NOSA

Nordic Society for Aerosol Research

NOSA Aerosol Symposium

Helsingør, Denmark
8-9 November, 2007

Special focus of the symposium:

Airborne Nano-particles: New Technologies and impacts

In connection with NMR Workshop
”Organic particles in Nordic urban areas"
7 November 2007

Program
Conference Proceedings

Local organizers:

Sponsored by:

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[Tom side]

Introduction

NOSA (the Nordic Society for Aerosol Research)

NOSA has the ambition to arrange Nordic Aerosol conferences annually in one of the Nordic countries.
The first steps towards the founding of NOSA were taken in 1978 in Stockholm. The first NOSA scientific meeting was arranged in Göteborg in 1982. Before the NOSA-2007 Aerosol Symposium, Sweden hosted eleven meetings and Finland, Denmark and Norway have each arranged three meetings.

NOSA is an organization consisting of members from the Nordic countries as well as other countries that are involved in aerosol research. The purpose of NOSA is:

- to strengthen the cooperation within the Nordic aerosol research community;
- to offer a network and a meeting place for Nordic aerosol scientists;
- to disseminate the results of Nordic aerosol research to other scientists;
- to widen the awareness regarding Nordic aerosol research among public and policymakers;
- to encourage a multi-disciplinary dialogue between aerosol scientists and scientists within other fields of science where aerosol expertise is needed.

In particular, NOSA wants to encourage young scientists in the beginning of their scientific careers. Membership in NOSA is free of charge.

NOSA-2007 Local Organizing Committee

The local organizing committee consists of the following persons:

Matthias Ketzel, Finn Palmgren	National Environmental Research Institute (DMU), University of Aarhus, Department of Atmospheric Environment
Merete Bilde, Ole John Nielsen	University of Copenhagen, Chemistry Department
Marianne Glasius	University of Aarhus, Chemistry Department
Jacob Klenø Nøjgaard	National Research Centre for the Working Environment

The NOSA board

The board of NOSA assists the local organizing committee in arranging the NOSA-2007 conference, and currently consists of the following persons:

Mattias Hallquist (NOSA President)	Göteborg Atmospheric Science Centre, Göteborg University
Merete Bilde	Department of Chemistry, University of Copenhagen
Douglas Nilsson	Atmospheric Science Unit, Stockholm University
Jacob Klenø Nøjgaard	National Research Centre for the Working Environment
Erik Swietlicki	Lund Institute of Technology, Lund University
Hanna Vehkamäki	Dept. of Physical Sciences, University of Helsinki
Karl Espen Yttri	Norwegian Institute for Air Research (NILU)

Conference Location

Lo-skolen Conference Center
Gl. Hellebækvej 70
3000 Helsingør
Tel: +45 4928 0900
http://www.loskolen.dk

A direct train connection from Copenhagen Airport to Helsingør departs every 20 minutes and takes about 1 hour and 10 minutes. Bus 803 departs from the Helsingør station to (Hellebo Park) every 30 or 60 minutes.

NMR workshop “Organic particles in Nordic urban areas”

PROGRAM

Helsingør, Denmark, 7 November 2007

Wednesday, November 7th

9:30 - 10:00 Registration and coffee/tea

Session 1 10:00 - 12:05 Chair: Marianne Glasius, AU, Denmark

10:00 - 10:05
M. Glasius, AU, Denmark
Welcome

10:05 - 10:50 **Invited Talk**
P.H. McMurry, University of Minnesota, USA
Novel Approaches for measuring physical and chemical properties of particulate organics **(70)**

10:50 - 11:15
E. Swietlicki, University of Lund, Sweden
Characterization of organic aerosol components at a European aerosol super-site in southern Sweden **(100)**

11:15 - 11:40
K.E. Yttri, NILU, Norway
Carbonaceous aerosols in the Norwegian environment **(114)**

11:40 - 12:05
R. Hillamo, Finnish Meteorological Institute, Finland
Studies on carbon content of fine particle ambient aerosol in Finland **(36)**

12:05 - 13:00 **LUNCH**

Session 2 13:00 - 17:30 Chair: Finn Palmgren, DMU, Denmark

13:00 - 13:45 **Invited Talk**
M. Kalberer, ETH Zurich, Switzerland
Ultra-high resolution mass spectrometry as a tool to advance organic aerosol characterization **(42)**

13:45 - 14:10
M. Glasius, AU, Denmark
Molecular tracers in organic particles - results from measurements in Danish urban areas **(26)**

14:10 - 14:35
P. Wåhlin, DMU, Denmark
Source apportionment of PM10 in Copenhagen urban background **(106)**

14:35 - 15:00 **Coffee/tea**

15:00 - 15:30 **Invited Talk**
A. Mayer, TTM Technik Thermische Maschinen, Switzerland
PM10-Toxicity-Equivalent – New Approach to a Health-Oriented PM-Characterization **(65)**

15:30 - 15:55
D. Simpson, EMEP MSC-W, METNO, Norway
Modelling of organic aerosol in Europe **(92)**

15:55 - 17:30 **Discussion**

18:00 - **Dinner**

2007 NOSA Aerosol Symposium

PROGRAM

Helsingør, Denmark, 8-9 November 2007

Speakers and poster presenters please see the end of this page for practical information related to your presentation.

Thursday, November 8th

9:00 - 10:00 Registration and Welcome coffee

Session 1 10:00 - 12:05 Atmospheric Aerosols - Chair: P.H. McMurry and M. Hallquist

10:00 - 10:15 Welcome and Opening
M. Hallquist and M. Ketzel
10:15 - 11:05 **Invited Talk**
P.H. McMurry
Nucleation and Growth of Atmospheric Aerosols (**68**)
11:05 - 11:25 (O1)
N. Kivekås, M. Zhan, H. Lihavainen, M. Komppula, J. Sun, Y. Viisanen
Preliminary results from DMPS-measurements at Mount Waliguan, Inland China (**46**)
11:25 - 11:45 (O2)
S. Saarikoski, H. Timonen, K. Saarnio, M. Aurela, R. Hillamo
Filter and on-line measurements of fine particle organic carbon in Helsinki, Finland **(88)**
11:45 - 12:05 (O3)
L.L. Sørensen, S. Larsen, S. Pryor, T. Kristensen
Measurement of primary marine aerosols using the dissipation technique **(94)**

12:10 - 13:00 **LUNCH**

Session 2 13:00 - 14:50 Particles from traffic - Chair: A.C.R. Mayer and F. Palmgren

13:00 - 13:50 **Invited Talk**
A.C.R. Mayer
Elimination of Combustion Generated Nanoparticles – Why and How **(64)**
13:50 - 14:10 (O4)
A. Frey, K. Teinilä, A. Virkkula, H. Lihavainen, R. Hillamo
Black carbon levels in fine and ultrafine particle size fractions (**22**)
14:10 - 14:30 (O5)
C.S. Hak, E. Ljungström, M. Hallquist, M. Svane, J.B.C. Pettersson
Determination of particle emission factors of individual vehicles under real-life conditions (**30**)
14:30 - 14:50 (O6)
A. Gudmundsson, A. Dahl, E. Swietlicki, G. Blomqvist, P. Jonsson, M. Gustafsson
Studies of wear particle emissions using a road simulator (**28**)

14:50 - 16:20 **Coffee, exhibitions and poster presentations**

Session 3 16:20 - 17:20 Fundamental aerosol physics - Chair: M. Bilde and E. Swietlicki

16:20 - 16:40 (O7)
K. Hansen, P. Aandersson, E. Uggerud
Extracting the magic numbers of water clusters from abundance spectra (**34**)
16:40 - 17:00 (O8)
T. Kurtén, I.K. Ortega, M. Salonen, V. Loukonen, H. Vehkamäki, M. Kulmala
Quantum chemical studies on atmospheric sulfuric acid nucleation (**50**)
17:00 - 17:20 (O9)
P.U. Andersson, M.T. Suter, L.S.E. Romero Lejonthun, J.B.C. Pettersson
Molecular beam studies of ice properties and ice-adsorbate interactions (**10**)

17:30 - 18:30 **NOSA Annual Meeting**

19:00 - 22:00 **Dinner**

Friday, November 9th

Session 4 09:00 - 10:30 Health aspects of aerosols - Chair: L. Asking and O.J. Nielsen

09:00 - 9:50 **Invited Talk**
L. Asking
Current status of inhaled insulin (**13**)
09:50 - 10:10 (O10)
A. Yilmaz, P. Glarborg, H. Livbjerg
Particle formation from gas cookers (**110**)
10:10 - 10:30 (O11)
J. Löndahl, E. Swietlicki, J. Pagels, A. Masssling, C. Boman, J. Rissler, E. Vaclavik-Baüner, S. Loft, A. Blomberg, T. Sandström
Respiratory tract deposition of nano-particles from biomass combustion and traffic, impact of size-distribution and hygroscopicity on the deposited dose (**56**)

10:30 - 10:50 **Coffee and exhibitions**

Session 5 10:50 - 12:10 Aerosol chemistry and physics - Chair: T. Krinke and M. Glasius

10:50 - 11:10 (O12)
K.E. Yttri, W. Aas, C. Dye, C.L. Myhre, N.J. Schmidbauer, D. Simpson, L.H. Slørdal, S. Solberg, T.M. Svendby
SORGA (Secondary Organic Aerosols in the Urban Environment) - Modelling and measurements of carbonaceous aerosols at a rural and an urban site in Norway (**114**)
11:10 - 11:30 (O13)
J. Pagels, A. Khalizov, M. Emery, P.H. McMurry, R.Y. Zhang
Processing of soot by controlled sulphuric acid and water condensation - growth and mass transfer to aggregates and spheres (**80**)
11:30 - 11:50 (O14)
M. Messing, K.A. Dick, K. Deppert
Generation of nanometer-sized gold particles by spark discharge - for growth of GaP nanowires (**72**)
11:50 - 12:10 (O15)
M.A. Miettinen, V. Suonmaa, U. Tapper, U. Backman, J. Joutsensaari, A. Auvinen, J.K. Jokiniemi
Controlled synthesis of nanoparticles for inhalation exposure studies (**74**)

12:10 - 13:10 **LUNCH**

Session 6 13:10 - 15:05 Chamber and laboratory experiments - Chair: M. Kalberer and J. K. Nøjgaard

13:10 - 14:00 **Invited Talk**
M. Kalberer, M. Savi, D. Lang, A. Gaschen, M. Fierz, M. Ryser, J. Ricka
Investigation of health effects of organic aerosol particles: First results using a new particle deposition chamber (**40**)
14:00 - 14:20 (O16)
M. Frosch, O. Faurskov Nielsen, M. Bilde
Raman spectroscopy and formation of cloud droplets (**24**)
14:20 - 14:40 (O17)
M. Dal Maso, T. Mentel, A. Kiendler-Scharr, T. Hohaus, E. Kleist, M. Miebach, R. Tillmann, R. Uerlings, R. Fisseha, P. Griffiths, Y. Rudich, E. Dinar, J. Wildt
An overview of the Jülich plant chamber experiments: Aerosol formation from plant emissions (**20**)
14:40 - 15:00 (O18)
J. Joutsensaari, P. Yli-Pirilä, J. Heijari, J.K. Holopainen, P. Miettinen, T. Raatikainen, J. Rautiainen, D.R. Worsnop, A. Laaksonen
Secondary organic aerosol formation by ozonolysis of volatiles emitted from trees (**38**)

15:00 - 15:05 **End of Symposium**

Information for Speakers:

OH projector will be available. A computer with PowerPoint will also be available. We ask you to bring your presentations on CD-R or a memory stick. Please don't use your own computer.
The total length of an oral presentation, including time to get to the podium, introduction by the chairman and time for questions, is 20 minutes. The talk must be no longer than 15 min. and will be followed by a five min. question and answering session. Invited speakers will get 50 min. in total.

The chairman will get three pieces of coloured paper which will be used to give information to the speaker (green, yellow and red). A time schedule for a 20 minutes talk can be:

0-13 minutes	Green
13-16 minutes	Yellow, time to state the conclusions
16-18 minutes	Red, stop now
after 20 minutes	Questions over, change to the next speaker.

Information for Poster Presenters:

Poster boards and stickers will be available. The dimensions of the poster boards are: width 100 cm and height 140 cm.

Exhibitors / Sponsors

The following companies involved in the sale and development of aerosol instrumentation and applications will present their products witin an exhibition during the conference:

TSI GmbH, Web: http://particle.tsi.com
Danalytic ApS, E-mail: danalytic@post.tele.dk
Grimm Aerosol Technik GmbH & Co. KG Web: http://www.grimm-aerosol.com
C. I-Analyse Web: http://www.ihle-andersen.dk
Oleico AB Web: http://www.oleico.se/
ZenZors A/S Web: http://www.zenzors.com/
OPSIS AB Web: http://www.opsis.se/

The conference was additionally sponsored by:

CCAR - Copenhagen Centre for Atmospheric Research
Web: http://www.kiku.dk/ccar

Invited Speakers

Peter McMurry
University of Minnesota
USA

Andreas Mayer
TTM, Niederrohrdorf
Switzerland

Markus Kalberer
ETH Zurich // Paul Scherrer Institute
Switzerland

Lars Asking
Novo Nordisk
Denmark

Abstracts

The scientific contributions presented at the NOSA-2007 Aerosol Symposium and the NMR Workshop “Organic particles in Nordic urban areas” are documented in this collection of abstracts which are arranged in an alphabetical order according to the surname of the first author.

MOLECULAR BEAM STUDIES OF ICE PROPERTIES AND ICE-ADSORBATE INTERACTIONS

P.U. ANDERSSON[1], M.T. SUTER[1], L.S.E. ROMERO LEJONTHUN[1] and J.B.C. PETTERSSON[1]

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412 96 Göteborg, Sweden.

Keywords: ICE, DESORPTION, MOLECULAR BEAM, SCATTERING.

INTRODUCTION

The dynamics of molecular interactions with water ice surfaces are studied using molecular beam techniques. The experimental method allows for detailed investigations of interaction between molecules and ice surfaces under single collision conditions, and we characterize collision dynamics, energy transfer, trapping and sticking probabilities, and the kinetics of desorption. The molecular beam scattering technique is also used as a sensitive probe of structural changes of the ice surface.

METHODS

A molecular beam apparatus has been constructed for the present studies. An ice surface is prepared by deposition of water vapor on a cold substrate and the surface is maintained in a differentially pumped vacuum chamber with a partial water vapor pressure up to 10^{-4} mbar, which allows for experiments with ice surfaces in the temperature range 100-200 K. At the higher surface temperatures employed, the ice has a very dynamic character and undergoes rapid evaporation and condensation. A molecular beam is directed towards the surface, and the molecular flux from the surface is detected by mass spectrometry.

RESULTS AND CONCLUSIONS

Results for He, Ar, CO, CO_2, CH_4, C_2H_6, C_3H_8, HCl and Cl_2 interactions with ice surfaces at 100-191 K are presented (Suter *et al.*, 2006; Andersson *et al.*, 2000; Suter *et al.*, 2006; Suter *et al.*, 2004; Andersson *et al.*, 2004; Andersson *et al.*, 2000; Lejonthun *et al.*, 2006). Angular-resolved intensity and time-of-flight distributions are measured with mass spectrometry, and the effects of surface temperature, incident kinetic energy, incident angle, and adsorbate coverage are investigated. The results confirm that molecular collisions with ice are highly inelastic and characterized by efficient transfer of energy to surface modes. The trapping of all atoms and molecules (except He) on the surface is found to be very effective under typical thermal conditions. Ar, CO, CH_4 and C_2H_6 accommodate to the temperature of the ice, but rapidly leave the surface by desorption because of the low binding energy to the surface. We conclude that accommodation of molecules with a mass similar to or larger than CO on water ice surfaces should be highly efficient under all conditions of relevance for atmospheric chemistry.

