Emissions and Their Molecular Biological Effects on Air/Liquid-Interface Exposed Lung Cells (in-Vitro) as well as on Aerosle Exposed Mice (in-Vivo).*

6th Int. Symposium on Ultrafine Particles – Air Quality and Climate, Brussels, Belgium, May 20th-21st 2017 (Invited plenary lecture, fully funded)
- Zimmermann *et al., Investigation of the toxicity of combustion aerosols within the HICE-project: Chemical composition of ship-, car- and wood combustion-emissions and their molecular biological effects on air/liquid-interface exposed lung cells.*

2016

EAC 2016, Tours, France, 4th-9th September 2016
- Zimmermann et al., *Studying the biological effects of combustion aerosols on air/liquid-interface exposed human and murine lung cells within the HICE-project: Composition and molecular biological effects of emissions from wood combustion, ship emissions and car engines.*

Seminar at Institute of chemicalkinetics and combustion SB RAS, Novosibirsk, Russia, March 17th 2016
- Zimmermann et al., The HICE Project: Composition and biological effects of ship diesel engine, wood combustion and car engine emission aerosols.

2015

Aerosols and Health, Russian-German Worksshop, IAO, Tomsk, Russia, 29th-31st July 2015
- Zimmermann and the HICE consortium, *Research initative on wildfire aerosolemisions and dangereous imacts on environment and health – Introduction on the HICE concept.*

HICE Summer School: Data Structure & Data Integration Cardiff, UK July 2nd-4th, 2015
- Zimmermann and the HICE consortium, *Combustion-derived aerosols and their health effects: Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) –the ship emission study.*

HICE Summer School: Data Structure & Data Integration, Cardiff, UK July 2nd-4th, 2015
- Zimmermann, *Introdutionary remarks and overview on the HICE-project*
- Rüger, *Chemical particle analysis by high resolution mass spectrometry – GC-APCI-FT-ICR-MS*

International Workshop of Helmholtz Zentrum München and US-EPA: "Comprehensive Evaluation of Acute and Chronic Environmental Factors and Their Interaction with Genetic, Epigenetic and Social Factors in Germany and the U.S.", München and Chiemsee, Germany, March 17th-19th 2015
- Zimmermann, *Aerosol analysis within the HICE framework.*

HICE on web, news and TV: Highlights

5 years of HICE research resulted in more than 40 publications, in which the findings and the progress of our research on the impact of anthropogenic aerosols on human health are summarized in scientific peer-reviewed journals. In addition, our research created a stir on web, news and TV. Highlights from 2015 – 2017 are listed below. Last but not least, the HICE website summarizes the whole dimension of 5 years of research from the vision to the publications: https://www.hice-vi.eu/index.html.

WEB

Inside Science
December 2016. 'Clean-burning'-Fuels May be Worse for the Lungs. Artificial lung reveals surprising dangers from pellet burners and diesel-fueld ships.

The article describes the effect of different fuel exhausts on artificial lung cells and their response to exhaust exposure. The so called 'clean' fuels, however, induced distinct detrimental effects. By exposing artificial lungs to ship exhausts, inflammation was triggered; diesel caused an even stronger response than heavy fuel. According to Markus Kalberer, an atmospheric chemist at the University of Cambridge in England, Zimmermann's team used an impressive suite of techniques to analyze the response patterns of the cells, gaining detailed information about metabolism and gene activity.

Link to the online article: https://www.insidescience.org/news/clean-burning-fuels-may-be-worse-your-lungs#overlay-context=users/nrogers

Spiegel Online
June 2015. Leise rieselt der Ruß: Ship exhaust gases harm human's health. Why are they still allowed to pollute the air?

Exhaust gases of low-sulfur fuels can be sent through catalizors and soot particle filters and hence lower the threat on human health. Nevertheless, most ships are driven on heavy oil. The article describes the ignorance of the International Maritime Organisation with environment and health although recent scientific results reveal ship exhausts to impair human lung cells.

