Department of Aerosols and Laser Studies

HEAD
VLADIMÍR ŽDÍMAL

DEPUTY
RADEK FAJGAR

RESEARCH STAFF
IRENA BENEŠOVÁ ŠEVČÍKOVÁ, DAVID BRUS, VLADISLAV DŘÍNEK, JOSEF KUGLER, VALERI V. LEVDANSKI, PAVEL MORAVEC, JAKUB ONDRÁČEK, LUCIE ONDRÁČKOVÁ (DŽUMBOVÁ), DANA POKORNÁ, JOSEF POLA, JAROSLAV SCHWARZ, JIŘÍ SMOLÍK, DANIELA ŘIMNÁČOVÁ, TEREZA TRÁVNÍČKOVÁ, MARKÉTA URBANOVÁ, PETR VODIČKA
Part time: JAROSLAV KUPČÍK

PHD STUDENTS
VĚRA JANDOVÁ, MARTIN KOŠTEJN, OTAKAR MAKEŠ, LUDMILA MAŠKOVÁ (ANDĚLOVÁ), JAN PUŠMAN, LENKA ŠKRABALOVÁ, NADĚŽDA ZÍKOVÁ, LUBOŠ KRABÁČ

TECHNICAL STAFF
DARIA BARTLOVÁ

Fields of research

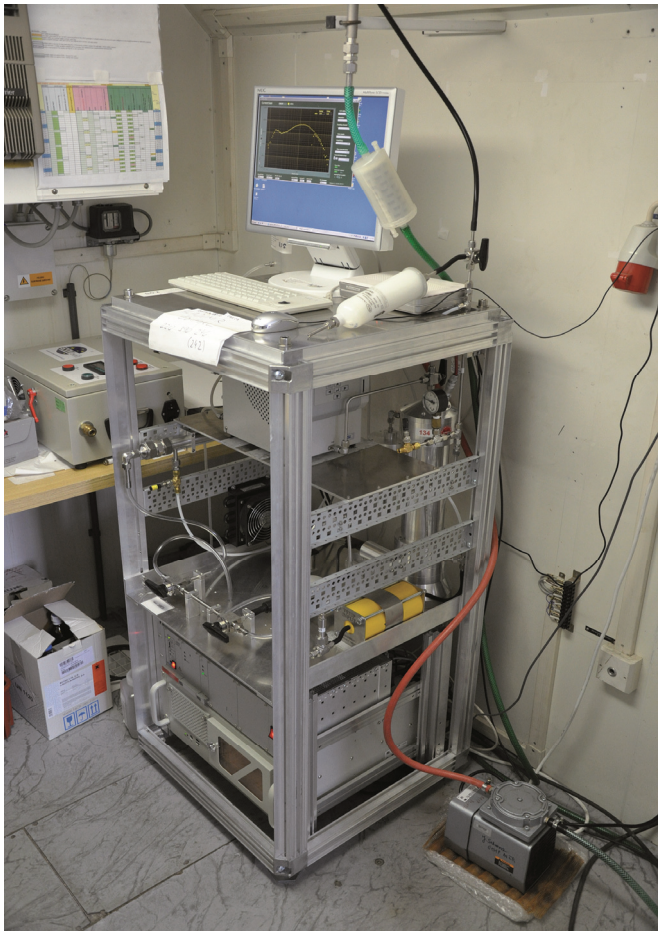
- Atmospheric aerosols
- Indoor/outdoor aerosols
- Nucleation phenomena
- Synthesis of nanoparticles *via* aerosol processes
- Heat and mass transfer in aerosol systems
- Interaction of aerosols with electromagnetic radiation
- Emissions sampling
- Nanoparticles and health
- Aerosol technology
- IR and UV laser induced chemistry
- Chemical vapor deposition of novel C-, Si- and Ge-based nanostructured materials
- IR laser-induced carbothermal reduction of oxides
- IR and UV laser photopolymerization in the gas phase
- UV laser chemical liquid deposition of metal nanosols and nanocomposites
- CVD of nanostructured objects (nanowires, nanoplatelets)
- IR and UV laser deposition of TiO_2-based materials
- IR and UV laser ablation for deposition of thin films