The residence time on the surface is measured for CO_2, C_3H_8, HCl, and Cl_2. The desorption kinetics can be described by the Arrhenius equation, and pre-exponential factors and activation energies for desorption are determined from the data. In case of CO_2, the desorption kinetics are found to be significantly different on amorphous ice than on crystalline ice.

Low energy He scattering is used to study the surface properties of water ice at 150-191 K. The elastic scattering data for the temperature range 150-180 K are consistent with the results expected for crystalline ice. Above 180 K the elastic He scattering signal decreases rapidly with increasing temperature. This effect is concluded to be due to either strongly anharmonic surface vibrations or the onset of disorder in the ice surface, or a combination of the two.

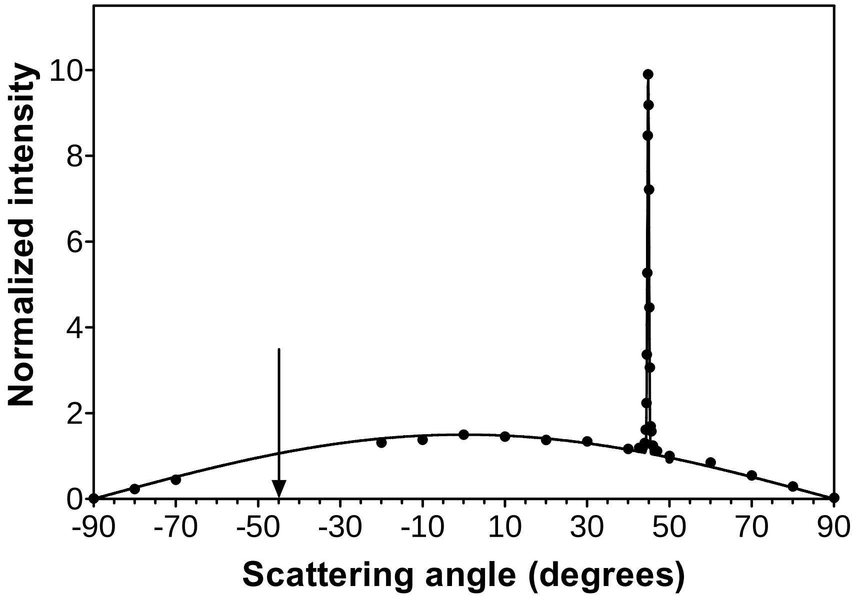

Figure 1. Angular distribution for helium scattering at an incident angle of 45° (indicated by arrow) from crystalline ice at 165 K. A narrow peak due to elastic scattering of helium from the surface is observed in the specular direction. The broad distribution due to inelastic and incoherent scattering from the ice is well described by a cosine distribution (solid line).

ACKNOWLEDGEMENTS

This work was supported by the Swedish Research Council.

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Lejonthun L.S.E. Romero, Andersson, P.U., Någård, M.B., and Pettersson, J.B.C. (2006). Chlorine interactions with water ice studied by molecular beam techniques. *Journal of Physical Chemistry B* **110**, 23497.

CURRENT STATUS OF INHALED INSULIN

L. ASKING

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Keywords: inhalation, insulin

Evidence exists for the use of the inhaled route for administration of medication from already 4000 years ago. Aqueous nebulisation was the main technology until the launch of the pressurized metered dose inhaler in 1956. In 1970, the first dry powder inhaler entered the market and with effective and safe drugs as beta-agonists and steroids, asthmatic and COPD patients are now efficiently treated and have a good quality of life. The inhaled route for insulin was already proposed in the 1920ies but it is not until the last 10 years that any major progress has been made. Several companies are now in late stage development of products and the first product has already reached the market in 2006. Inhaled insulin possesses several challenges. From a clinical perspective, the bioavailability of macromolecules including insulin is lower than for small molecules and about 10 to 15% of the dose becomes available to the systemic circulation. Clinical safety has to be assessed particularly as insulin is a life-long therapy for diabetic patients. From a technical perspective, accurate dosing to the deep lung possesses a challenge. From a marketing perspective, product cost needs to be competitive to other routes of administration with subcutaneous being the main alternative route. The technologies for inhaled insulin on the market and late stage development include both dry powder inhalers and small volume nebulizers. These technologies will be further discussed in the presentation. Inhaled insulin is a relevant alternative for a group of patients that for various reasons cannot be well controlled with injected modern insulin (i.e. analogues). The majority of insulin users can be well controlled with a few daily injections of modern insulin.

ACCELERATED SOLVENT EXTRACTION FOR DETERMINATION OF BENZO(a)PYRENE IN DIESEL PARTICULATE MATTER

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Keywords: PAH, Benzo(a)pyrene, diesel particulate matter, ASE.

INTRODUCTION

One group of compounds with high mutagenic and carcinogenic properties found in diesel particles are polycyclic aromatic hydrocarbons (PAH) (Boström *et al*., 2002). The most well known PAH is benzo(a)pyrene (B(a)P) which is the only PAH classified by International Agency for Research on Cancer (IARC) as carcinogenic to humans (group 1) (Straif *et al*., 2005). Analysis of B(a)P and other high molecular weight PAH in diesel particulate matter have shown lower extraction recoveries compared to extraction of ambient air particles when using common extraction methods such as ultrasonically assisted extraction and Soxhlet extraction (Schantz *et al*., 1997; Turrio-Baldassarri *et al*., 2003; Christensen *et al*., 2005; Bergvall and Westerholm, 2006). The aim of this present study was to evaluate the extraction recovery of B(a)P from diesel particulate matter using Accelerated Solvent Extraction (ASE).

METHODS

The diesel particulate matter investigated was Standard Reference Material (SRM) 2975 obtained from the National Institute of Standards and Technology (NIST) (NIST, 2000). Extraction of the diesel Standard Reference Material was performed using an ASE 200 instrument (Dionex, USA). Samples were placed in 5 ml extraction cells and the deuterated internal standard B(a)P-d_{12} was added to the particulate matter. The extraction times, e.i. static times, tested were 5, 20 and 30 minutes. Other extraction conditions used: oven temperature 200ºC, 3000 psi, 9 minutes heat time, 3 minutes preheat time and four or five extraction cycles using toluene as solvent. Four consecutive particulate samples were extracted for each extraction time. Each sample was also extracted an additional extraction cycle to investigate the extraction recovery of the first analytical extraction (4 or 5 extraction cycles). The extracts were then cleaned up using silica solid phase extraction (SPE) cartridges. Deuterated coronene was added to the SPE eluate as a volumetric internal surrogate standard for calculation of the extraction recovery. The samples were then analyzed using online hyphenated LC/GC/MS according to Bergvall and Westerholm (2006).

CONCLUSIONS

The analytical results for B(a)P are shown in Table 1. Results published by Bergvall and Westerholm (2006) and Christensen *et al*., (2005) using ultrasonically assisted extraction are comparable with the certified NIST value (NIST, 2000). The results obtained using ASE shows generally higher relative concentrations compared to the certified NIST value. The highest relative concentrations were obtained in the present study using ASE 5x20 min (20 min extraction time and 5 extraction cycles) and ASE 5x30 min. However, no significant difference was seen when the extraction time was increased from 5x20 min to 5x30 min. The result reported by Schantz *et al*., (1997), Table 1, is intermediate between the certified NIST value and the present study. They used lower extraction temperature, shorter extraction time and only one extraction cycle in their experiments compared to the present study.
Furthermore, comparing the additional extraction cycle with the previous analytical extraction (4 or 5 extraction cycles) the recovery of B(a)P were larger than 90% for both 5x20 min and 5x30 min. The

recovery obtained when extracting for 4x5 min was 85%. It was noticed that the recovery of deuterated B(a)P used as internal surrogate standard was higher than that of the analyte B(a)P. This indicates that added deuterated B(a)P is more easily extracted compared to the non labeled analyte B(a)P. This could partly explain the lower determined concentrations using ultrasonically assisted extraction.

Extraction	Relative conc %	Reference
Ultrasonication	130	Bergvall and Westerholm, 2006
Ultrasonication	150	Christensen *et al.*, 2005
ASE 1x5 min	420	Schantz *et al.*, 1997
ASE 4x5 min	1350	
ASE 5x20 min	1650	
ASE 5x30 min	1650	

Table 1. Determined concentration of B(a)P in SRM 2975 relative to the certified NIST value, which is set to 100%.

ACKNOWLEDGEMENTS

Lena Elfver is acknowledged for skilful laboratory assistance. This work was financed by Stockholm University and the Swedish Emission Research Programme (Svenska Emissionsforskningsprogrammet, EMFO).

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SRM 2975. Diesel Particulate Matter (Industrial Forklift). Certificate of Analysis, National Institute of Standards and Technology (2000) Gaithersburg, USA

IN WANT OF MEASUREMENTS OF AIR POLLUTION FROM WOOD SMOKE

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Keywords: Wood smoke pollution, Health problems, Regulations, Need for local measurements.

INTRODUCTION

In many residential areas woodstoves and fireplace inserts have become very popular in the past ten years - even as primary heating technology. Especially asthmatic people experience wood smoke as strongly bothering. The smoke from neighbouring chimneys enters houses through windows, systems of ventilation and fine cracks in the outer walls. In the night people can not air the bedrooms without getting the rooms filled with wood smoke. Until now the regulations of wood smoke have been ineffective. - It would be a great step forward, if local authorities and smoke affected people could have effective, handy measuring instruments at their disposal, so that the inconvenience from smoke could be analytically documented.

WOOD SMOKE POLLUTION

Already in 1980 the American Journal “Environmental Science and Technology” discussed a study about air pollution from woodstoves. The study concluded that measured emissions from correctly fired woodstoves were very large, both concerning fine particles and cancer promoting PAH. Woodstoves caused larger air pollution with PAH and particles than any other form of heating by atmospheric burning and they were uncontrollable (Environmental Science & Technology, July 1980). Recent Danish studies have proved the same results for particles, PAH and dioxin (Glasius *et al.* 2007; Schleicher, 2001). NERI statistics for UN show that emissions to the air from wood burning in residences account for approximately 60 % of fine particles (PM 2,5) from Danish sources against 14% from traffic; approximately 90 % of PAH to the air from Danish sources; as well as 50 % of dioxin to the air from Danish sources (C. – Dupont, 2007).

HEALTH PROBLEMS

The Danish Health Interview Survey 2000 has shown, that about 300.000 people within a fortnight had been bothered from wood smoke in their neighbourhood (Keiding *et al.,*2003). In 2000 there were ca. 300.000 wood stoves. Today there are 600.000 or more, and they are used more frequently than before because of high energy prices. - When you ask people how it bothers them, they point at pains around eyes and the nose, respiration problems, fit of coughing, headache, palpitation and insomnia. But you can get much worse illnesses. It is specially children, elderly people and people with heart diseases, asthma and other forms of dyspnoea, who are particularly sensitive to air pollution.

It has also been known for years, that chronic PAH influence may cause cancer and hurt our genes (Karlson *et al.*, 2006). Just as serious are health effects from dioxin. It is acknowledged, that dioxin may reach the brain through breathing (Fabig, 2000). Especially in residential areas you have long term influences. You are in your home most of the time.

In other words, there is a real conflict between cheap room heating and public health.

REGULATIONS

According to the Danish Environmental Protection Law § 42,1 local authorities may order air pollution from private, stationary systems for energy production to be reduced, if the production involves essential pollution (Danish: væsentlig forurening). – If the threats can not be stopped, local authorities may close the activity according to § 42,4. Therefore, the controversial question in local wood smoke cases is, whether there is an essential pollution or not. This judgement is usually lacking measurements.

The Statutory Order on Air Pollution 2001 from the Danish Ministry of Environment and Energy makes it absolutely clear, that air pollution is essential, when the emissions consist of category 1-substances including PAH and dioxin and there is not implemented effective emissions reduction. The Statutory Order 2001 claims, that an essential air pollution demands effective emissions reduction, so that there will be free dilution (Danish: fri fortynding). It means, that the smoke is able to move away unimpeded (free) from any whirls, which could draw wood smoke down to dwelling level. Especially for wood stove chimneys in densely built-up areas it has to be proven that free dilution is what happens.

NEED FOR LOCAL MESUSUREMENTS

One can distinguish between:
1. Air pollution from neighbouring wood stoves.
2. Air pollution in local districts (’smoke pockets’)
3. Omnipresent air pollution contributing to fine particles, PAH and dioxin loads in the environment.
This abstract concentrates on themes 1. and 2.

Ad 1) In relation to neighbour conflicts it would be of help for the local authorities, if they have at their disposal improved measurement equipment to verify the presence of small particles over time and improved calculation models to ensure optimal dimensioning and locating of the chimneys at small distances and low elevations. It would promote objective and uniform considerations in the whole country.

Ad 2) Air pollution in local districts may signify smoke pockets. In an investigation to measure the level of dioxins in the atmosphere in Denmark, dioxin concentrations in the ambient air were measured in Frederiksborg and Copenhagen and periodically in a village close to residences with wood stoves. The village winter maximum was very pronounced, being the highest measured in the programme (J. Vikelsøe *et al.*, 2006). The residence area in the village could be called a smoke pocket. The problem is to define the limits of such a pocket and how to stop the smoke problems. –A combination of GIS mapping and particle measurements with a handy, effective device could help local authorities to define the problem areas for regulation purposes concerning an essential improvement of public health.

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ONE-YEAR OBSERVATIONS OF PARTICLE FORMATION EVENTS AT TWO SIBERIAN STATIONS

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Keywords: ATMOSPHERIC AEROSOLS, OBSERVATIONS, NUCLEATION.

INTRODUCTION

Formation of new atmospheric aerosol particles by nucleation events is a significant source of new atmospheric particles (Kulmala *et al.,* 2004). The formed particles have, after growing by condensation, the potential to act as cloud condensation nuclei and thus affect the Earth's radiative balance as well as the hydrological cycle.

The western part of the boreal forest area has been an area where particle formation has been studied intensively, in part because it has been an area where time series of atmospheric submicron size distributions have been measured continuously for years (eg. Dal Maso *et al.,* 2007). Studies on these measurements have revealed that the boreal forest is a frequent source of new particles (eg. Tunved *et al.,* 2006). However, these studies are concentrated on the western part of the European boreal forest area, while data of the vast forested areas of the Siberian forests is still scarce.

In this work we present two one-year datasets from the Siberian boreal forest, where submicron aerosol size distributions have been measured. The analysis of the time series demonstrates that new particle formation and growth is occurring also in Central Siberia, providing evidence that the studies performed on atmospheric particle formation in the Nordic countries can be extrapolated to the Siberian boreal forest as well.

MATERIALS AND METHODS

Aerosol size distribution measurements were performed at two sites in Central Siberia, Tomsk and Listvyanka. (see Table 1 for locations). The aerosol size distribution data was measured using Diffusion Aerosol Spectroscopes (DAS, see eg. Julanov *et al., 2002,* Eremenko and Ankilov, *1995*). The DAS consists of a set of grid diffusion batteries and a condensation particle counter. The particle concentration at both the inlet and outlet of the diffusion battery is measured to determine the penetration though the diffusion grid. By measuring the penetration with varying numbers of grids, and with knowledge of the size-dependent particle diffusion, one can obtain the size distribution of atmospheric particles.