Link to the online article: http://www.spiegel.de/spiegel/print/d-135434730.html

NEWS

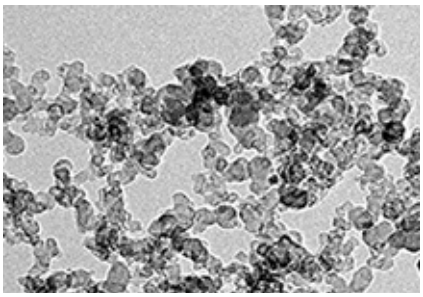
Experiments on wood combustion
October 2016. HICE searches for new insights into the health effects of burning wood in households. From 19 September to 7 October 30 scientists from Germany and Finland ran an experimental campaign at the University of Eastern Finland (UEF) in Kuopio.

Source: University of Eastern Finland (UEF)

The researchers burned spruce and pine logs as well as softwood pellets in wood stoves to see how the combustion directly affects lung cells. Therefor two air-liquid interface systems were used. The cells were also exposed to diesel emissions. By this the differences between the effects of wood and diesel should be shown under the same experimental conditions. Further understanding about the effects of wood and diesel combustion on human health will be gained by tests with animals that were also pursued during the campaign. The first HICE experimental campaign on wood combustion took place in 2013 and focused on beech, birch and pellets. The results are expected by the end of 2016.

Ship emissions affect lung macrophages

July 2016. Exhaust emissions from ships affect the health of people living nearby coasts. Scientists from the Helmholtz Virtual Institute HICE have shown the effects on lung macrophages. These are immunocompetent cells and play an important role concerning lung diseases like COPD. The results have been published in the renowned open access journal PLOS ONE.



Source: University of Rostock

"The macrophages react more sensitive than lung epithelial cells on inhaled particles", explains Sean Sapcariu, the first author of the paper and PhD Student at the University of Luxembourg, a cooperation partner in HICE. "They represent the 'first line of response' in fighting against foreign objects like germs or aerosol particles that intrude the lung." In their experiments the scientists exposed the cells to two different types of ship fuel: heavy fuel oil and diesel. "We found different strengths of inflammatory responses and other molecular biological pathways, but similar toxic effects", Sapcariu adds. With this the previous results of HICE from 2015 concerning the biological reactions of human epithelial lung cells to diesel and heavy fuel oil have been confirmed and further validated.

Link to news release:

http://www.helmholtz-muenchen.de/aktuelles/uebersicht/pressemitteilungnews/article/35186/index.html
https://www.aerztezeitung.de/medizin/krankheiten/asthma/article/915761/feinstaub-schiffsmotoren-schaden-lunge.html

Link to Publication: http://journals.plos.org/plosone/article?id=10.1371%2Fjournal.pone.0157964

Wood and diesel experiments in 2016

March 2016. The annual HICE Consortium Meeting took place in Munich on the 25th and 26th of February. Over 40 scientists from 13 different partner organisations participated in the meeting and planned the activities of the upcoming year.

Source: Helmholtz Zentrum München

In 2016 HICE will perform experiments with wood and diesel. The experiments will take place at the Helmholtz Zentrum in Munich as well as at the University of Eastern Finland. It is intended to look for the effects of wood and diesel combustion on lung cells and to perceive further understanding about the effects on human health. The scientists also work on the finalization of the results from the experiments with gasoline and ethanol hold at the University of Rostock in 2015.

Studies on gas and bio-fuel exhausts

October 2015. The current discussions on harmful exhausts emitted by cars shows that the research on the emissions from diesel and gas fuel has been not completed by far. In April and May 2015 the HICE scientists examined the effects of gasoline at the University of Rostock. They also investigated bio-ethanol as the current favored alternative to fossil fuels.

Source: IT- und Medienzentrum/ Universität Rostock

The scientists used the set-up and the methodology that was developed in HICE and already applied for ship diesel emissions as well as for emissions from wood combustion. For this they ran an engine with bio-ethanol and gasoline. Lung cells were exposed to the fuels under realistic in vitro conditions in an air-liquid interface exposure system. The interdisciplinary work of HICE was again the main part of the campaign: Chemists and physicians analyzed the chemical composition and physical properties of the particles and gas phase. Biologists will analyse the cellular responses at the transcriptome, proteome and metabolome level. First Results are expected for 2016.

Summer school on data integration
July 2015. The young scientists in HICE learned about the challenges of data integration at the Summer School 2015 hosted by the University of Cardiff. Regarding the interdisciplinarity of the project the topic of integration is crucial for the common results.