Research projects

European supersites for atmospheric aerosol research

(J. Schwarz, schwarz@icpf.cas.cz; supported by EC, project No. FP6-026140-EUSAAR)

European infrastructure project EUSAAR is focused on improving the current state of aerosol measurement on European supersites for atmospheric aerosol measurement. This aim is being reached by dissemination of knowledge from basic technical level to setting-up a state of the art of experimental methods on selected sites. QA/QC procedures, intercalibration of both basic and advanced measurement methods together with development of new aerosol instrumentation are the ways to fulfill the aims of the project. [Refs. 1, 8, 18, 52, 53, 66, 67]



A photo of scanning mobility particle sizer measuring size distribution of particles at background site Košetice

Thermophysical properties of water in unexplored, technologically significant regions

(V. Ždímal, zdimal@icpf.cas.cz; joint project with Institute of Thermomechanics of the ASCR, v. v. i., CTU, and University of West Bohemia, Plzeň, supported by GA ASCR, grant No. IAA4200760905)

This project focuses primarily on liquid water and solutions of selected salts below the freezing point (supercooled water), and water in nano-droplets. Existing hypotheses include the possibility of phase separation of supercooled water into two liquid phases below the second critical point. Density of supercooled water is only known at 0.1 MPa. Suggested measurements up to 100 MPa will provide first data. A new method and apparatus will be developed. The surface tension of supercooled water and a salt solution will be measured. The

surface tension of nano-droplets will be estimated from nucleation experiments. A range of theoretical approaches including phenomenological methods, simplified microscopic models, and molecular simulations, will be used with experimental data to obtain fundamental findings and engineering models. [Refs. 9, 10, 23, 32-41]

New ways to synthesize nanoparticles of various oxides

(V. Ždímal, zdimal@icpf.cas.cz; joint project with the ICT and Spolchemie a.s., supported by MIT, grant No. FR-TI1/548)

The aim of the project is to seek new ways how to synthesize nanoparticles of various oxides, characterize produced particles and perform a process scale-up. [Refs. 27, 68]

Comparison of aerosol composition, source region profiles and types observed in 1994 and 2009 at rural background site in Central Europe

(J. Schwarz, schwarz@icpf.cas.cz; joint project with Nuclear Physics Institute of the ASCR, v. v. i., supported by GACR, grant No. 205/09/2055)

The objectives of project can be summarized as follows: Atmospheric aerosol elemental composition on daily based samples will be analyzed using high sensitive non-destructive multi-elemental analytical technique (Proton Induced X-ray Emission PIXE), using multivariate statistical methods the main aerosol source types and their elemental profiles as well as magnitude of their influence on receptor site will be identified. Main source regions and their impact on regional air quality will be studied by combining the aerosol composition analysis with air mass transport history study. The obtained results will be compared with data available from 1990s to assess the impact of economical and structural changes in Central European economy on air pollution. [Refs. 21, 55-58, 61]

Influence of surface processes and electromagnetic radiation on transfer phenomena in aerosol systems with nanoparticles and porous bodies with nanopores

(V.V. Levdanski, valerij@icpf.cas.cz; supported by GA ASCR, grant No. IAA400720804)

The aim of the proposed project is to perform a theoretical study of the influence of surface processes, size effects and electromagnetic radiation on transfer phenomena in aerosol systems with nanoparticles and in capillary-porous bodies with nanoscale pores taking into account physicochemical transformations on the particle and pore surface. It is assumed to study the joint influence of size effects, electric charge and adsorbable foreign gases on formation of nanoparticles. Novel methods of the membrane purification of gases under influence of resonance radiation are assumed to be considered. The effect of radiation on mass transfer and storage of hydrogen in metallic nanoparticles will be investigated. The influence of electromagnetic radiation on coagulation, coalescence of nanoparticles and their deposition on a surface will be studied. [Refs. 9, 10, 23, 32-41]