The diameter size range covered by the DAS measurements is from 3nm to ca. 250 nm for the Tomsk setup and from 3 nm to 50 nm at Listvyanka. The time resolution was 7 and 3 minutes per size distribution for the Tomsk and Listvyanka stations, respectively. The size and time resolutions were such that they enabled the analysis of the size distribution time series for the occurrence of particle formation events. To quantify the occurrences of new particle formation, the size distributions resulting from the data inversion were analyzed visually. Because the particle formation events were mostly occurring near noontime, and more than one event a day was rarely observed, the data analysis was performed on a day-to-day basis.

RESULTS

The mean particle concentration during the measurements at the Tomsk station was 2480 cm-3, while the median was 1950 cm-3 and the standard deviation 2000 cm-3. In Listvyanka, the mean particle concentration measured by the DAS was 4690 cm-3. The median concentration was 4090 cm-3 and the standard deviation 3150 cm-3. The Tomsk total numbers are comparable with measurements at Finnish background sites, while the Listvyanka measurements, in contrast, show that the site is influenced by another particle source, very probably local pollution.

We found 32 days that fulfilled the criteria of a regional-scale particle formation event for the Tomsk station. This is approximately 10% of all days that could be classified. 147 days (44% of the total) were classified as undefined. In Listvyanka, we observed 31 event days of 253 analyzable days (12%). Most of these events happened in the spring—summer period from April to July.

CONCLUSIONS

We present one-year time series of aerosol size distribution measurements measured at two Central Siberian sites. On of the sites, Tomsk, can be considered a background site, while the other is influenced by anthropogenic sources.

We found occurrences of particle formation events, in which new particles are nucleated and subsequently grow by condensation, at both stations. The occurrences were recorded predominantly during springtime. The formation and growth rates of new particles were of the same order than observed at other stations in the boreal forest.

These findings give tentative evidence that not only the western part, but also the wide areas of Central and Eastern Siberia are sources of aerosols produced by processes involving both biogenic and anthropogenic precursors.

ACKNOWLEDGEMENTS

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AN OVERVIEW OF THE JÜLICH PLANT CHAMBER EXPERIMENTS: AEROSOL FORMATION FROM PLANT EMISSIONS

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KEYWORDS: SOA,AEROSOL FORMATION, NUCLEATION RATES, MODELING

INTRODUCTION

Biogenic volatile organic compounds (BVOC) are major participants in atmospheric chemistry, both due to their large emissions and their influence on O_3 and OH radical budgets. They also to play an important part in atmospheric particle formation events, in which new particles are produced from precursor vapors and then grow to larger sizes (Kulmala *et al.*, 2004; Tunved *et al*, 2006).

Plant emissions, e.g. monoterpenes and sesquiterpenes, are a major source of VOCs in the troposphere (Guenther *et al.*, 1995). BVOC emissions commonly depend on light and temperature (Saathoff *et al.*, 2003). So far most laboratory investigations on the potential to form secondary organic aerosols (SOA) from plant emissions focused on single VOCs such as α-pinene. In this study we investigated the formation of SOA from the mixture of VOCs emitted by spruce, pine and birch trees by oxidation with ozone and OH.

MATERIALS AND METHODS

The experiments were performed in the Jülich plant chamber in order to provide well defined conditions for plants. The experimental setup consisted of two chambers, both approximately 1.5 m^3 in volume, which are constantly being stirred. The plants were put in one of the chambers and fed with CO_2. They were also irradiated in a 24-hour cycle to cause emissions of VOCs.

A fraction of the air carrying plant emissions was transferred from the plant chamber to a second camber, the reaction chamber. The reaction chamber was constantly flushed with ozone, and was equipped with a UV-lamp. When the UV lamp was switched on, photolzsis of O_3 produced OH-radicals and particle formation was initiated. This led to a short nucleation peak, producing a rapid increase in particle number. After the nucleation peak, no new particles were produced and the condensable vapours condensed on the existing particle surface.

VOC measurements were conducted both in the plant and reaction chamber with a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS), to determine the emission kinetics, and an online-GC-MS system for compound identification. VOC mixing ratios were in the lower ppbv to pptv range. Identification by GC-MS was based on mass spectra and retention times of pure chemicals (Fluka / Aldrich, purity > 93 %). The total number of particles formed was measured with an UCPC (TSI3025A). The size distribution of the aerosols in the chamber was measured by a TSI SMPS3936. The resulting SOA was analysed with an Aerodyne aerosol mass spectrometer (Q-AMS).

RESULTS

The nucleation rates observed during the particle formation bursts varied between 0.04 to 260 cm^{-3} s^{-1}, derived from from the UCPC data. These values are high compared to ambient observations which range from 0.01 – 10 cm^{-3} s^{-1} (Kulmala *et al.*,2004). The growth rates were of the order of a few tens of nm h^{-1}, calculated from the SMPS size distributions. They compare reasonably well with growth rates observed in mid latitudes with a range of 1-20 nm h^{-1} (Kulmala *et al.*,2004).

The maximum volume produced as well as the the growth rates of particles showed a linear dependency of the total carbon entering the reaction chamber. The growth behaviour was quite similar for the pine, spruce and α-pinene events, while birch produced more effectively growing particles. The nucleation rates also increased with increasing total carbon, but the dependency varied much more between the species. Again, birch was the most effective particle producer with respect to total carbon emitted.

MODELING

The chamber setup, with inflow of VOC-laden air form the plant chamber and outflow from the reactor chamber to the instrumentation, leads to dilution of the aerosol concentration over time, with the aerosol lifetime being of the order of 1 h. Due to this, a model taking this effect into account has to be used in evaluating the chamber data.

The chamber setup can be considered a continuously stirred tank reactor (CSTR, Schmidt 1998). This means that we assume that there exists perfect mixing inside the tank volume, and the concentration in the reaction chamber are determined by the inflow and outflow rates. Changes in the inflow will result in changes in the chamber concentration after a time lag determined by the in- and outflow. The model results demonstrated that the gas phase concentration of monoterpenes in the chamber is well understood.

The aerosol was simulated with a simple moving sectional model with only condensation, coagulation and dilution taken into account. Assuming a accommodation coefficient of unity and a negligible vapor pressure for the condensing vapor, we found that ca 1% of the oxidized monoterpene was enough to explain the observed growth rate of the particles for a pine event.

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BLACK CARBON LEVELS IN FINE AND ULTRAFINE PARTICLE SIZE FRACTIONS

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Keywords: traffic emissions, black carbon (BC), PSAP, light absorption.

INTRODUCTION

Traffic is a significant emission source of fine particulate matter (aerodynamic diameter D_a below 2.5 µm, $PM_{2.5}$) in urban and urban background areas. Soot is one of the most important component of the traffic related particulate emissions. The number concentration of ultrafine (D_a < 100nm) soot particles in the areas influenced by the traffic can be high (Rose *et al*., 2005). Ultrafine particles, including soot, play an important role in aerosol-induced adverse health effects (Ibald-Mulli *et al*., 2002, Lighty *et al*., 2000). In addition, soot is the most efficient particulate light absorber, and has an effect on global radiative balance. When optical methods are used to analyze absorbing properties of fine particles, soot is often called black carbon (BC). In this study, BC levels in urban background aerosol were investigated using instrumentation based on light absorption of particles.

METHODS

The measurements were done in Helsinki, Finland, at an urban background station SMEAR III (60º20'N, 24º97'E, 26m above se level). The site is located on the outskirt of Helsinki, 5 km northeast from the city centre. Absorption coefficients σ_{AP} were measured using two 3-wavelength (λ = 467 nm, 530 nm, and 660 nm) Particle Soot Absorption Photometers (3λ PSAP, Radiance Research, Seattle, WA, USA, Virkkula et al., 2005). Selection of the particle size fraction was made by using impactors with 1 µm and 0.170 µm cut-off diameters (Fig. 1). The sample air for PSAPs was diluted with the dilution ratio of about 1:3. The sample flow rates were adjusted to 1.7 and 1.3 l min^{-1} for PSAP with the 0.170µm and 1µm cut-off impactors, respectively. A Multi-Angle Absorption Photometer (MAAP) measured BC mass concentration for particle smaller than 1 µm. The MAAP flow rate was 6.6 l min^{-1}. In addition, a 3-wavelength (λ = 450 nm, 550 nm, and 700 nm) nephelometer (TSI model 3563, St Paul, MN, USA) with a flow rate of 20 l min^{-1} was used to detect scattering coefficients $\sigma_{SP..}$ This information is used for the iterative correction procedure of PSAP data as presented by Virkkula *et al*. (2005). The data was averaged to 15 minute.

The measurement setup described above was used to study the BC levels in different particle size fractions between June 12 and end of August 2007.

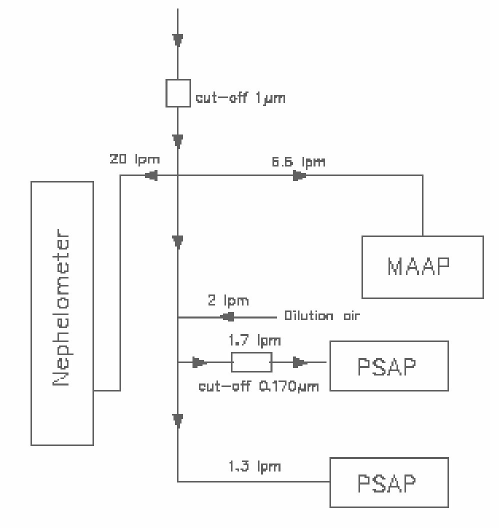

Figure 1 Schematic picture of the instrumentation.

RESULTS AND CONCLUSIONS

This investigation showed a clear difference between σ_{AP}s in two different size ranges. σ_{AP} with cut-off diameter 0.170 ($\sigma_{AP,0.170\mu m}$) were approximately 60% of the σ_{AP} values with 1µm cut-off ($\sigma_{AP,1\mu m}$). This already shows that significant fraction of the BC particles of urban background aerosol occurs near the ultrafine size range. On the other hand, vehicular rush-hours did not show a clear increase of $\sigma_{AP,0.170\mu m}$ fraction compared to $\sigma_{AP,1\mu m}$. This is most likely because of the fact that long-range transported or regional black carbon dominates at the location. The situation is probably different when fresh traffic aerosols will be measure inside the traffic (next step of this study).

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RAMAN SPECTROSCOPY AND FORMATION OF CLOUD DROPLETS

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Keywords: Raman spectroscopy, cloud condensation nuclei, water activity, van't Hoff factor.

INTRODUCTION

The aim of this work is to obtain a microscopic understanding of the interactions between solute molecules and water in growing cloud droplets.

Adipic acid and ammonium sulphate are ubiquitous components of atmospheric particulate matter. Both compounds have been found to act as cloud condensation nuclei (Cruz and Pandis, 1997). Cloud droplet activation is described by Köhler theory (Köhler, 1936; Seinfeld and Pandis, 2006), in which the water activity of the growing droplet is a key parameter. Often the van't Hoff factor is used to account for non-ideality of the aqueous solutions (e.g. Bilde and Svenningsson, 2004; Henning *et al.*, 2005).

In this work we take a different approach and try to understand intermolecular interactions between adipic acid, ammonium sulfate and water on the microscopic level.

METHODS

Model systems of cloud droplets have been studied using Raman spectroscopy. The model systems consisted of aqueous solutions of ammonium sulphate (with concentrations varying between 0.1 M and 3.6 M) and adipic acid (with concentrations varying between 7 mM and 100 mM). The Raman spectra of these solutions were obtained with a Bruker RFS 100 with a Germanium-diode laser detector and laser excitation from a Nd^{3+}/YAG laser at wavelength 1064 nm. The laser intensity was 281 mW. The spectral resolution was 4 cm^{-1}.

The low-frequency parts of the spectra (with wavenumber below 400 cm^{-1}) was transformed into the $R(\nu)$-representation (Nielsen, 1993). One broad band was seen with a maximum at 175 cm^{-1}. It has been assigned to the O-O deformation of pentamer structure (Nielsen *et al.* 2000), which is very abundant in pure water and many aqueous solutions at room temperature (Walrafen, 1964; see figure 1). It is considered to be characteristic of bulk water (Gniadecka *et al.*, 2003; Greve *et al*, 2007, Hetényi *et al.*, 2004). These bands were fitted to Gaussian functions, and the functional dependence between the height of the band and the concentration of ammonium sulphate was examined for solutions containing various amount of adipic acid.

CONCLUSIONS

From the $R(\nu)$-representations of Raman spectra of aqueous solutions, it could be seen that addition of ammonium sulphate led to an increase in the concentration of the water pentamer species, whereas the concentration of the water pentamer decreased upon addition of even small quantities of adipic acid to an aqueous solution of ammonium sulphate. This effect was evident even when the concentration of adipic acid was below 10 mM. In contrast, the addition of adipic acid to pure water had no observable influence on the concentration of the water pentamer species. A similar effect was observed for aqueous solutions containing ammonium chloride and adipic acid, but it was not seen for solutions of for example sodium chloride and adipic acid. This indicates that the water structure is dependent not only on the amount of solutes, but also on the identity of the present solutes. Furthermore, when the solution contains more than

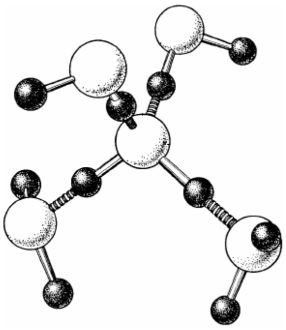

Figure 1: Model of the water pentamer. Oxygen atoms are connected to hydrogen atoms through covalent bonds (white) and hydrogen bonds (striped) (Walrafen, 1964).

one solute, the effect on the intermolecular interaction may differ greatly from the corresponding interactions in solutions containing only *one* solute. To determine the water activity, it is therefore not always sufficient to use the van't Hoff factors of the solutes. It is also necessary to describe the combined influence of the solutes on water.

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MOLECULAR TRACERS IN ORGANIC PARTICLES – RESULTS FROM MEASUREMENTS IN DANISH URBAN AREAS

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Keywords: PAHs, hopanes, levoglucosan, traffic, wood combustion.

INTRODUCTION

We investigated the sources and concentrations of organic compounds in particles by measurements of polycyclic aromatic hydrocarbons (PAHs), hopanes and levoglucosan. These compounds are molecular markers of their origin, and their levels in particles thus reflect the influence of different sources to particle mass. PAHs are emitted to air as byproducts from combustion of both wood and fossil fuels. Hopanes are mainly tracers of engine lubricating oil and thus vehicle emissions of particles (Rogge et al., 1993), while levoglucosan and mannosan are major combustion products of cellulose and hemicellulose ((Simoneit et al., 1999), and these compounds are thus tracers of wood smoke emissions.

We studied the concentrations of molecular markers and their correlations with other pollution tracers in two measurement campaigns. One campaign was aimed at particles and tracers from traffic emissions, while the other campaign was aimed at particles and tracers from residential wood combustion. Emissions from traffic and wood combustion are the two major Danish sources to $PM_{2.5}$.

METHODS

Particles from traffic emissions were studied in a campaign in October-November 2004. Measurements were carried out at a busy street and a background site in Copenhagen, Denmark. Particles from wood combustion were studied in a campaign in March-April 2005. In this campaign, measurements were carried out in a residential area with detached houses and a background site. Active woodstoves were present in about one fourth of the houses in the residential area (Glasius et al., 2007).