For that all students were given the opportunity to present their data from omics analyses as well as from chemical particle and gas phase analyses. A poster session specified the data they gained from the measurement campaign on wood combustion that took place at the University of Eastern Finland. Experts from the Helmholtz Zentrum München, the Max Delbrück Centre Berlin, the University Mainz and from the University of Rostock referred to the comprehensive work of the students and presented approaches for solutions in data integration and system modelling.

Ship emissions stress lung cells
June 2015. Emissions from ship fuels have massive impact on lung cells – these results were published by scientists of HICE in the journal PLOS one. Both Heavy Fuel Oil (HFO) and Diesel have similar strong effect on the cells. This is especially interesting as the diesel is seen by regulation authorities as the "cleaner" fuel. Ships have to use it in areas close to harbors, while the use of HFO is only allowed on the open sea.

„Surprisingly the cells reacted stronger towards the Diesel, that contains more soot but less toxic compounds than the Heavy Fuel Oil", says Dr. Sebastian Öder, first author of the paper. The Diesel emissions affected essential cellular pathways such as energy metabolism, protein synthesis and chromatin modification. The biological response of the cells was all in all broader than the response on the Heavy Fuel Oil. The reactions to HFO emissions were dominated by oxidative stress and inflammatory responses. The HFO emissions contained high concentrations of toxic compounds such as metals and polycyclic aromatic hydrocarbon, and were higher in particle mass. These compounds were lower in the Diesel emissions, which in turn had higher concentrations of elemental carbon ("soot"). Common cellular reactions included cellular stress responses and endocytosis.

"We highly recommend to reduce the emissions from ships by installing exhaust filters like it is common for road traffic", says Prof. Dr. Ralf Zimmermann, the speaker of HICE. "To replace Heavy Fuel Oil with Diesel is with regard to our results not an adequate method to reduce the health effects from ship emissions." In future studies the scientists want to focus on the role of the soot and on emissions of Marine Gas Oil.

Link to news release: https://www.helmholtz-muenchen.de/en/press-media/press-releases/all-press-releases/press-release/article/26995/index.html
Link to publication: http://journals.plos.org/plosone/article?id=10.1371/journal.pone.0126536

TV PROGRAM

Health effects of cruisers
Prof. Ralf Zimmermann, the speaker of HICE, contributed to TV reports showing the health effects of cruise ships for passengers, crew and the people living in coastal areas.

"Particle filters for modern cars are required by law, particle filters for ships are not", says Prof. Zimmermann. "We see a large number of fine particles, nanoparticles that contain pollutants like polyaromatics which are carcinogenic and cause inflammations." The results of the scientific research on ship emissions have been published in the journal PLOS ONE in 2015 (see above link to the publication). The TV report "Dicke Luft durch Kreuzfahrtschiffe" and "Stinkende Kreuzfahrt- und Ausflugsschiffe – Freie Fahrt für Feinstaubschleudern?" ran on the German broadcasting station ARD on the 8th of March 2017 and the 30th of August 2016, respectively.

March 3rd, 2017

Link to the corresponding reports: http://www.daserste.de/information/wirtschaft-boerse/plus-minus/sendung/schadstoffe-kreuzfahrschiffe-100.html

August 30th, 2016

https://report-muenchen.br.de/2016/12075/stinkende-kreuzfahrt-und-ausflugsschiffe-freie-fahrt-fuer-feinstaubschleudern.html

All press releases from 2015-2017

26.08.2017
tagesschau24 – Alles Öko auf dem Traumschiff?: Alles Öko auf dem Traumschiff? (26.08.2017: 11:15 h – 12:00 h)

05.06.2017
ARD-Alpha – Alles Öko auf dem Traumschiff?: Alles Öko auf dem Traumschiff? (05.06.2017: 17:00 h – 17:45 h)

08.03.2017
Plusminus: Dicke Luft durch Kreuzfahrtschiffe

05.03.2017
tagesschau24 – Alles Öko auf dem Traumschiff: Alles Öko auf dem Traumschiff (05.03.2017: 01:15 h – 02:00 h)