Study of transport of inhaled nano-sized particles (Pb, Cd) and their allocation in organs

(J. Smolík, smolik@icpf.cas.cz; supported by GACR, grant No. 503/11/2315)

All of the evidence from animal and human studies showed that there are risks associated with inhalation of nano-sized particles (NSP). The alveolar translocation of NSP is likely the pathway how NSP can be transposed from air to the blood vessels, and distributed throughout the body to organs. In spite of the fact that an extrapulmonary translocation is highly dependent on particle surface characteristics/chemistry, in addition to particle size, the study of transport of inhalated nano-particles Pb, Cd (elements, oxides), their allocations in organs, as well as study of toxicity these nanoparticles will be carry out with nanoparticles (10, 20 and 60 nm). The nonbiogenous elements (Cd, Pb) have been selected as products of

technological processes and due to their presence in ambient aerosol. The research will give us more information for a proper understanding of risks of technologies producing Cd and Pb nano-sized particles and ambient aerosol risk. [Refs. 6, 20, 50, 51, 60]

Development and application of new experimental methods to measure heterogeneous particles in superheated steam

(V. Ždímal, zdimal@icpf.cas.cz; joint project with CTU and Institute of Thermomechanics of the ASCR, v. v. i., supported by GACR, grant No. 101/09/1633)

The aim of the project is to determine some properties of heterogeneous nuclei present in the superheated steam of steam turbines. In this project, the sampling device, coupled to advanced aerosol instrumentation (condensation particle counter, scanning mobility particle sizer), will be used to measure heterogeneous particles at selected power stations. To enable measurements of particles down to about 1 nm, a fast expansion chamber will be developed, enabling resolution of particle size by variable supersaturation. Collected data will serve as a basis for understanding the transport and the state of agglomeration of chemicals present in the steam circuit, for quantifying their effect on condensation, and, consequently, on the efficiency and reliability of steam turbines. [Refs. 9, 10, 23, 32-41]

Methodology of evaluation of air quality effect on library and archival collections

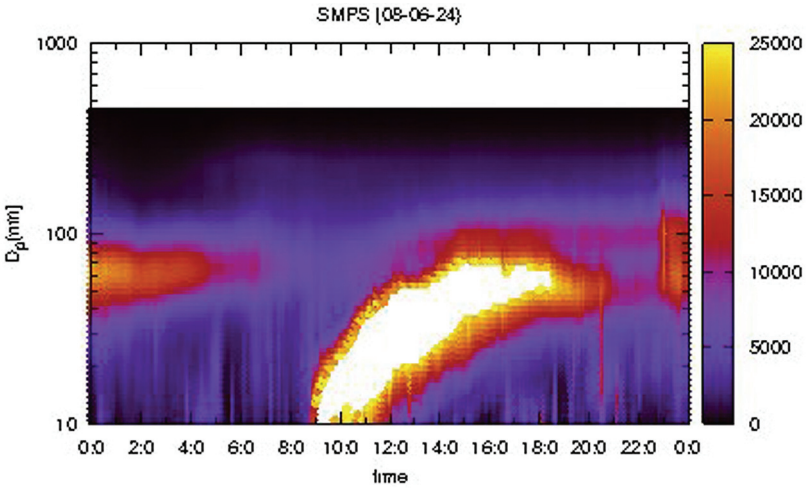
(J. Smolík, smolik@icpf.cas.cz; supported by the Ministry of Culture of the CR, project No. DF11P01OVV020)

The aims of the project are: a) development of evaluation methods for indoor air quality in libraries and archives, targeted at reduction of damages on library and archival collections caused by adverse effects of environment and b) gaining detailed knowledge of direct dependences between damage of library and archival collections and surrounding environment, leading to precautions reducing the adverse effects of deteriorated environment. [Refs. 11, 42, 43, 44, 59]

Advanced study of physical and chemical properties of atmospheric aerosols in high time resolution

(V. Ždímal, zdimal@icpf.cas.cz; supported by GACR, grant No. 209/11/1342)