Particulate and semivolatile compounds were sampled on quartz fibre filters followed by polyurethane foam plugs. Sampling time was 12 hours (06-18) on working days in the traffic emission study and 2x12 hours (15-03) in the wood combustion study. Filters for analysis of PAHs and hopanes were extracted in dichloromethane, and the extracts were cleaned on silicic acid glass columns. The columns were first eluted with hexane (extracting hopanes) followed by dichloromethane (extracting PAHs). The solvent of the dichloromethane fraction was exchanged to toluene. PAHs and hopanes were analysed with GC-MS. Further analytical details are available in Glasius et al. (2007). The analysis of levoglucosan and mannosan was performed with the method described by Zdrahal et al. (2002).

CONCLUSIONS

Samples were collected during periods of expected maximum emission in both areas, in order to characterize the sources. In addition sources were identified by simultaneous measurements at a background site. The results listed in Table 1 show considerable differences between average concentrations in background area and source area. The relatively large standard deviations are due to differences in emissions and meteorological conditions. There is e.g. a clear increase in hopane concentrations at low wind speeds (2-3 m s^{-1}) (data not shown).

Study	Compounds	Source area	Background
Traffic	PAH	12.5±8.1 ng m^{-3}	4.7±2.9 ng m^{-3}
	Hopanes	35±23 ng m^{-3}	5.2 ±2.4 ng m^{-3}
Wood combustion	PAH	10.9±7.1 ng m^{-3}	5.9±2.9 ng m^{-3}
	MAs	313±237 ng m^{-3}	168±89 ng m^{-3}

Table 1. Average concentrations (± one standard deviation) of molecular markers during the two measuring campaigns. MAs are levoglucosan and mannosan. 12 samples were analysed from the traffic campaign and 10 from the wood combustion study. Only 10 particulate PAH are reported here.

In the traffic study both PAHs and hopanes from traffic show high correlations (R>0.75) with simultaneous measurements of $PM_{2.5}$, CO and NO_x from traffic. The correlation between PAHs and hopanes from traffic are 0.67.

In the wood combustion study, PAHs from wood combustion show high correlations with $PM_{2.5}$ and CO, while the correlations are lower for monosaccharide anhydrides (levoglucosan + mannosan). Both types of tracers show negative correlations with NO_x, as expected since wood combustion does not emit NO_x in considerable amounts. The correlation between PAH and monosaccharide anhydrides is 0.53. The results indicate that wood combustion particles are best traced using an array of molecular markers (Glasius et al., 2007).

The conclusion is that molecular markers such as PAHs, hopanes and monosaccharide anhydrides are suitable as tracers of specific sources, also at Danish conditions. Results of the present study can be used to evaluate source contributions to organic particles in future studies.

ACKNOWLEDGEMENTS

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STUDIES OF WEAR PARTICLE EMISSIONS USING A ROAD SIMULATOR

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Keywords: PM measurements, Ultrafine particles, Vehicles emissions, Wear particles

INTRODUCTION

During the last years it has become evident that wear particles from road pavements and tyres strongly contribute to episodes with very high concentrations of inhalable particles in outdoor air. These episodes normally occur during dry periods in winter and spring when accelerated wear and particle production occurs due to the use of studded tyres and winter gritting. This problem has attracted attention in countries were studded are frequently used. The resulting wear and production of inhalable particles is dependent on a number of factors that are difficult to quantify in real world environments. Therefore, the objective of this study was to investigate the effects of pavement type, tyre type and speed on pavement wear in a controlled environment.

METHODS

At the Swedish National Road and Transport Research Institute (VTI) a circular road simulator was used to generate wear particles. Particle sampling in the simulator hall makes it possible to sample pure wear particles, with very low contamination from ambient particles. The road simulator runs four wheels around a circular track. Each wheel axle is equipped with an electrical motor which drives the rotation of the simulator. The speed can be varied between 0–70 km/h. The simulator track can be equipped with any type of pavement and any type of light-duty vehicle tyre can be mounted on the axles. Three different sets of measurements were made in order to elucidate the effect of three factors on pavement wear and generation of PM_{10}; these were 1) type of pavement, 2) type of tyres and 3) speed.

1) These included an asphalt concrete consisting of granite stone material with 16 mm maximum aggregate size (hereafter denominated “Granite <16”), a stone mastic asphalt of quartzite stone material with 16 mm maximum aggregate size (“Quartzite <16”) and another stone mastic asphalt (“Quartzite <11”) of another quartzite stone material with 11 mm maximum aggregate size.
2) Three types were chosen; studded winter tyres, friction (non-studded winter) tyres and summer tyres.

3) Speed was varied from 0–70 km/h in the road simulator. The increase between these speeds is made quickly in less than two minutes. Once the desired speed has been reached the road simulator is left to run for ~1.5 h.

Particle size distribution in the road simulator hall was sampled using a PM10-inlet and measured using different instrument as APS (model 3321, TSI), SMPS (CPC 3010 and DMA 3071, TSI), DustTrak (model 8520, TSI) and TEOM.

RESULTS AND CONCLUSIONS

A granite pavement resulted in 70 % higher PM_{10} concentration than a quartzite pavement of the same aggregate size. Out of two quartzite pavements with different aggregate sizes, the one with smaller stone material (Quartzite <11) led to lower PM_{10} concentration than larger (Quartzite <16), indicating that other aggregate properties than size are more important for PM_{10} production.

Studded tyres cause extreme concentrations of PM_{10} that are tens of times higher than those associated with non-studded winter tyres. Summer tyres have a very little effect on PM_{10} production in contrast.

Using a simple box model assumption mass emission and number emissions factors were estimated. Our estimated PM10 emission for studded tyres at 70 km/h agrees with field measurements carried out in two cities in Sweden. The PM10 emission was determined to ~1 g per vehicle kilometre.

Apart from the expected wear particle size ranges (>1 µm), an ultra-fine (<100 nm) fraction with a number maximum around 20–40 nm was found for studded tyres. No ultra-fine particle emission was detected from friction or summer tires. The composition of the emitted particles is assumed to be winter tyre fillers and softening oils, which differ from summer tyres. For a given tyre the velocity and thereby the tyre temperature was the most significant parameter that affected the amount of generated particles.

ACKNOWLEDGEMENTS

The Swedish National Road Administration is acknowledged for financial support.

DETERMINATION OF PARTICLE EMISSION FACTORS OF INDIVIDUAL VEHICLES UNDER REAL-LIFE CONDITIONS

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Keywords: ultrafine particles, traffic, urban pollution, vehicle emissions.

INTRODUCTION

Road traffic constitutes an important source of particular matter and trace gases. Most particles in vehicle exhaust are in the ultrafine size range. In contrast to large particles which are a result of wear of road pavement, tyres and brakes, ultrafine particles are respirable and penetrate deep into the lungs, posing a threat to health. Especially in the densely populated urban areas, road traffic can lead to severe pollution of the ambient air. Since today half of the global population lives in urban areas, it is a matter of public and scientific concern to examine the emissions under real-life conditions. Particularly the measurement of the particle emissions from individual vehicles that form a car fleet delivers insight into the variability of particle emissions among cars and might allow the assignment of emission properties according to vehicle type, age, fuel technology etc.

EXPERIMENTAL

Here we present an experimental setup for the measurement of particle emission factors (EF) from individual vehicles, which was designed for continuous on-road sampling. The system has been applied in two test experiments conducted in the Göteborg area. The measurement sites were at a rather busy major street in Göteborg (Western Sweden) and a sparsely frequented two-lane country road 25 km from Göteborg, respectively. The measurements were each performed monitoring the traffic on one of the two lanes. The inlet of a sampling line was installed in the centre of the lane and attached to the street surface to extract air directly (*in-situ*) from the plumes of passing vehicles. To measure CO_2 and number density of particles > 10 nm simultaneously, the collected air was distributed to a CO_2 monitor and a condensation particle counter (CPC, TSI 3010), respectively. The additional registration of licence plate numbers from the vehicles driving past gives information about the vehicle type, engine power and further technical data provided by the National Road Administration.
While during the first experiment everyday traffic was observed to prove the applicability of the described approach, the second experiment served to study the intra-vehicle variability of particle emissions under predetermined driving conditions (specified speed and gear). A set of four selected vehicles, consisting of a diesel car, an older medium-sized petrol car and two compact cars was applied.

METHOD

Although the sampled air volume was diluted with a known amount of particle-free background air, the very high particle numbers within the vehicle exhaust plumes gave concentrations exceeding the upper limit of the particle counter. A solution to nevertheless quantify the excess particle numbers in the plume is presented and the particle EF's are derived from the enhancement ratios of particle number to CO_2 mixing ratio in the exhaust plumes of passing vehicles.

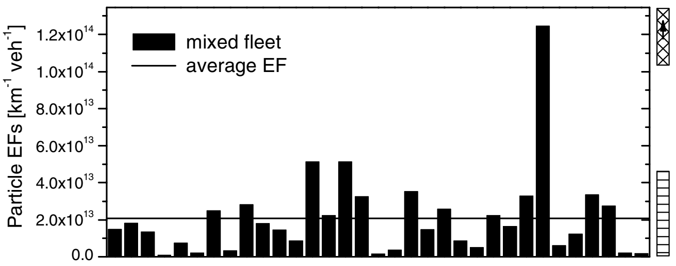

Figure 1. Single vehicle number particle emission factors derived from measurements in Göteborg.

When assuming a CO_2 emission of 164 g km^{-1} veh^{-1}, which is an average value for petrol-fuelled vehicles (cp. www.starterre.fr/voiture-auto/emission_co2), particle emission factors of the order 2×10^{13} part km^{-1} veh^{-1} were derived from the observed car passages (cp. Figure 1). This value agrees well with those published in the literature for petrol-driven vehicles (e.g. Jones and Harrison, 2006; see also lower side bar in Figure 1), which constitute more than 90% of the Swedish fleet (Ahlvik, 2002). Emission factors for diesel driven passenger cars are one order of magnitude higher (cp. upper side bar in Figure 1). Given the obtained results, the used setup proved appropriate to quantify particle emission factors from road traffic.

CONCLUSIONS

The measurements and observations of this study demonstrated that the simultaneous measurement of CO_2 and particle number for the purpose of characterising individual vehicles' emissions is a feasible approach. Furthermore, by using the described method, the particle emission can be linked to other indicators for traffic exhaust such as NO_x, VOC or CO in order to better understand real-world vehicle to vehicle variation in particle production.

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A COMPARISON OF NEW PARTICLE FORMATION AT DIFFERENT SITES IN THE EUROPEAN BOUNDARY LAYER

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Keywords: NEW PARTICLE FORMATION, FORMATION RATE

INTRODUCTION

Secondary aerosol formation from gas phase precursors is considered as an important source of new particles. Considerable attention has been paid to the sources and sinks of atmospheric particles because they influence particle number concentrations, which are of great concern as the particles effect global radiative forcing and human health. New particle formation has been observed almost everywhere in the atmosphere, in clean areas as well as rural, coastal and polluted areas (Kulmala et al., 2004). In this work we compare new particle formation at different sites in the European boundary layer; in Central Europe (Melpitz, Eastern Germany), in Southern Europe (San Pietro Capofiume "SPC" in the Po Valley) and in Northern Europe (Hyytiälä station in Finland) for the period of one year (July 2003-June2004). In particular; we identified occurrences of new particle formation bursts (NPF) focusing mainly on studying the similarities and differences of NPF for those different locations.

MATERIAL

Data sets of particle size distribution and number concentrations were compared based on one year data of continuous measurements in three different sites. The sites span latitudinal range from (44^{o}3'N, 11^{o}37'E, 10 m a.s.l.) for SPC; (51^{o}32'N, 12^{o}54'E, 87 m a.s.l.) for Melpitz and (61^{o}51'N, 24^{o}17'E, 170 m a.s.l.) for Hyytiälä (see Fig.1). The anthropogenic impact at the sites varies from polluted rural (SPC) to moderate rural (Melpitz) to clean conditions (Hyytiälä). New particle formation events were distinguished from nonevents days by applying the same criteria as previously shown in Hamed et al. (2007).

RESULTS

Monthly frequencies of NPF ranged from 3 to 67% depending on location and season (see Fig. 2a). In spring seasons it was common that new particle formation days were more frequent; maximum was for Hyytiälä, on average, 42% from March till May while for SPC and Melpitz maximum event frequencies were seen in summer (28% in July for SPC and 38% in August for Melpitz). Surprisingly, during November 2003 no particle formation was observed at all in those sites (see Fig.2a). Generally, in all three sites the minimum values of event frequencies occur in the winter. Figure 2b shows the new particle formation rates as a function of month for the different sites. We have estimated the formation rate of 3 nm particles from the increase of 3–20 nm particle number concentration between the nucleation event start time and the time when the particle concentration exhibits a maximum during the event. Remarkable gradient was found between the more polluted sites (SPC and Melpitz) that exhibit high formation rates and less polluted (Hyytiälä) that exhibits low formation rates. Generally in spring time the particle formation rates were higher for all stations than in winter time. In Hyytiälä the highest formation rates occur in spring whereas in Melpitz and in SPC the highest values are seen in summer. In general, the trend of the formation rates in different seasons was almost the same as the nucleation event frequency trend. More data analysis is still ongoing to further understand the differences and similarities of NPF events in different European boundary layers environments, including a comprehensive statistical comparison of the data sets with respect to variation of meteorological parameters and trace gases during nucleation events, in order to elucidate the different process that govern nucleation at those sites.

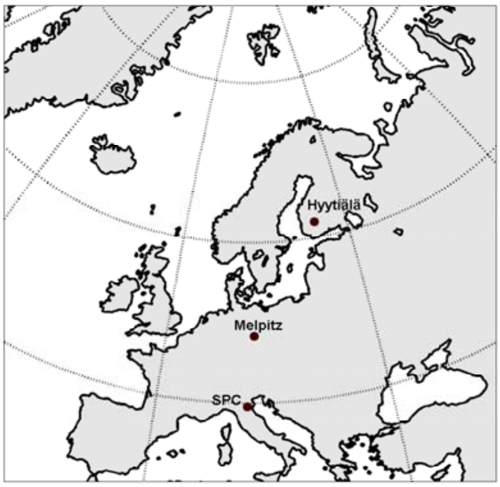

Figure 1. Map shows the locations of the stations that were compared in this study.

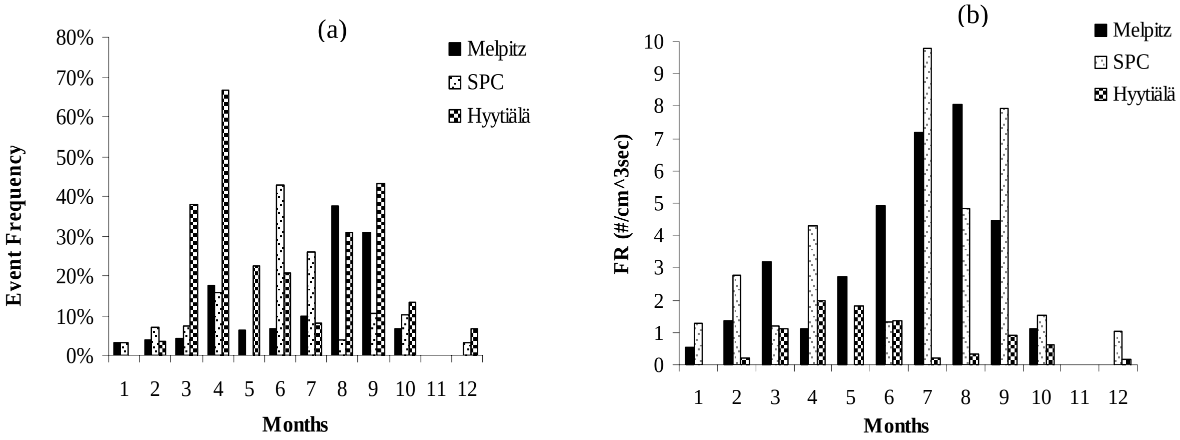

Figure 2. (a) Monthly event frequency and (b) Monthly mean of formation rate ($cm^{-3}sec^{-1}$) in Melpitz, SPC and in Hyytiälä stations respectively. (Note: June 2004 for SPC was statistically poor)

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EXTRACTING THE MAGIC NUMBERS OF WATER CLUSTERS FROM ABUNDANCE SPECTRA

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Keywords: Protonated water clusters, binding energy, unimolecular reactions.