03.03.2017
Ostsee-Zeitung: Weniger Lust auf Dieselautos

18.11.2016
MDR Sachsen-Anhalt – LexiTV – Wissen für alle: LexiTV – Wissen für alle (18.11.2016: 15:00 h – 16:00 h)

01.10.2016
medical special: Schiffsabgase beeinflussen Makrophagen

01.09.2016
Wirtschaftsmagazin FÜR DEN UROLOGEN: Schiffsabgase beeinflussen Makrophagen

01.09.2016
Wirtschaftsmagazin FÜR DEN HAUTARZT: Schiffsabgase beeinflussen Makrophagen

01.09.2016
Wirtschaftsmagazin FÜR DEN ORTHOPÄDEN: Schiffsabgase beeinflussen Makrophagen

01.09.2016
Wirtschaftsmagazin FÜR DEN FRAUENARZT: Schiffsabgase beeinflussen Makrophagen

31.08.2016
tagesschau24 – Report München: Report München (31.08.2016: 10:30 h – 11:00 h)

30.08.2016
ARD – Report München: Report München (30.08.2016: 21:45 h – 22:15 h)

23.08.2016
shz.de: Schifffahrt: Schweröl-Rückstände im Wasser: Kreuzfahrt-Schiffe werden sauberer

23.08.2016
Flensburger Tageblatt: Kreuzfahrt-Schiffe werden sauberer

22.08.2016
Der niedergelassene Arzt: Schiffsabgase beeinflussen Makrophagen

05.08.2016
Bundesregierung: Umweltschutz ist mit an Bord

01.08.2016
F & S: Gesundheitsbelastung durch Schiffsabgase

01.08.2016
Naturheilkunde: Mythos gesunde Seeluft: Schiffsabgase beeinflussen Makrophagen

22.07.2016
VDI nachrichten: Gesundheit: Schiffsabgase schädigen die Lunge

20.07.2016
Ostsee Zeitung: Forscher fordern Partikelfilter-Pflicht für Schiffe

15.07.2016
NDR Info – Logo: Logo (15.07.2016: 21:05 h – 22:00 h)

15.07.2016
3sat – Alles Öko auf dem Traumschiff?: Alles Öko auf dem Traumschiff? (15.07.2016: 20:15 h – 21:00 h)

13.07.2016
scinexx.de: Schiffsabgase beeinträchtigen Immunabwehr

12.07.2016
Kompakt Pneumologie: Schiffsabgase beeinflussen Makrophagen

12.07.2016
Ärzte Zeitung App: Feinstäube schaden der Lunge

12.07.2016
Ärzte Zeitung Online: Schiffsmotoren schaden der Lunge

11.07.2016
wissenschaft.toppx.de: Schiffsabgase beeinflussen Makrophagen

11.07.2016
lifepr.de: Schiffsabgase beeinflussen Makrophagen

25.04.2016
NDR 2 – Der NDR 2 Abend: Der NDR 2 Abend (25.04.2016: 19:00 h – 21:00 h)

01.12.2015
enorm: LUXUSDAMPFER BLEIBEN UMWELTKILLER

27.09.2015
NDR Info – LOGO: Logo: Das Wissenschaftsmagazin
(27.09.2015: 14:05 h – 15:00 h)

25.09.2015
NDR Info – LOGO: Logo: Das Wissenschaftsmagazin
(25.09.2015: 20:05 h – 21:00 h)

25.09.2015
Main-Echo Aschaffenburg: Umweltschutz an Bord nimmt Fahrt auf

04.09.2015
Schwäbische Zeitung Leutkirch: Sauberer Luxusdampfer

03.09.2015
Schwäbische Zeitung: Sauberer Luxusdampfer

24.08.2015
Labor Praxis: Wie Schiffsabgase auf Lungenzellen wirken

18.07.2015
Hamburger Abendblatt – Die Woche Alstertal & Walddörfer: Schiffabgase noch giftiger als angenommen

17.07.2015
Die Zeit: Schifffahrt Mit Filter ist gesünder

16.07.2015
ZEIT Hamburg: Mit Filter ist gesünder

10.07.2015
NDR: Schiffsdiesel weit giftiger als bisher gedacht

15.06.2015
springerprofessional.de: Gesundheitsgefahr durch Schiffsdiesel-Abgase

13.06.2015
Der Spiegel: Leise rieselt der Ruß

11.06.2015
LaborPraxis: Wie Schiffsabgase auf Lungenzellen wirken

11.06.2015
Gefahrstoffe/Reinhaltung der Luft: Wie Schiffsabgase auf Lungenzellen wirken

06.06.2015
schattenblick.de: UMWELT/758: Abgase von Schiffsdieselmotoren erzeugen starke biologische Effekte in menschlichen Lungenzellen (idw)