Advanced physical and chemical properties of Central European atmospheric aerosol at rural background and urban background sites will be studied in high time and size resolution. Parallel measurement of aerosol volatility will be carried out using a C-ToF-AMS equipped with a thermodenuder inlet, aerosol hygroscopicity using an HTDMA, and particle number size distribution using an SMPS. The information about aerosol particle density will be extracted from the SMPS and AMS. Hygroscopicity closure will be obtained from the combined HTDMA and AMS chemical composition data allowing to study the influence of organic aerosol on particles' hygroscopicity. The content of primary and secondary organic aerosol and the extent of aerosol ageing will be determined using AMS data at each site. In addition, at least a year-long time evolution of number size distributions obtained using the SMPS and OC/EC concentrations from the OC/EC analyzer will be delivered to the EBAS database, to be available for global atmospheric modeling groups [Refs. 13, 19, 22, 52-54, 56, 62-67].



Daily course of number and size of the new aerosol particles „banana“ type recorded by spectrometer SMPS

New laser induced process for production of novel carbon-based nanomaterials and carbon-based nanomaterials with incorporated Si, N, and B heteroatoms

(J. Pola, pola@icpf.cas.cz; supported by GA ASCR, grant No. IAA400720619)

Megawatt KrF laser gas-phase photolysis of benzene and acetonitrile–benzene mixture was studied by using mass spectroscopy-gas chromatography and Fourier transform infrared spectroscopy for analysis of volatile products, and by Fourier transform infrared, Raman and X-ray photoelectron spectroscopy, electron microscopy and magnetization measurements for analyses of solid products deposited from the gas-phase. The results are consistent with carbonization of benzene and decomposition of non-absorbing acetonitrile in carbonizing benzene through collisions with excited benzene and/or its fragments. The solid products from benzene and acetonitrile-benzene mixture have large surface area and are characterized as nanomagnetic amorphous carbonaceous soot containing unsaturated C centers prone to oxidation. The nanosoot from acetonitrile-benzene mixture incorporates CN groups, confirms reactions of benzene fragments with CN radical and has a potential for modification by reactions at the CN bonds.

Pulsed infrared laser-irradiation of titanium monoxide leads to ablation and when carried out in gaseous benzene (1-5 Torr) to simultaneous dielectric breakdown of benzene into low molecular carbonaceous species which allow carbothermal reduction of ablated TiO_x particles and their protection by carbonaceous shell. The deposited particles are characterized by Fourier transform infrared Raman and X-ray photoelectron spectroscopy and by electron microscopy and shown to be stable towards oxidation in air. The reported process can find use in protection of gas-phase produced reactive nanoparticles by carbon phase. [Refs. 5, 15, 25, 26]

Laser approach to metal nanoalloys, its optimization & search for novel alloy nanostructures

(J. Pola, pola@icpf.cas.cz; no support)

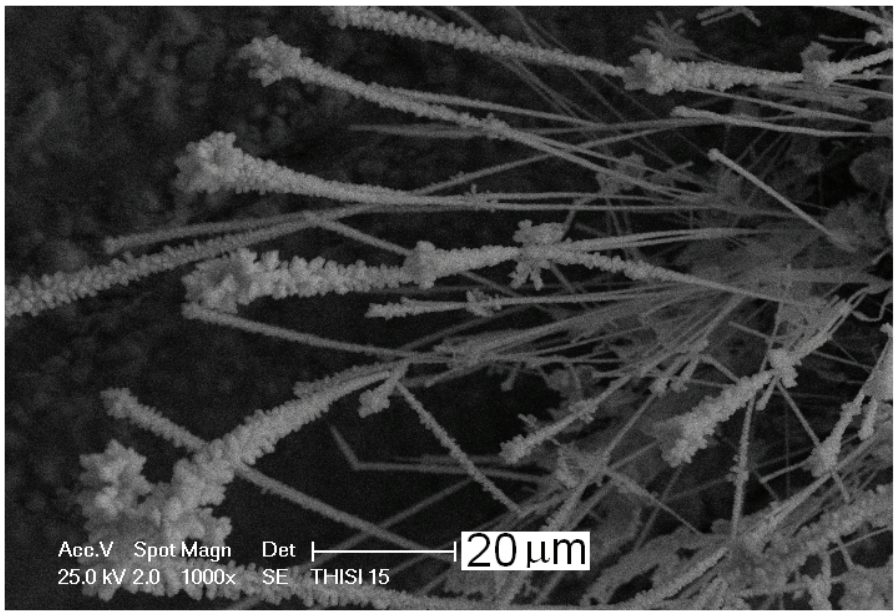
Pulsed IR laser irradiation of $SmCo_5$ alloy in vacuum and in adjacent dielectric breakdown (DB) of benzene has been examined as a tool for modifying phase and composition of this alloy and for suitability to serve as a laser deposition technique of Sm-Co nanoparticles and Sm-Co/C films. The composition of solid deposits was determined by FTIR, X-ray photoelectron and Raman spectroscopy and electron microscopy, and gas-phase chemical changes upon irradiation in gaseous benzene were analyzed by gas-chromatography