INTRODUCTION

Ionic species have an enhanced ability to act as nucleation centers in the atmosphere relative to their neutral counterpart due to the reduced critical size and barrier height. In addition to the special energetic and thermodynamic properties endowed to water clusters in general due to the presence of hydrogen bonds and the concomitant highly non-trivial approach to bulk properties, this makes the thermal properties of these clusters particular interesting objects. The present study deals with the stability of protonated water clusters in the size range up to hundred molecules, probed by molecular beam experiments in vacuum.

Clusters are usually produced with broad mass distributions that reflect the kinetics of formation and which reflect specific experimental conditions. Superposed on the broad envelope abundance distributions one observes size-to-size variations in the abundances. These are caused by evaporative processes in the molecular beam and contain information about the underlying size-to-size variations of the cluster stability. Spectra such as those measured in this study are well known (Shi, 1993) and the anomalies have been discussed extensively theoretically (see e.g. Svanberg 1998), but seemingly no attempt has been made to quantify the effect based on the observed abundance spectra.

EXPERIMENTAL PROCEDURE AND RESULTS

Our experimental set-up consists of an electrospray ion source, which produces cluster ions from pure water. After electrospray at atmospheric pressure, the ions pass through two differentially pumped chambers before entering the high vacuum region of the instrument. The operating parameters of the source were optimized for production of a wide distribution of clusters. After having entered the high vacuum region of the apparatus, the ions are focused into the quadrupole mass filter which acts as a high pass filter in these experiments. The ions are then transferred into the time-of-flight (TOF) region which is operated at $2\cdot10^{-7}$ mbar. The TOF is of the reflectron type, and the ion beam is extracted and accelerated in a direction orthogonal to the ion optical axis applying pulses of high voltages (9.1 kV) to the acceleration electrodes. The duty cycle of the TOF is set to allow all ions in a wide mass range to arrive before sending off the next burst of ions and the ion count rate is adjusted to allow for a sufficiently wide linear dynamic range. The mass resolution of the time-of-flight analyzer was $m/\Delta m = 5000$ (FWHM). Typically, time-of-flight spectra are accumulated for 1–2 minutes for positive ions and 5 minutes for negative ions.

A typical spectrum is shown in Fig.1. The abundance anomalies, including the strongly enhanced peaks at 379 and 505 amu which are the N=21 and 28 cluster, have been described previously and interpreted in terms of increased stability of these species.

ANALYSIS

The method used to analyze the data has been developed elsewhere and used for the quantitative analysis of shell structure in metal and rare gas clusters (Hansen, 1999). The relation used is

$$I_N \propto \frac{D_N + D_{N+1}}{2} + \frac{C_v}{G}(D_N - D_{N+1}),$$

where I_N are the observed abundances, D_N the evaporative activation energy of $(H_2O)_NH^+$ and G is approximately 25. The heat capacities, C_V, are not known experimentally for these species and two different parameterizations were used, both based on extrapolations from bulk values. One is the high temperature (constant) value, and the other the low temperature value which grows linearly with temperature. The outcome of the analysis gives the relative differential binding energies vs. size. To translate these to absolute energies the bulk parameters for cohesive energy and surface tension were used. The presence of the second term on the right hand side of the equation has important consequences for the interpretation of the prominent peaks at N=21 and 28 in terms of their stability.

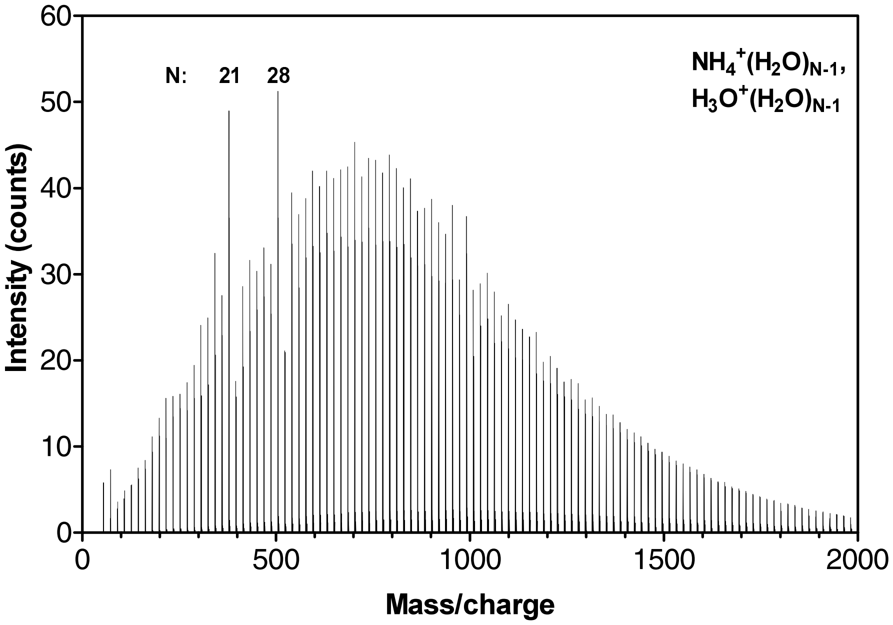

Figure 1. Measured cluster abundances. Note that the spectrum also includes ammonia containing species, as indicated.

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STUDIES ON CARBON CONTENT OF FINE PARTICLE AMBIENT AEROSOL IN FINLAND

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Keywords: ATMOSPHERE, FINE PARTICLES, CARBONACEOUS AEROSOL

INTRODUCTION

Half of the fine particle mass in typical urban air is made of carbonaceous material. Major part of this is organic carbon (OC). Soot (called elemental carbon, EC or black carbon, BC) from incomplete combustion has lower concentrations, but it forms an important fraction of carbonaceous material. In urban ambient air organic carbon is primary or secondary, but elemental carbon is always primary. For ambient soot concentrations there are several direct measurement methods, which mostly are based on the measurement of light absorption of particles, and therefore the parameter they measure is called black carbon (BC) concentration. Organic carbon is usually measured using thermal-optical measurement methods. In this work a set of campaign-based and a long-term measurement data on carbonaceous material in fine particle aerosol in Helsinki will be presented. Most of the data is from an urban background station close to Helsinki downtown (SMEAR III, 60°20'N, 24°97'E, 26 m above sea level).

METHODS

In Helsinki, of carbonaceous particulate matter there are the longest time series for black carbon as measured with the aethalometers. The time series covers several years since 1996. This enabled a study on the trends of BC concentrations in Helsinki (Järvi et al., 2007). Comparison between different years was done for selected periods, when data from all campaigns existed in an equal manner. The effect of traffic and meteorological variables to the measured BC concentrations were taken into account.
Recently the BC measurements with an aethalometer were completed with the measurements by using two Particle Soot Absorption Photometers (PSAP). Use of preimpactors allows PSAPs to measure different size fractions, one thought to represent fresh diesel soot ($PM_{0.17}$) and the other (PM_1) the sum of fresh and aged (long-range transported) BC.
Organic carbon has been studied using various sampling and analytical methods. Thermal-optical transmission method has been used for size-selected ($PM_{2.5}$, PM_1) and size-segregated samples. The offline methods were completed with an online (semi-continuous) set up in summer 2006. The water-soluble fraction of organic carbon (WSOC) analyses were done from filters and impactor substrates using the TOC-V_{CPH} organic carbon analyzer (Shimadzu) with a high sensitive catalyst. Chemical speciation has been till now limited. Some organic acids have been determined from PM_1 samples using an ion chromatography (IC) and a liquid chromatography mass spectrometry (LC-MS). The latter have been used also to identify organic biomass burning tracers, monosaccharide anhydrides (mainly levoglucosan), from filter and impactor samples.

RESULTS

In the BC trend study, a small decrease of BC concentrations (from 1.11 to 1.00 $\mu g\ m^{-3}$) was found from 1996 to 2005 for the considered periods. The diesel engine technology and diesel fuel have developed much during ten years, but the anticipated clear decrease in BC concentrations is compensated by increasing number of vehicles. When looking at the BC in two size fractions using the PSAP setup, the data did not show big differences in the diurnal variation between the two fractions. This is most likely due to the fact that the measurement site is a few hundred meters from the major roads, and long range transported and especially regional aged aerosol dominates BC mass. During high concentration periods of organic carbon long range transported or regional secondary aerosol dominates which can be seen from the same concentration levels in Helsinki as in Hyytiälä (SMEAR II) station 200 km north from Helsinki (Figure 1). Annual WSOC contributes 30-80% of OC in Helsinki. Levoglucosan was found to be good tracer for both natural and anthropogenic biomass burning. Combining emission rates of levoglucosan and OC from a laboratory scale wood combustion experiment (one fireplace) to corresponding ambient concentrations, it was possible to estimate how much wood combustion contributes the particulate matter concentrations in Helsinki. This crude calculation suggests that during winter months (October-March) typically 40% of organic carbon is from biomass combustion.

CONCLUSIONS

The studies carried out on carbonaceous particulate matter in Helsinki, Finland, show that offline analysis can gather useful data when conducted on long-term basis, and online measurements are needed for source- or process-specific considerations. As shown in connection of biomass burning tracer (levoglucosan), organic speciation is sometimes useful in assessing contribution of sources of ambient particulate matter.

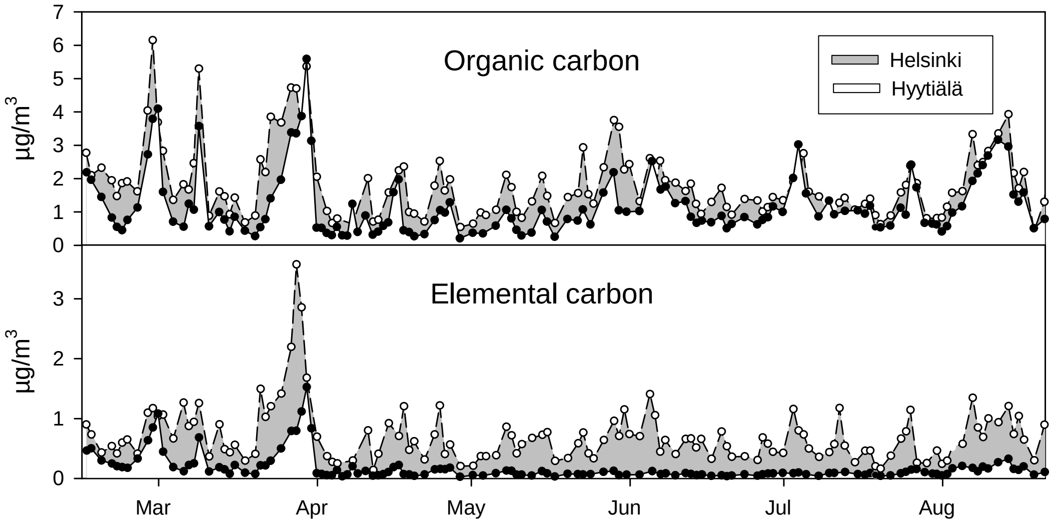

Figure 1. High concentration periods of OC display similar concentrations in Helsinki (SMEAR III station) and in Hyytiälä (SMEAR II station), which are more than 200 km apart from each other.

ACKNOWLEDGEMENTS

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SECONDARY ORGANIC AEROSOL FORMATION BY OZONOLYSIS OF VOLATILES EMITTED FROM TREES

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Keywords: secondary organic aerosols, plant volatiles, ozonolysis

INTRODUCTION

The formation of secondary organic aerosols (SOA) is one of the main processes that affect the composition and properties of atmospheric aerosols. Volatile monoterpenes and isoprene are the main biogenic VOCs (BVOCs) in the atmosphere and they are known to contribute to SOA formation (Kanakidou et al., 2005). The current evidence from reaction chamber studies (Bonn and Moortgat, 2003) suggests that inducible VOCs (e.g., sesqui- and homoterpenes) might be even more effective in reactions with O_3 and subsequent formation of aerosol particles. We have recently studied SOA formation from oxidation of volatile organic species emitted by living plants, white cabbages (Joutsensaari et al., 2005, Pinto et al., 2007). Those studies showed that particle nucleation by ozonolysis of plant volatiles takes place more efficiently when the plants are emitting inducible VOCs after elicitor triggering or herbivore damages compared to intact plants. In this paper, we present results from the experiments of SOA formation by ozonolysis of VOC emitted from Scots pine and Norway spruce seedlings.

METHODS

We have studied SOA formation in a continuous flow reactor (Teflon chamber, ~2 m^{-3}, residence time ~1 h). Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) seedlings were used as VOC emitters. In some experiments, the trees were treated with methyl jasmonate (MeJa) or damaged by herbivores (large pine weevil, *Hylobius abietis*) to induce the production of monoterpenes and certain less-volatile sesqui- and homoterpenes. Plant-emitted VOCs were conducted into the separate reaction chamber and they were mixed with an air-flow enriched with ozone (target concentration 200 ppb) at the inlet of the reactor. At the beginning of the trials, VOCs from trees were introduced to the chamber for about one hour before ozone addition. During nighttime (22-06), the lights over plants were off. Particle size distributions were measured with scanning and fast mobility particle sizers (SMPS, FMPS). Ozone and VOC concentrations were measured at the reactor inlet and outlet. VOC samples were collected on Tenax-TA adsorbent and subsequently analyzed by gas chromatography-mass spectrometry (GC-MS). Furthermore, composition of formed particles were analysed with an Aerosol mass spectrometer (AMS, Aerodyne).

RESULTS AND DISCUSSION

The preliminary results show that monoterpenes (e.g. α-pinene, β-pinene, myrcene, limonene and β-phellandrene) were identified as the most abundant compounds in the emission of Scots pine and Norway spruce seedlings. The total BVOCs and sesquiterpene emissions were about 5-fold and 10-fold higher, respectively, from the herbivore-damaged/MeJa-treated plants compared to the intact plants. Figure 1 shows particle number size distributions as a function of the hour of day for control and herbivore-damaged spruce seedling. After the start of the ozone introduction, clear particle formation was observed and subsequently more particle formation events were determined but they were less intensive. During nighttime particle production were lower due to lower VOC emissions. In the experiments with the herbivore-damaged spruce seedlings, total number concentration of formed particles were about 3-fold higher than control ones due to higher VOC emissions. Preliminary results for spruce seedlings indicated that higher sesquiterpene emission led higher particle formations which suggest that sesquiterpenes play an important role in new particle formation. AMS results shows that there is significant similarity between chamber mass spectra and mass spectra obtained during particle growth events in Boreal forest, Hyytiälä. However, there the chamber results have an extra series of peaks - possibly reflecting a specific set of VOC precursors emitted from seedlings. In future we will study SOA formation also by photochemical reaction of VOC from different types of plants, e.g., isoprene, monoterpene and sesquiterpene emitters.