03.06.2015
solarify.eu: Schiffsdiesel machen krank

03.06.2015
Universität Rostock: Abgase von Schiffsdieselmotoren erzeugen starke biologische Effekte in menschlichen Lungenzellen

28.05.2015
juraforum.de: Internationale Messkampagne an der Uni Rostock

28.05.2015
innovations-report.de: Gesundheitsauswirkungen von Feinstäuben

29.01.2015
EinsPlus – 45 Min: 45 Min: Alles Öko auf dem Traumschiff?
(29.01.2015: 06:15 h – 07:00 h)

02.02.2015
tagesschau24 – Sendung unbekannt: Auswirkungen von Dieselabgasen auf den Menschen

13.02.2015
tagesschau24 – 45 Min – Alles Öko auf dem Traumschiff?:

28.01.2015
EinsPlus – Sendung unbekannt: Ohne Titel

26.01.2015
NDR (inkl. R. NDS) – 45 Min: 45 Min: Dokumentation
(26.01.2015: 21:00 h – 21:45 h)

Outlook

The HICE research program was a forerunner and has established itself in a renowned and very successful research initiative in aerosol and health research. In this context the HICE research strategy will be sustained and expanded in excess of the initial project duration. Based on the recommendation of the midterm review, a part of the HICE activities has been transferred to the basic funding scheme of HMGU. Cooperation contracts between the HMGU and the University of Rostock as well as with the University of Eastern Finland in Kuopio (UEF) ensure a continuation of studies and measurement campaigns according to the HICE-concept ("newHICE"). Further HICE partner are associated in newHICE via third party funding (e.g. from the German Ministry of Education and research, BMBF or EU programmers) and the cooperation network is expanded by further international partners, including the Polytechnic University of Hong Kong, the Jinan University in Guangzhou (China) and the National Autonomous University of Mexico (UNAM). During the HGF-funding period of HICE, primarily direct emissions of different combustion sources were investigated. In the framework of the HICE-continuation, these concepts will be transferred to novel topics and aspects, such as to secondary aerosols (SOA) and non-combustion generated particles and gas phase compounds (e.g. entrainment or mechanical abrasion). The long-term goal is to expand the HICE-concept and to refine the technologies to enable a direct investigation of ambient aerosols. Further new topics are the development and application of improved, disease-specific (multi-)cellular assays for health-effect evaluation, and the improvement of analytical, molecular biological and instrumental methods, including statistical data analysis, data mining and system biological models.

A new project granted by BMBF utilizing HICE methodologies investigates aerosol emissions from the mechanical treatment of carbon concrete composite. Together with other partners at the HMGU the HICE concept is also expanded within a focus network in direction of allergy research (addressing exposure with bio aerosols such as pollen and anthropogenic air pollution). Further research proposals of the HICE partners (DFG, EU) addressing "Aerosols and Health" topical field have been submitted or are in preparation. In 2018 the first newHICE campaign in Finland is focusing on the aging of wood and lignite combustion aerosols and on diesel emissions (electrical power generator). Furthermore, also for the first time direct ALI-exposures from an aerosol aging chamber are performed.