and FTIR and GC/MS spectroscopy. IR laser ablation in vacuum leads to deposition of amorphous $Sm_{1.00}$ $Co_{2.1\text{-}2.2}$ films containing uniformly dispersed Co_2Sm_5 nanocrystals and to formation of residual Sm_2Co_{17} target phase, both of which indicating disproportionation of $SmCo_5$ and Sm-enrichment of ablated particles. IR laser ablation in benzene results in formation of ultrafine powders consisting in fully amorphous $Sm_{1.00}Co_{4.2\text{-}4.6}$ nanoparticles embedded in amorphous hydrogenated carbonaceous phase and is in keeping with minor structural changes in ablated $SmCo_5$ particles. Both deposited materials are shown to differ in magnetic properties and the carbonaceous shell serves as a protection of Sm-Co nanobodies towards atmospheric oxidation. [Ref. 16]

Green chalcogenation of metals by laser-prepared poly(silachalcogenide)

(J. Pola, pola@icpf.cas.cz; supported by GACR, grant No. 203/09/0931)

UV laser photolysis of thiirane allows chemical vapor deposition of sulfur-containing solid which undergoes room-temperature reaction with copper and yields sub μm-sized amorphous filamentary $CuS/Cu_2S/C/H$ structures incorporating CuS and Cu_2S nanograins. Properties of these structures were examined by FTIR, Raman and X-ray photoelectron spectroscopies, X-ray diffraction and by electron microscopy. The results demonstrate the first example of reaction between solid sulfidizing reagent and copper at room temperature. [Ref. 17]

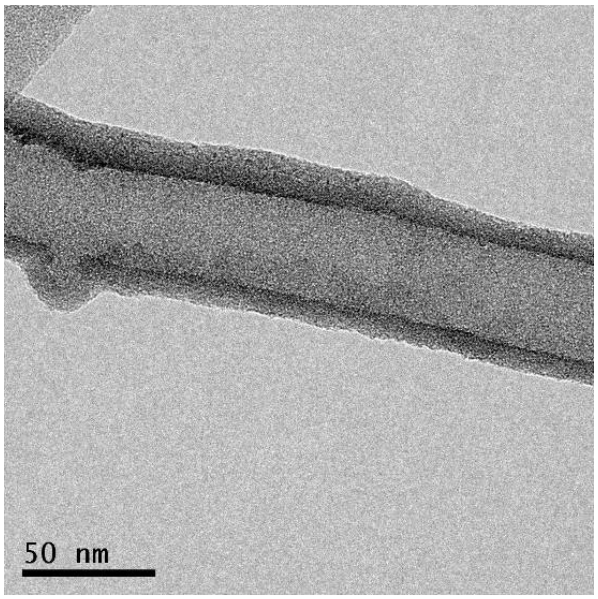


Laser deposited sub-μm-sized flower-like filamentary CuS_x features

Preparation of Si/O/C nanotubes using germanium nanowires as templates

(V. Dřínek, drinek@icpf.cas.cz; supported by GACR, grant No. 203/09/1088)