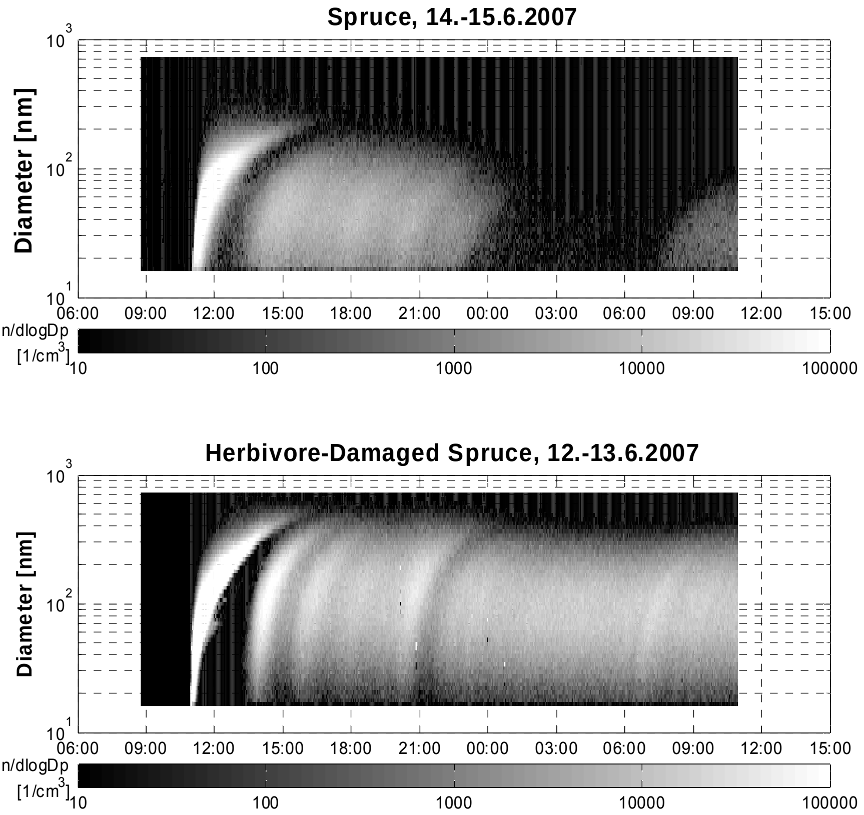

Figure 2. A contour plot of aerosol particle number size distributions for control (upper panel) and herbivore-damaged (lower panel) spruce seedling.

ACKNOWLEDGEMENTS

The work was supported by the Academy of Finland (decisions no. 202300, 105209, 111360, and 110763). The authors want to thank T. Oksanen for his help during the experiments and the staff at the Kuopio University Research Garden for maintaining the plants.

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INVESTIGATION OF HEALTH EFFECTS OF ORGANIC AEROSOL PARTICLES: FIRST RESULTS USING A NEW PARTICLE DEPOSITION CHAMBER

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Keywords: health effects, organic aerosol, electrostatic deposition, secondary organic aerosol.

INTRODUCTION

Adverse health effects associated with exposure to particles in the (sub-) micrometer range in ambient air are well documented by epidemiology and supported by mechanistic animal studies. The particle properties responsible for these effects are only poorly understood, but particle surface characteristics and chemical composition are likely important parameters. To elucidate the features of particle-cell interactions in cell culture systems representing the respiratory surface, it is essential to mimic the in-vivo interactions of particles with cells as closely as possible. However, commonly used model systems for in-vitro studies deviate significantly from the in-vivo situation such that responses are possibly not representative of those induced by the particles in vivo.

METHODS

A new deposition chamber is presented where particles are deposited onto the cells directly out of a conditioned air-flow, simulating accurately the physiological conditions in the lung, i.e., the aerosol is humidified to about 90% relative humidity, the CO_2 concentration is increased to 5% $^v/_v$ and the aerosol is heated to 37°C. This assures that all cellular reactions are due to particle deposition and not due to other stress factors.

One of the most important features of the chamber is the electrostatic particle deposition. After passing a bipolar charger (Kr-85 source) particles are efficiently deposited by an alternating electrical field of 4kV/cm. To avoid accumulation of particles with one polarity on the cells, the polarity of the electrical field alternated at 1Hz. For on-line monitoring of the state of the cell culture, the chamber is equipped with a device detecting the mucociliary activity, whose most conspicuous signature is the ciliary beat frequency. A fiber optic probe placed above the cell culture acts as an optical bistatic radar and detects the vertical movement of the mucus induced by the beating cilia within the illuminated and observed area with a high sensitivity (Figure 1).

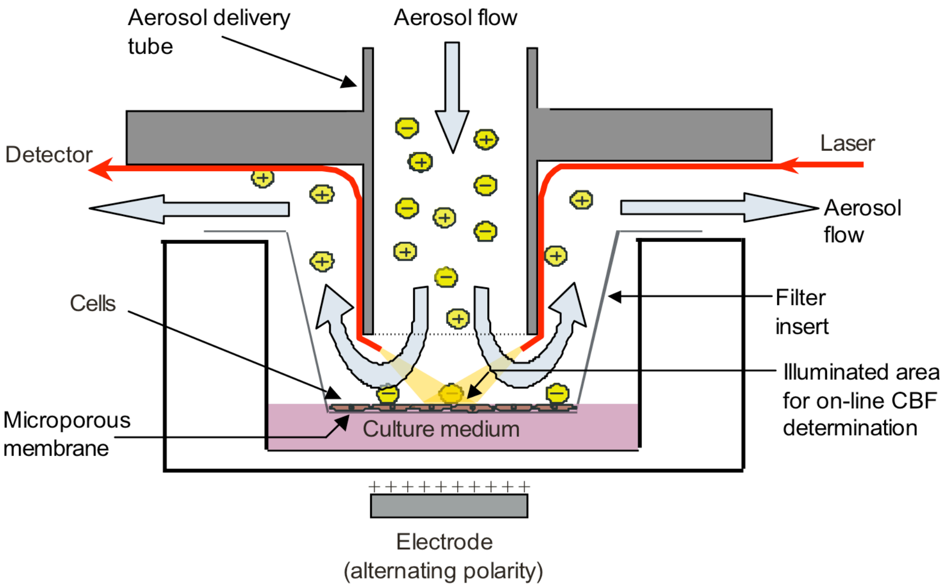

Figure 1. Schematic design of the new particle deposition chamber for lung cell cultures. Particles are deposited in an electrical field between the particle delivery tube and the electrode placed directly beneath the cell culture. A part of the cell culture is illuminated to detect on-line reactions of the cells during particle deposition.

CONCLUSIONS

This new particle deposition chamber was extensively characterized to assure that particles are evenly and efficiently deposited on the cell culture. The even distribution of the particles on the filter was determined by counting deposited particles off-line with a microscope on randomly selected locations along the filter insert radius and with modeling results. Particle deposition efficiency was tested with monodisperse standard particles (polystyrene particles (PSL), Polysciences) and with modeling calculations. At a field of 4kV/cm 15–30% of all particles (50-600nm) are deposited. The deposition efficiency is about 5-45 times higher than comparable existing particle deposition systems.
We tested the new deposition chamber on microdissected porcine tracheal epithelia, a human bronchial-epithelial cell line (BEAS-2B) and on porcine bronchoalveolar lavage macrophages using 200nm PSL at a concentration of about 10^4 particles/cm^3 and secondary organic aerosol (SOA) particles generated in a smog chamber for an exposure time of 2hrs. While the inert PSL particles did not provoke any cell reactions first results with SOA show a tendency to increased release of lactate dehydrogenase and (pro)inflammatory cytokines.

ACKNOWLEDGEMENTS

This work was supported by the Swiss State Secretary for Education and Research (SER), Grants No. C06.0075 and C03.0052 as part of the EC COST Action 633 and by EC Project POLYSOA, Contract No 12719.

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ULTRA-HIGH RESOLUTION MASS SPECTROMETRY AS A TOOL TO ADVANCE ORGANIC AEROSOL CHARACTERIZATION

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Keywords: Chemical analysis, Mass spectrometry, Smog chamber, Secondary organic aerosol.

INTRODUCTION

It has been shown in the last years that high molecular weight compounds make up a significant fraction (20-50%) of the water-soluble organic carbon (WSOC) in ambient aerosols. To better understand formation processes of organic aerosol mass and estimate their influence on climate and health related issues a more complete knowledge of the organic components in the ambient aerosol is necessary.

Novel Mass spectrometric techniques such as high resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), allows determining unambiguously the elemental composition of compounds. Secondary organic aerosol (SOA) samples generated in a smog chamber were analyzed with FTICR-MS.

METHODS

SOA particles were generated in the indoor smog chamber at the Paul Scherrer Institute (PSI), which consists of a 27-m^3 transparent Teflon bag placed in a temperature-controlled housing. alpha-pinene SOA was produced in dark ozonolysis experiments without seed particles, NO_x (<2ppb), water vapor (relative humidity < 2%) and OH scavenger.

The particles were sampled on Teflon membranes filters. After sampling, the filters were extracted for 45 min in a sonication bath in 1 ml acetonitrile:water (50:50) mixture. The extracts were then directly introduced in the mass spectrometer for analysis.

All FTICR-MS measurements were carried out on a 7 Tesla LTQ-FT mass spectrometer (Thermo Electron, Germany) equipped with a Nanomate electrospray source in positive and negative ion mode (Advion Biosciences, UK). Mass accuracy was typically better than 2 ppm. Spectra were acquired at a resolution of 400’000 at m/z 400.

CONCLUSIONS

Several hundred peaks in a mass range between m/z 200-700 were detected. Often within a few millidalton 2-3 peaks with totally different elemental composition are measured emphasizing the necessity for high resolution measurements to elucidate the components in complex samples such as SOA.

The mass spectrum is clearly divided in a range with low-molecular weight compounds (m/z < 300) and a high molecular weight (or oligomer) range (m/z > 300). In the oligomer mass range a dimer and trimer range is distinguishable.

Using advanced data analysis techniques (e.g., the Kendrick and van Krevelen analyses) the elemental composition of the majority of all peaks in the entire mass spectrum could be assigned.

Van Krevelen diagrams show that most of the compounds in alpha-pinene-ozonolysis-SOA have high O:C ratios in the range of 0.4 - 0.6. Monomers have on average a higher O:C ratio than dimers and trimers, suggesting a condensation reaction leading from the monomers to the small co-oligomers as shown in Figure 1 (Reinhardt et al., 2007).

A program developed in-house, MonomerHunter, was used to calculate the abundance of exact mass differences throughout the spectrum to identify potential monomers. Up to 80 different monomers were identified with this procedure. Most of the peaks measured in the monomer mass region of the spectrum (m/z < 300) is found in the calculated results of the MonomerHunter, indicating that this mathematical procedure gives mostly chemically meaningful results.

For the first time ultra-high resolution MS data from aerosol samples were analyzed for a wide mass range (m/z 200-700) with advanced data analysis methods to examine the elemental composition of monomers and oligomers and to investigate possible oligomer formation mechanisms in secondary organic aerosols.

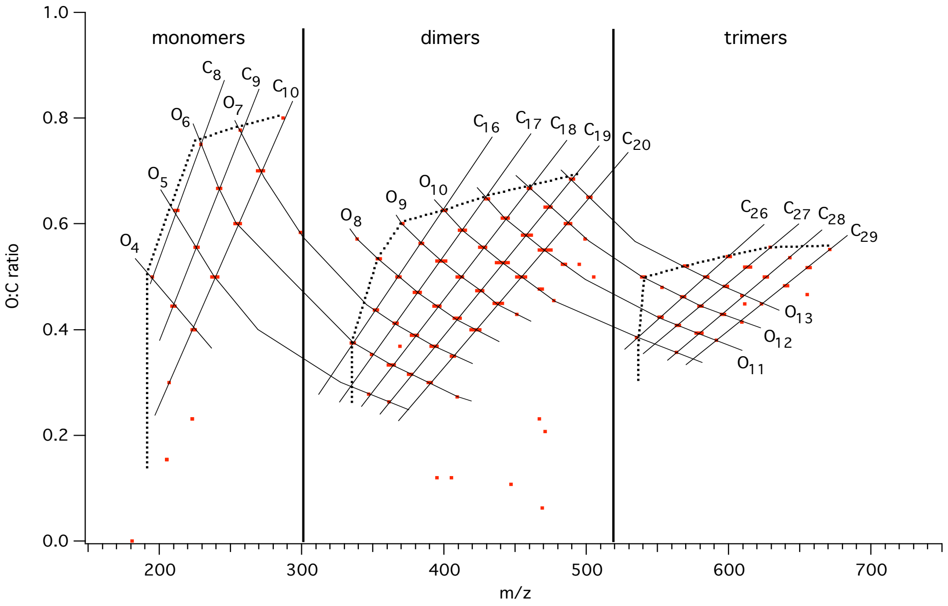

Figure 1. O:C ratio as a function of m/z for all compounds >m/z200 for alpha-pinene-ozonolysis-SOA. Dimers and trimers have a lower maximum O:C ratios than monomers suggesting condensation reactions as possible formation pathways of SOA oligomers as indicated with the dotted lines. Compounds with the same number of carbon and oxygen atoms are connected with solid lines.

ACKNOWLEDGEMENTS

The Functional Genomics Center is greatly acknowledged for providing their infrastructure. This work was supported by ETH Grant TH-14/04-2 and the Swiss National Science Foundation (No. 200020-108095).

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MODELLING TRAFFIC PARTICLES IN URBAN ENVIRONMENTS

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Keywords: aerosol modelling, particle mass, ultrafine particles, traffic emissions.

INTRODUCTION

Fine particles (FP) and ultrafine particles (UFP) and their sources and fate in the atmosphere continue to be key subjects in the atmospheric research due to concerns about the effects on human health and global climate. Over the recent years intensive measuring activities were conducted to characterise the particle size distribution and composition at different ambient and indoor locations. Traffic emissions could be identified as a dominating source of UFP (aerodynamic diameter less than 0.1µm). This can be seen by the large gradient in particle concentration between rural and kerbside locations shown in Figure 1. Vehicle emission factors under real world driving conditions have been be estimated for particle number and size distribution (e.g. Ketzel et al., 2003), for soot particles (Rose et al. 2006) and for particle mass including non-exhaust emissions (Ketzel et al., 2007).

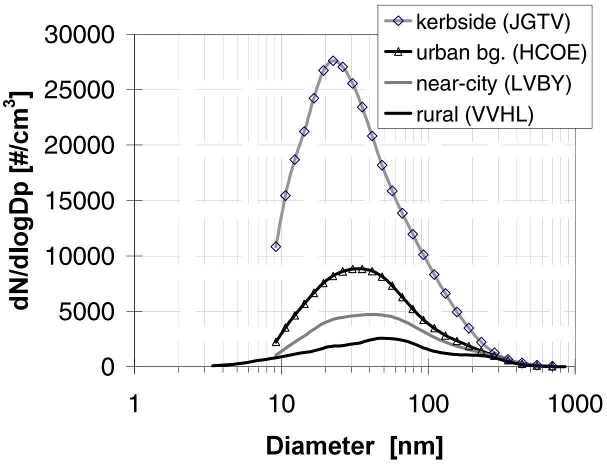

Figure 1. Measured particle size distribution at several locations in Denmark and Southern Sweden. (Based on Ketzel et al. 2004)

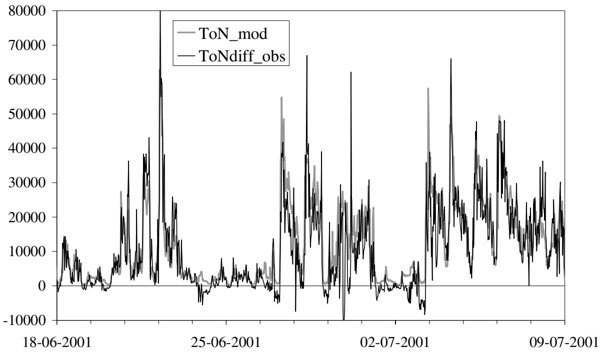

Figure 2. Time series of OSPM model predictions (grey) and measurements (black line) for total number concentration ToN [cm^{-3}] at a kerbside (Jagtvej) for a period of 3 weeks.