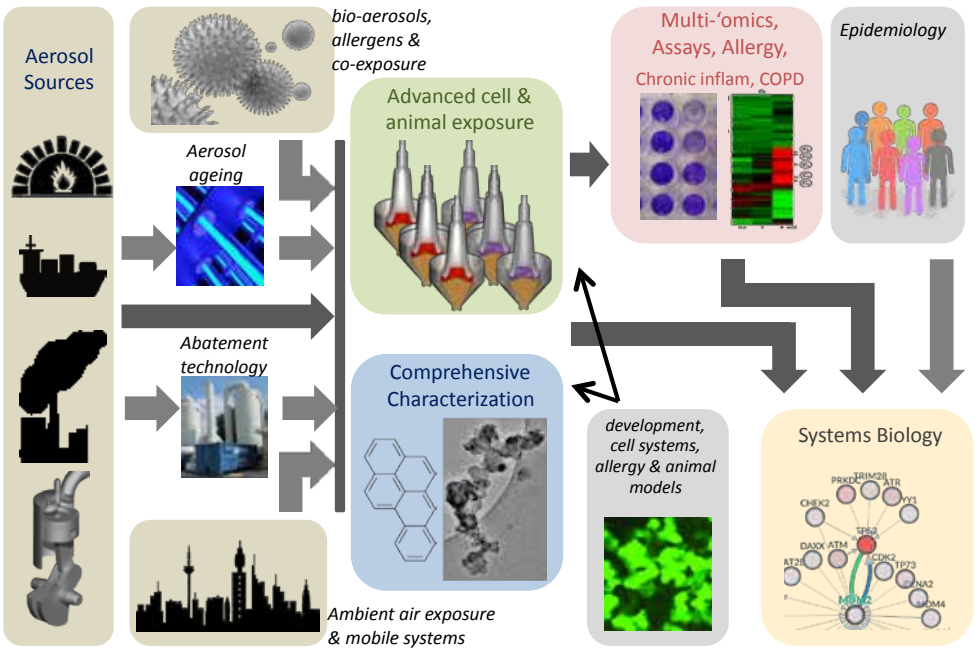


Fig. 1: Concept of newHICE: In addition to diluted combustion aerosols also aged aerosols as well as ambient aerosols will be targeted. A new focus is aerosol and allergy research (exposure with bio aerosols such as pollen). The ALI cell exposure results are validated with animal exposure in order to establish in the long run animal-free test systems. In order to be able to expand the HCIE-concept to ambient air monitoring applications, new cell systems and optimized ALI technology will be developed, e.g. for long time exposures. The data analysis is expanded via cooperation in direction of systems biology.

HICE-related Publications

2017

1. Czech, H.* et al.: A chemometric investigation of aromatic emission profiles from a marine engine in comparison with residential wood combustion and road traffic: Implications for source apportionment inside and outside sulphur emission control areas. Atmos. Environ. 167, 212-222 (2017)
2. Czech, H.* et al.: Chemical composition and speciation of particulate organic matter from modern residential small-scale wood combustion appliances. Sci. Total Environ. 612, 636-648 (2017)
3. Czech, H.*, Schnelle-Kreis, J., Streibel, T.* & Zimmermann, R.: New directions: Beyond sulphur, vanadium and nickel – About source apportionment of ship emissions in emission control areas. Atmos. Environ. 163, 190-191 (2017)
4. Czech, H. et al.: Time-resolved analysis of primary volatile emissions and secondary aerosol formation potential from a small-scale pellet boiler. Atm. Environ., 158:236–45 (2017)
5. Dragan, G.-C. et al.: On the challenges of measuring semi-volatile organic compound aerosols using personal samplers. Gefahrstoffe Reinhalt. Luft 77, 411-415 (2017)
6. Eichler, P.* et al.: Lubricating oil as a major constituent of ship exhaust particles. Environ. Sci. Technol. Lett. 4, 54-58 (2017)
7. Gruber, B. et al.: A minimal-invasive method for systemic bio-monitoring of the environmental pollutant phenanthrene in humans: Thermal extraction and gas chromatography – mass spectrometry from 1 µl capillary blood. J. Chromatogr. A 1487, 254-257 (2017)
8. Kasurinen, S.* et al.: Particulate emissions from the combustion of birch, beech, and spruce logs cause different cytotoxic responses in A549 cells. Environ. Toxicol. 32, 1487-1499 (2017)
9. Kohlmeier, V. et al.: Multi-channel silicone rubber traps as denuders for gas-particle partitioning of aerosols from semi-volatile organic compounds. Environ. Sci. Process Impacts 19, 676-686 (2017)
10. Passig, J. et al.: Aerosol mass spectrometer for simultaneous detection of polyaromatic hydrocarbons and inorganic components from individual particles. Anal. Chem. 89, 6341-6345 (2017)
11. Rüger, C.P.* et al.: Comprehensive chemical comparison of fuel composition and aerosol particles emitted from a ship diesel engine by gas chromatography atmospheric pressure chemical ionisation ultra-high resolution mass spectrometry with improved data processing routines. Eur. J. Mass Spectrom. 23, 28-39 (2017)
12. Streibel, T. et al.: Aerosol emissions of a ship diesel engine operated with diesel fuel or heavy fuel oil. Environ. Sci. Pollut. Res. 24, 10976-10991 (2017)
13. Wu, X. et al.: Determination of air pollution-related biomarkers of exposure in urine of travellers between Germany and China using liquid chromatographic and liquid chromatographic-mass spectrometric methods: A pilot study. Biomarkers 22, 1-27 (2017)