Low Pressure CVD of hexamethyldigermane Ge_2Me_6 and tetramethyldisilazane $(SiMe_2H)_2NH$ resulted in the growth of Ge nanowires wrapped in Si/O/C material. Nitrogen in the grown structure was replaced by oxygen due to its traces in the vacuum chamber. Subsequent annealing to 850 °C under vacuum lead to evaporation of germanium so that silicon oxycarbide nanotubes were formed. The nanotubes diameter was up to 80 nm, the length several microns. The nanotubes of such kind are very promising in the chemical catalysis. [Refs. 7, 14, 30, 31]



High resolution TEM image of the Si/O/C nanotube

Excimer laser-induced CVD of carbon encapsulated cobalt nanoparticles

(R. Fajgar, fajgar@icpf.cas.cz; supported by GACR, grant No. 203/09/1117)

Decomposition of acetylene/$Co(CO)_3(NO)$ mixtures induced by excimer ArF laser pulses is an efficient technique for preparation of amorphous cobalt nanoparticles encapsulated in carbon. Vacuum annealing up to 1170 K leads to structural changes both in the metal core and carbon shells. The cobalt core crystallizes in a face-centered cubic (β) form as revealed by X-ray and electron diffraction techniques and carbon affords graphite outer part. Properties of the Co(core) - carbon(shell) nanocomposites were examined by spectroscopy and microscopy techniques. Magnetization studies revealed superparamagnetic behaviour of the as-prepared amorphous deposit up to 150 K while annealed samples are ferromagnetic due to the size of the cobalt cores larger than 20 nm.

Excimer laser deposition and characterization of cerium doped TiO_2

(R. Fajgar, fajgar@icpf.cas.cz; supported by GACR, grant No. 203/09/1117)

Thin layers of Ti/Ce/O photocatalyst were deposited by ArF excimer laser ablation of oxide targets. Pellets of TiO_2 and CeO_2 were alternately irradiated by laser beam (193 nm) with fluence 6.0 $J.cm^{-2}$. Non-stoichiometric titanium oxides with 1-10% cerium were deposited on glass, quartz and tantalum substrates as thin multilayers and characterized by spectroscopic, microscopic and diffraction techniques. The as-prepared films with thickness 150 nm possess good adhesion to substrates and very poor degree of crystallization, as demonstrated by broad diffusion rings in selected area electron diffraction (SAED) pattern. Heating of the oxides in air (450 ^{o}C / 2h) leads to crystallization of the deposited material and its superhydrophylic behaviour. The nanocrystalline film shows the discrete SAED rings of anatase TiO_2 and cubic CeO_2 nanocrystallites. The Raman spectrum of the annealed deposit revealed bands attributable to anatase form of TiO_2 and cubic CeO_2. UV-VIS spectroscopy demonstrates successful shift of the absorption edge to the visible region. [Ref. 29, 47]

International co-operations

Division of Nuclear Physics, Department of Physics, Lund University, Lund, Sweden
Finnish Meteorological Institute, Helsinki, Finland: Studies on homogeneous nucleation using diffusion chambers
Ghent University, Institute for Nuclear Sciences, Ghent, Belgium: OC/EC in urban and suburban PM10 aerosol in Prague, Hygroscopic properties of urban and suburban carbonaceous aerosols
Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan
Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Switzerland
Norwegian Institute for Air Research, Kjeller, Norway: Indoor aerosol behaviour
Southern Illinois University Carbondale, Carbondale, IL, USA: Friction materials based on polymer matrix containing metals and their impact on environment
Technical University of Crete, Chania, Greece: Aerosols in the environment
University of Helsinki, Division of Atmospheric Sciences, Helsinki, Finland
Tampere University of Technology, Tampere, Finland: Synthesis and characterization of nanosized metal/ceramic particles
University of Eastern Finland, Kuopio, Finland: Novel aerosol generation processes focused on medical treatment and nanotechnology
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodź, Poland: UV laser-induced cross-linking of polysiloxanes
Faculty of Technology and Metallurgy, University of St. Cyril & Methodius, Skopje, Republic of Macedonia: Novel preparation and photocatalytic study of titania-based catalysts
Instituto de Estructura de la Materia, CSIC, Madrid, Spain: Studies on IR laser deposition of nanosized metal chalcogenides and polycarbosilathianes
King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia: Laser degradation of contaminants in fuel oils
National Institute for Lasers, Plasma and Radiation Physics, Bucharest, Romania: Laser-induced CVD of Fe/polymer nanocomposites
National Institute of Advanced Industrial Research and Technology, Tsukuba, Japan: Laser control of organic reactions
POLYMAT, Institute for Polymer Materials, San Sebastian, Spain: Laser ablation of graphene-based composites
University of Crete, Heraklion, Greece: Laser induced chemical vapour deposition of polycarbosilathianes