METHODS

Here we apply these emission factors together with a street pollution model OSPM (Berkowicz, 2000) to predict time series of total particle number, PM_{10} and NOx at street level. Moreover we identify the relevant particle dynamic processes acting at different time scales.

CONCLUSIONS

The time scales for particle dynamic processes (e.g. coagulation, deposition, dilution, condensation) are estimated for urban street and background environment and discussed in their relevance for influencing the particle size distribution. In agreement with the literature it can be concluded that coagulation is too slow to alter the size distribution in the exhaust plume and dilution is the dominating process. A similar conclusion can be drawn for the street scale. In a more confined environment as e.g. a road tunnel the removal processes coagulation and deposition might play an important role.

We show that for model predictions at street level the total particle number and PM2.5/PM10 can be treated as 'inert tracer', i.e. particle transformation has not to be modelled in detail and rather considered as part of the emission process. Using OSPM we obtain high correlation (R=0.8) between measured and modelled total particle number assuming constant emission factors (Figure 2). If we account for a temperature dependence of the particle emissions the model results improve slightly (R=0.82). For modelling particle mass concentrations the non-exhaust emission factors play a crucial role and are increasingly dominating the emissions as new exhaust after-treatment technology is reducing direct exhaust emissions of vehicles (Figure 3).

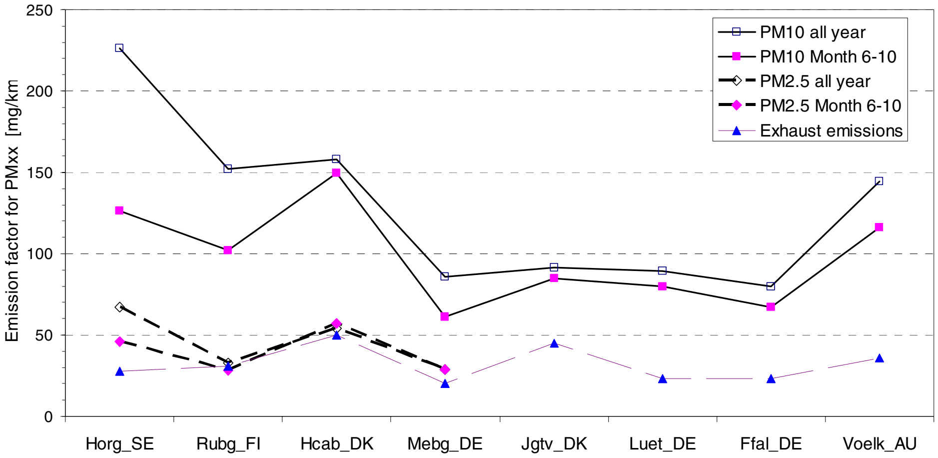

Figure 3. Average PM$_{10}$ and PM$_{2.5}$ emission factors for 8 street locations in 5 European countries separated for all year and summer month estimated by using NO$_x$ as tracer. The estimated values for exhaust emissions are given as well. (Ketzel et al. 2007)

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PRELIMINARY RESULTS FROM DMPS-MEASUREMENTS AT MOUNT WALIGUAN, INLAND CHINA

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Keywords: Aerosol, Background, China.

METHODS

A set of continuous aerosol measurements were carried out at Mount Waliguan Global Atmosphere Watch station during the time period August 2005 – May 2007. The station is located in inland China (100.92 East, 36.27 North, 3810m asl.) in the province of Qinghai. The nearest cities are located some 300 km east and north-east of the station. The measuring site is located on top of a local Mount Waliguan, rising several hundread meters above the surrounding area. The area is dry grassland with an annual average rainfall of 350 mm, mostly during summer months.

Aerosol size distribution was measured with a DMPS system (Komppula *et al*., 2003) covering the particle size range from 9 to 600 nm in mobility diameter. There were also long gaps in the data due to instrument failures. Meteorological parameters were also measured at the station, and air back-trajectories (FLEXTRA) were used to find out the history of the air masses arriving to the station. All data were converted to one- hour averages to make the data analysis easier.

RESULTS AND DISCUSSION

The average one-hour total particle number concentration at the station was 2280 cm^{-3}. The corresponding median and range were 1497 cm^{-3} , and from 224 to 34550 cm^{-3}, respectively. These particle concentrations are quite large for background air (Tunved *et al*., 2003). The monthly- median number concentration varied from 1130 to 3550 cm^{-3}, highest concentrations being observed in December 2005 and January 2006 (Figure 1.). The number concentration in May 2007 was also high, but there was data available for only the first nine days of the month.

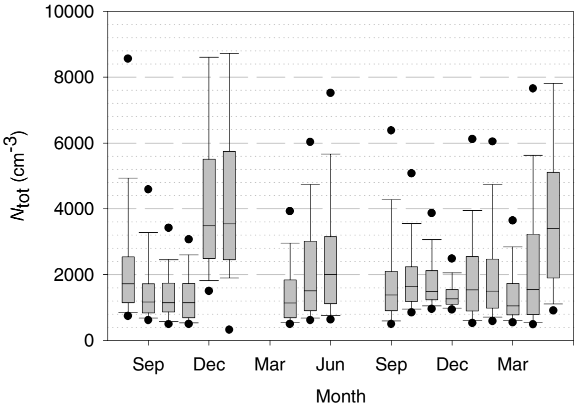

Figure 1. Monthly variation of total particle number concentration at Mount Waliguan between August 2005 and May 2007. The bars show the range from 25-percentile to 75-percentile, the line in the middle being median value. The error bars are 10- and 90-percentiles, and the dots show the 5- and 95-percentiles.

The data were sorted according to air mass arriving direction. The directions were divided to four sectors, being North (315 - 45°), East (45 – 180°), South (180-270°) and West (270-315°). A trajectory fell into a sector only if it had spent more than 50% of the time in that sector. This way some of the trajectories were left unclassified. After this procedure more than half of all the trajectories were located in the western sector. The trajectories were classified in the same way into higher- or lower troposphere, according to their height from sea level. The limit separating high and low air was 550mbar pressure level (4500m). There were no big differences between the total particle number concentrations from different sectors. The air masses coming from the western sector seemed to be associated with lower particle number concentrations than the rest of the air masses. The difference between the higher and lower tropospheric air was not significant.

The data was also separated according to which sector and height the air mass was located one day before arriving to Mount Waliguan. The sectors and heights were the same as above. This separation gave more differences between the sectors than the above trajectory analysis (Figure 2.). In lower tropospheric air the median total number concentration was higher in the air masses that had been in the northern and eastern sector one day before arriving to Mount Waliguan. In higher tropospheric air the highest median concentration was in the air masses coming from the eastern sector. This is probably caused by long range transport of pollutants from the industrial areas of China. The highest individual one-hour concentrations were, however, in the air masses coming from the southern sector. This is consistent with the fact that in the southern sector there are areas, where the ground is so high from sea level, that the ground level is actually in the upper troposphere.

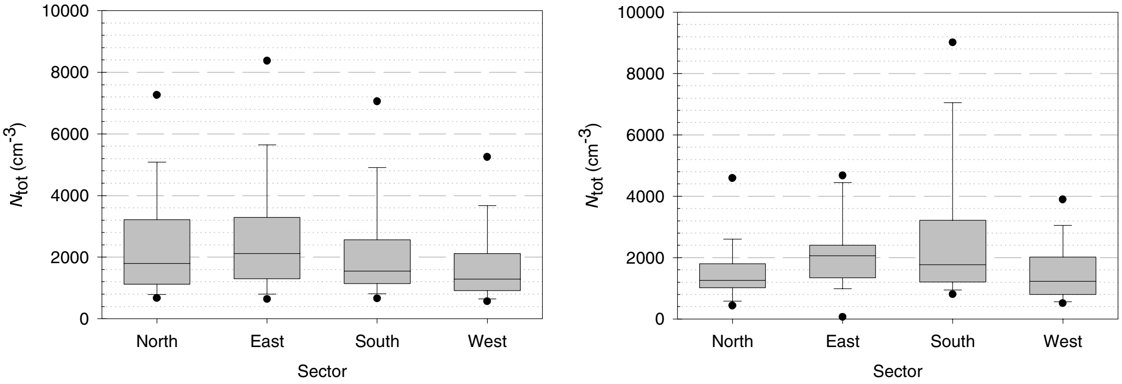

Figure 2. The variation of total particle number concentration at Mount Waliguan between August 2005 and May 2007 according to location of the air mass one day before arriving to the site. The left figure is for lower tropospheric air and the right figure for upper tropospheric air. The bars, error bars and dots are as in Figure 1.

ACKNOWLEDGEMENTS

This work was supported financially The Academy of Finland. Thanks also to the Chinese Academy of Meteorological Sciences and to the staff at the Mount Waliguan station.

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PHYSICAL PROPERTIES OF AEROSOL PARTICLES AT A BACKGROUND SITE IN INDIA

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Keywords: AEROSOLS, CLIMATE FORCING, BROWN CLOUD.

INTRODUCTION

Southern Asia including India is exposed to substantial quantities of particulate air pollution. This particulate air pollution is assumed to be originating from fossil fuel and biomass burning. The pollution aerosols are likely to have large influences on human health and regional climate over Southern Asia (e.g. Jayaraman *et al.*, 1998; Satheesh and Ramanathan, 2000; Singh *et al.*, 2004). The main purpose of this work is to conduct long term measurement program at a background site in India. Based on a continuous measurement program, we are able to study for example the basic properties, diurnal and seasonal variation of particulate matter, and contribution of natural and anthropogenic sources. This paper concentrates on the preliminary results of the particle size distribution measurements.

METHODS

Measurements are conducted at a background site, located in Mukteshwar (29°31'N, 79°39'E) about 350 km northeast of New Delhi in India. The site is located about 2000 meters above the sea level at the Himalaya mountains. No major local pollution sources affect the site. The instrumentation at the site includes DMPS (Differential Mobility Particle Sizer), CPC (Condensation Particle Counter), PM10, PM2.5, nephelometer, aethalometer and Milos weather station. Particle size distributions are measured with the DMPS in the size range 10-600 nm in about 5.5 minute cycles. The DMPS has been running since November 2005. This study presents the data from November 2005 until early June 2007.

RESULTS AND DISCUSSION

During the measuring period the one-hour average particle number concentration varied from 220 to 14900 cm^{-3}. The highest monthly average concentration was observed in April and the lowest in July and August, 4400 cm^{-3} and 1300 cm^{-3}, respectively. The spring time particle formation increases the concentrations and the rainy season (July-September) lowers them. The size distribution is mostly dominated by one mode with maximum around 100 nm.

Figure 1 points out the different features of the seasons. The new particle formation dominates the size distribution in spring (here April presented). The distribution shows more particles in the smaller sizes than in the other months and also the highest concentrations occur. On the other hand the rainy season (here August) lowers the concentration and especially in the larger sizes and shifts the maximum towards smaller sizes. In winter the size distributions are somewhere between these two, as well as the annual average.

The diurnal variation of the total number concentrations has also different patterns in different seasons (Figure 1). The highest concentrations appear in April throughout the day. The pattern in April is mainly driven by new particle formation occurring normally around midday during about half of the days in

April. In winter, the particle concentration seems to increase from morning to the evening and settle to lower levels again towards the night. This behavior might be a mixture of boundary layer evolution and the daily behavior patterns/activities, like cooking and heating, of habitants in the close by valley. During the rainy season, the concentration drop is notable and no diurnal pattern is seen when the rain "cleans" the atmosphere.

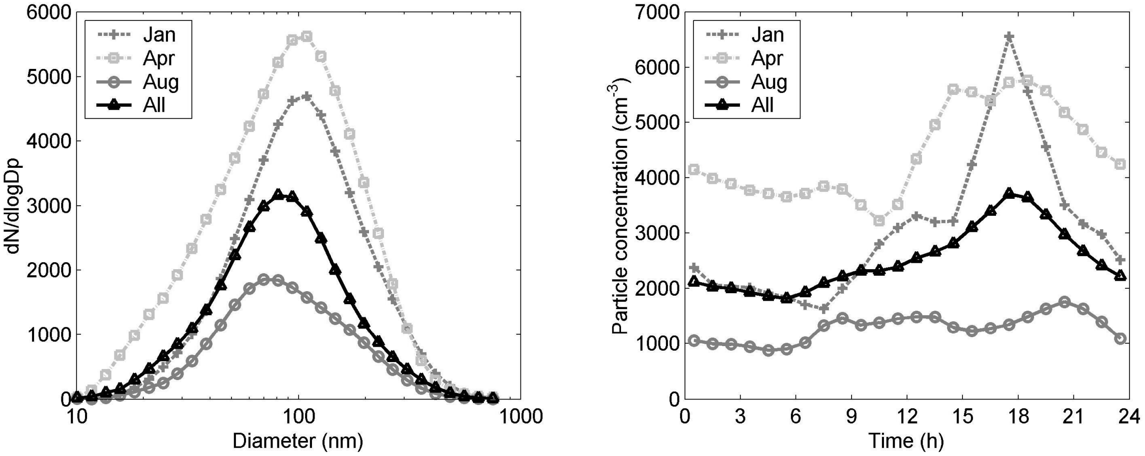

Figure 1. Average size distributions (on the left) and average diurnal variation of particle concentration (on the right) for three months: January (winter), April (spring) and August (rainy season), and the whole time period.

These preliminary results will be completed by taking a look to the modal features of the size distributions and by fitting one to three lognormal modes to the distributions. Some emphasis will be put on the new particle formation, which seems to be quite frequent during spring. More comparison between the rainy and dry seasons will be done. An attempt will be done to find out the features of the Brown cloud, the pollution cloud over India.

ACKNOWLEDGEMENTS

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QUANTUM CHEMICAL STUDIES ON ATMOSPHERIC SULFURIC ACID NUCLEATION

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Keywords: nucleation, molecular clusters, quantum chemistry, sulfuric acid

THE ROLE OF AMMONIA IN NEUTRAL AND ION-INDUCED NUCLEATION

The molecular-level processes by which gas-to-particle nucleation occurs in the Earth's atmosphere are currently not well understood. A strong correlation has been observed between sulfuric acid concentrations and new particle formation. However, as binary sulfuric acid - water nucleation cannot explain the observed new-particle formation rates, the participation of other species such as ammonia or ions has often been suggested. We have used the SIESTA (Sohler *et al.*, 2002) and TURBOMOL (Ahlrichs *et al.*, 1989; version 5.8) quantum chemistry programs to study the free energies of formation of small neutral and charged sulfuric acid - water - ammonia clusters. We employ a cost-effective multilevel computational strategy which allows the study of larger clusters than before without significant loss of accuracy. Figure 1 shows formation free energies calculated for small sulfuric acid - ammonia clusters. In atmospherically realistic conditions, the thermodynamic barrier for neutral particle formation is significantly lower for ammonia-containing clusters. For ion-induced nucleation, the presence of ammonia is thermodynamically unfavorable for the smallest clusters, but ammonia may still slightly assist the growth of clusters to larger sizes. It should be noted that though ion-induced nucleation is thermodynamically very favourable, experiments (Kulmala *et al.*, 2007) indicate that at least in boreal forest conditions, neutral nucleation mechanisms dominate particle formation.