2016

14. Czech, H.* et al.: On-line analysis of organic emissions from residential wood combustion with Single-Photon Ionisation Time-Of-Flight Mass Spectrometry (SPI-TOFMS). Fuel 177, 334-342 (2016)
15. Kasurinen, S. et al.: Particulate Emissions from the Combustion of Birch, Beech, and Spruce Logs Cause Different Cytotoxic Responses in A549 Cells. Environmental Toxicology 32, 5,1487–1499 (2016)
16. Mülhopt, S.* et al.: Toxicity testing of combustion aerosols at the air-liquid interface with a self-contained and easy-to-use exposure system. J. Aerosol Sci. 96, 38-55 (2016)
17. Sapcariu, S.C.* et al.: Metabolic profiling as well as stable isotope assisted metabolic and proteomic analysis of RAW 264.7 macrophages exposed to ship engine aerosol emissions: Different effects of heavy fuel oil and refined diesel fuel. PLoS ONE 11:e0157964 (2016)
18. Tiitta, P.* et al.: Transformation of logwood combustion emissions in a smog chamber: Formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging. Atmos. Chem. Phys. 16, 13251-13269 (2016)

19. Weggler, B.A. et al.: Untargeted identification of wood type-specific markers in particulate matter from wood combustion. Environ. Sci. Technol. 50, 10073-10081 (2016)

2015

20. Kanashova, T.* et al.: Differential proteomic analysis of mouse macrophages exposed to adsorbate-loaded heavy fuel oil derived combustion particles using an automated sample-preparation workflow. Anal. Bioanal. Chem. 407, 5965-5976 (2015)

21. Kleeblatt, J. et al.: Needle trap sampling thermal-desorption resonance enhanced multiphoton ionization time-of-flight mass spectrometry for analysis of marine diesel engine exhaust. Anal. Methods 7, 3608-3617 (2015)

22. Müller, L. et al.: Characteristics and temporal evolution of particulate emissions from a ship diesel engine. Appl. Energy 155, 204-217 (2015)

23. Müller, L. et al.: Online determination of polycyclic aromatic hydrocarbon formation from a flame soot generator. Anal. Bioanal. Chem. 407, 5911-5922 (2015)

24. Oeder, S. et al.: Particulate matter from both heavy fuel oil and diesel fuel shipping emissions show strong biological effects on human lung cells at realistic and comparable in vitro exposure conditions. PLoS ONE 10:e0126536 (2015)

25. Radischat, C.* et al.: Real-time analysis of organic compounds in ship engine aerosol emissions using resonance-enhanced multiphoton ionisation and proton transfer mass spectrometry. Anal. Bioanal. Chem. 407, 5939-5951 (2015)

26. Reda, A. et al.: Analysis of gas-phase carbonyl compounds in emissions from modern wood combustion appliances: Influence of wood type and combustion appliance. Energy Fuels 29, 3897-3907 (2015)

27. Reda, A. et al.: Corrigendum to „Gas phase carbonyl compounds in ship emissions: Differences between diesel fuel and heavy fuel oil operation“. Atmos. Environ. 112, 369 (2015)

28. Reda, A. et al.: Corrigendum: Gas phase carbonyl compounds in ship emissions: Differences between diesel fuel and heavy fuel oil operation. Atmos. Environ. 112, 370-380 (2015)

29. Rüger, C.P. et al.: Characterisation of ship diesel primary particulate matter at the molecular level by means of ultra-high-resolution mass spectrometry coupled to laser desorption ionisation – comparison of feed fuel, filter extracts and direct particle measurements. Anal. Bioanal. Chem. 407, 5923-5937 (2015)

30. Schwemer, T. et al.: Gas chromatography coupled to atmospheric pressure chemical ionization FT-ICR mass spectrometry for improvement of data reliability. Anal. Chem. 87, 11957-11961 (2015)

31. Zimmermann, R.: Aerosols and health: A challenge for chemical and biological analysis. Anal. Bioanal. Chem. 407(20), 5863-5867 (2015)

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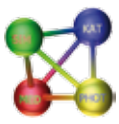

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