Visits abroad

D. Brus: Finnish Meteorological Institute, Helsinki, Finland (12 months)
L. Škrabalová: Finnish Meteorological Institute, Helsinki, Finland (1 month)
V. Jandová: Instituto de Estructura de la Materia, CSIC, Madrid, Spain (3 months)

Visitors

T. Hussein, University of Helsinki, Helsinki, Finland
V. Nororos, University of Helsinki, Helsinki, Finland
J. Blazevska-Gilev, University of St. Cyril & Methodius, Skopje, R. Macedonia
Nguyen Thanh Danh, Institute of Chemical Technology, VAST, Ho Chi Minh City, Vietnam

Ta Anh Tuan, HCM City Institute of Physics, VAST, Ho Chi Minh City, Vietnam
Radmila Tomovska, POLYMAT, Institute for Polymer Materials, San Sebastian, Spain
Xiaofeng Chang: Nanking University of Aeronautics and Astronautics, Nanking, China

Teaching

V. Ždímal: Faculty of Mathematics and Physics, Charles University in Prague, undergraduate course: "Aerosol Engineering"
V. Ždímal: ICT, Faculty of Chemical Engineering, graduate course "Aerosol Engineering"

Publications

Original papers

[1] Asmi A., Wiedensohler A., Laj P., Fjaeraa A.-M., Sellegri K., Birmili W., Weingartner E., Baltensperger U., Ždímal V., Zíková N., Putaud J.-P., Marinoni A, Tunved P., Hansson H.-C., Fiebig M., Kivekäs N., Lihavainen H., Asmi E., Ulevicius V., Aalto P.P., Swietlicki E., Kristensson A., Mihalopoulos N., Kalivitis N., Kalapov I., Kiss G., de Leeuw G., Henzing B., Harrison R.M., Beddows D., O'Dowd C., Jennings S.G., Flentje H., Weinhold K., Meinhardt F., Ries L., and Kulmala M.: Number Size Distributions and Seasonality of Submicron Particles in Europe 2008-2009. *Atmos. Chem. Phys.* 11(11), 5505-5538 (2011).

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Nemitz E., O'Donnell D., Panwar T.S., Pawlowska H., Petzold A., Pienaar J.J., Pio C., Plass-Duelmer C., Prévôt A.S.H., Pryor S., Reddington C.L., Roberts G., Rosenfeld D., Schwarz J., Seland Ø., Sellegri K., Shen X.J., Shiraiwa M., Siebert H., Sierau B., Simpson D., Sun J.Y., Topping D., Tunved P., Vaattovaara P., Vakkari V., Veefkind J.P., Visschedijk A., Vuollekoski H., Vuolo R., Wehner B., Wildt J., Woodward S., Worsnop D.R., van Zadelhoff G.-J., Zardini A.A., Zhang K., van Zyl P.G., Kerminen V.-M., Carslaw K.S., and Pandis S.N.: General Overview: European Integrated project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) – Integrating Aerosol Research from Nano to Global Scales. *Atmos. Chem. Phys.* 11(24), 13061–13143 (2011).

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