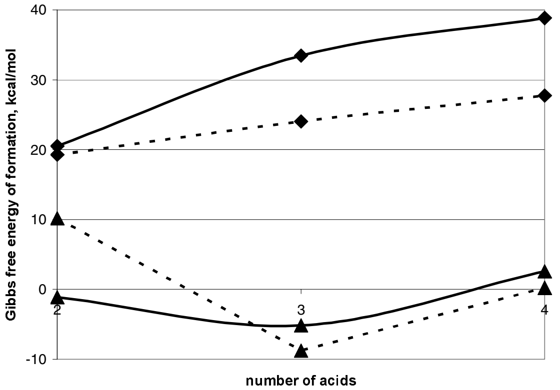

Figure 1. Formation free energies of clusters containing 2 to 4 H_2SO_4 molecules. Solid lines: clusters without NH_3; dashed lines: clusters with NH_3. Diamonds correspond to neutral clusters and triangles to charged clusters (where one H_2SO_4 has been replaced by HSO_4^-). Values computed at T=265 K, $[NH_3]=2.8\times10^{10}$ cm^{-3}, $[H_2SO_4]=1.0\times10^{7}$ cm^{-3} and $[HSO_4^-]=1.0\times10^{3}$ cm^{3}, using RI-CC2/aug-cc-pV(T+d)Z energies with BLYP/DZP geometries and frequencies.

POSSIBLE ROLE OF OTHER COMPOUNDS: AMINES AND SO_2 OXIDATION INTERMEDIATES

Some recent experimental evidence (Murphy *et al.*, 2007) indicates that amines, instead of or together with ammonia, might also participate in atmospheric nucleation reactions. Preliminary calculations on sulfuric acid - dimethylamine clusters (see Table 1) confirm that this is likely to be the case, as amines are significantly more strongly bound to sulfuric acid than ammonia is, and also promote cluster growth in the sulfuric acid co-ordinate more efficiently. The difference in binding energies is more than enough to overcome the mass-balance effect associated with the fact that atmospheric amine concentrations are likely to be 2-3 orders of magnitude lower than ammonia concentrations.

reaction	ΔE_0
$H_2SO_4 + NH_3 \Rightarrow H_2SO_4 \bullet NH_3$	-17.0 kcal/mol
$H_2SO_4 + (CH_3)_2NH \Rightarrow H_2SO_4 \bullet (CH_3)_2NH$	-26.7 kcal/mol
$H_2SO_4 \bullet NH_3 + H_2SO_4 \Rightarrow (H_2SO_4)_2 \bullet NH_3$	-29.5 kcal/mol
$H_2SO_4 \bullet (CH_3)_2NH + H_2SO_4 \Rightarrow (H_2SO_4)_2 \bullet (CH_3)_2NH$	-33.7 kcal/mol

Table 1. RI-MP2/aug-cc-pV(D+d)Z energies for reactions between sulfuric acid and ammonia or dimethylamine.

Berndt *et al.* (2006) recently found that the threshold H_2SO_4 concentration for particle formation was 10^7 molecules cm^{-3} if $H_2SO_4$was produced *in situ* via the reaction of OH radicals with SO_2 in the presence of water vapor (as it is in the atmosphere), and 10^{10} molecules cm^{-3} if the H_2SO_4 was taken from a liquid reservoir or produced *in situ* via the reaction of SO_3 with water vapor. This implies that intermediate or alternative products of the SO_2 oxidation chain also participate in nucleation. We have performed a series of test calculation on clusters containing sulfuric acid together with several such compounds: HSO_3, HSO_5, H_2SO_5 and $H_2S_2O_8$. Of these, only $H_2S_2O_8$ (peroxo-disulfuric acid) is bound more strongly to H_2SO_4 than another H_2SO_4 molecule. This implies that HSO_3, HSO_5 or H_2SO_5 - containing clusters are unlikely to explain the experimental results of Berndt *et al.*, but $H_2S_2O_8$-H_2SO_4-H_2O clusters (see Figure 2) might nucleate more efficiently than H_2SO_4-H_2O clusters alone.

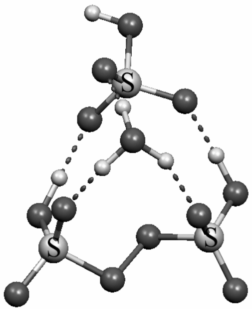

Figure 2. $H_2S_2O_8 \bullet H_2SO_4 \bullet H_2O$ cluster, optimized at the RI-MP2/QZVPP level.

CONCLUSIONS

Recent quantum chemical studies demonstrate that ammonia significantly enhances the formation of sulfuric acid - water clusters containing multiple sulfuric acid molecules. The role of ammonia in ion-induced nucleation is likely to be minor, though not necessarily negligible. In addition to sulfuric acid, ammonia and water, various amine species such as dimethylamine, and also peroxo-disulfuric acid, $H_2S_2O_8$, may be involved in atmospheric new-particle formation events.

ACKNOWLEDGEMENTS

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CHARACTERISATION OF A DENUDER FOR SEPARATION OF THE GAS-PHASE FROM NANOSIZED SECONDARY ORGANIC AEROSOLS IN LIMONENE OXIDATION MIXTURES

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Keywords: SOA, LIMONENE, DENUDER, PARTICLE

INTRODUCTION

Secondary Organic Aerosols (SOA) can be formed in the absence of sunlight, and therefore in both outdoor and indoor environments. Fast particle formation is observed during atmospheric oxidation of alkenes by ozone (O_3), nitrate and hydroxyl radicals. The particle yield depends on parameters like the particular alkene and oxidant, reaction time, concentration, temperature, humidity (Bonn et al., 2002) and less obviously, nitrogen oxides (Donahue et al., 2005). The particle phase is accommodated by a gas-phase which includes compounds of different volatilities and preference for the condensed phase. For purposes of studying the particle phase, only, separation methods are therefore necessary.

Human eye irritation (Klenø and Wolkoff, 2004) and airway irritation in mice (Wolkoff et al., 2000) have been reported during exposure to complex alkene oxidation mixtures. However, the particular species responsible for the observed effects have yet not been fully identified. Because these reactions are ubiquitous, it is desirable to identify the causative species and the phase in which they prevail. One approach is exposure of mice to alkene oxidation products with and without the gas-phase present by use of a denuder. This study characterizes the breakthrough of volatiles and reactive gasses, and deposition of the particles in a denuder developed to operate during an animal exposure scenario.

METHODS

The aluminum denuder (length 45.8 cm, with 5.1 cm) consists of an inlet- and outlet piece, which are connected to a middle section (Figure 1, left). An inner piece (Figure 1, right) slides into the middle section, which contains 14 sheets of activated carbon impregnated paper (37x250 mm) separated by stainless steel bars of diameter 2.4 mm. The metal parts were cleaned in methanol and oven dried for 2 hours at 90° C. Carbon sheets were disposed after use. The denuder was developed to retain the gas-phase of terpene/ozone reaction mixtures in concentrations of parts per million (ppm) and flows of 18 l/min during runs shorter than two hours.

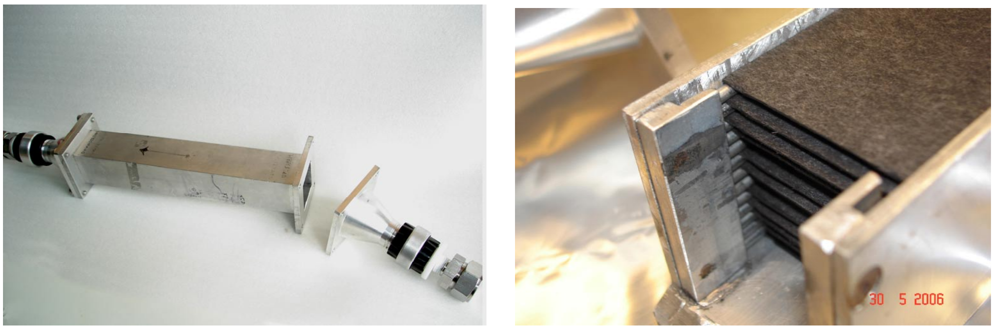

Figure 1. Particles exit the denuder (left), while the gas-phase is retained on activated carbon (right)

Experimental conditions were 40-60% relative humidity and 20-25 °C. The system dedicated for generation of ozone, limonene and terpene oxidation mixtures has been described elsewhere (Wolkoff et al., 2000; Clausen et al., 2001). Limonene was sampled on Tenax TA and measured by TD/GC/FID (PE

ATD 400 and HP 5890). O_3 was measured by chemiluminescense (API 265A). Particle number concentration and size distributions of 9.8-874.8 nm in 44 channels were measured by a Sequential (Stepping) Mobility Particle Sizer (Grimm) in fast scan mode (3 min 38 s/scan).

CONCLUSIONS

Limonene and O_3 were measured from multiple runs using different inlet concentrations (Figure 2, left). The break-through of limonene was 4-12 % after two hours and increasingly higher after 3 hours. Only 3-7%, however, exited the denuder after 30 minutes which was the duration used in previous animal exposure studies (Wolkoff et al., 2000). Less than 2 per mille of O_3 exited the denuder after two hours, evident of its high reactivity. The 16 s old limonene/O_3 reaction mixture produced $3.2 \cdot 10^7$ cm^{-3} particles with mode 80 nm in the range 30-180 nm (Figure 2, right). Only 5% of the 80 nm particles were retained in the denuder, but this became more pronounced for larger particles. As much as 30% of the 120 nm particles, although minor in number, were retained in the denuder.

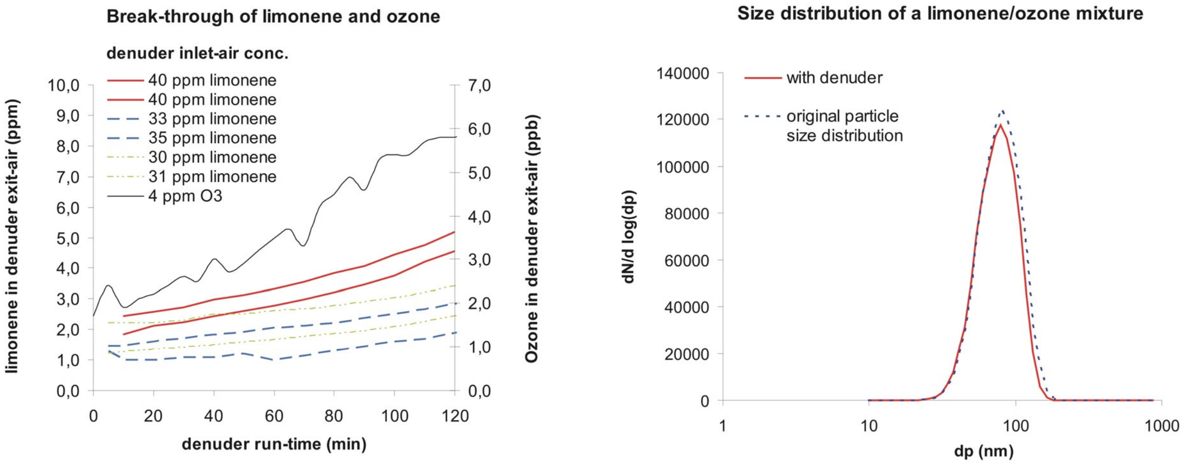

Figure 2. Examples of limonene and ozone breakthrough representative of multiple experiments (left), and particle size distributions of limonene/ozone reaction mixtures with and without denuder (right).

The low breakthrough of limonene and O_3 and the low deposition of particles appear to be sufficient to separate the gas-phase from the particle phase in future exposure studies. A higher efficiency may be desirable in other applications for which reason key parameters can be optimized, e.g. the number of carbon impregnated carbon sheets (the surface area) and the sample flow (exchange with the surface).

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AEROSOL DYNAMICS SIMULATIONS ON THE GROWTH RATES OF CHARGED AND NEUTRAL PARTICLES

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Keywords: particle growth rate, ions, modeling, aerosol dynamics

INTRODUCTION

The growth rate of freshly formed particles is one of the key parameters describing a new particle formation event in the atmosphere. There are multiple ways to determine the growth rate from measured data such as following the advancement of the peak of the growing nucleation mode (see e.g. Hirsikko *et al.* 2005), or calculating directly the growth rate from condensable vapor concentrations. Typically for particles smaller than 3 nm in diameter, the measurement data are available for charged particles only due to instrumental limitations. Below the detection limit of neutral particles, it cannot be verified whether the “apparent” growth rate of charged particles and the “real” growth rate of neutral particles are the same or not, and thus it is uncertain how well the charged particle data describe the growth of the whole particle population.

A series of aerosol dynamics model simulations was performed in order to study the performance of the methods used to determine the growth rates and how well the assumption that the apparent growth rates of charged particles are the same as the growth rates of neutral particles holds.

METHODS

The simulations were made using a newly-developed sectional box-model Ion-UHMA (University of Helsinki Multi-component Aerosol model for neutral and charged particles), which simulates the dynamics of multi-component tropospheric aerosol particles. Ion-UHMA is based on previous UHMA-model (Korhonen *et al.* 2004) on which we have added charge dynamics from model Aeroion (Laakso *et al.* 2002). The main dynamical processes in the model are condensation, coagulation, nucleation, ion-aerosol attachment and dry deposition. There are three particle charge classes in the Ion-UHMA: neutral, negative and positive. Particles with larger number of charges are treated in the same way as particles with one elementary charge. In addition to growing particles there are pools of neutral and charged clusters in the model. The attachment and recombination of clusters with growing particles are simulated and the formation of new (neutral or charged) particles acts as sink for the (neutral or charged) clusters.

In this study the formation rates of the particles were given as model inputs and not simulated. Particles were assumed to consist of sulfuric acid, ammonia, water and an organic compound. Sulfuric acid was assumed to be non-volatile. The Kelvin equation was used to calculate the saturation vapor pressure for the organic vapor, except for the particles smaller than 3 nm in diameter, onto which it was not let to condense at all.

Out of the simulated data, the apparent particle growth rates were determined following the advancement of the peak concentration of the nucleation mode. A straight line was fitted to the time and diameter coordinates of the peak values and the growth rate was obtained as the slope of the line. The procedure was repeated for three size ranges (1.7–3 nm, 3–7 nm and 7–20 nm) and for all charge classes. Respective growth rates were also calculated straight from vapor concentrations. The growth rates obtained from both aforementioned methods where then compared to the real growth rates calculated in Ion-UHMA during the simulations.

RESULTS AND DISCUSSION

The methods used to determine the apparent growth rate from the simulated data worked reasonable well in most of the cases. Both the apparent growth rate and the growth rate calculated from vapor concentrations were usually relatively close to the real one (see Figure 1.).

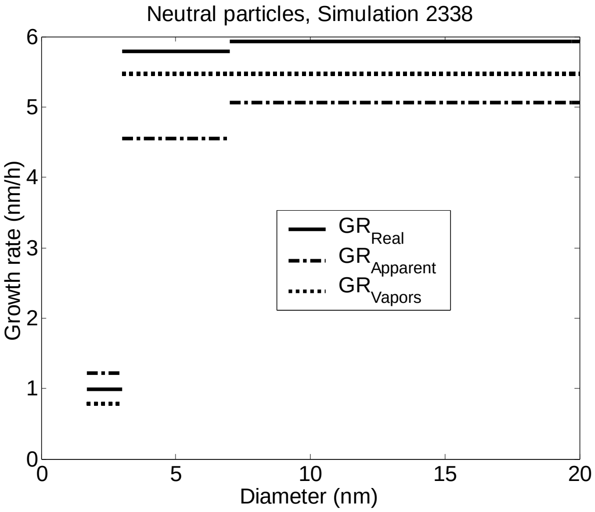

Figure 1. The growth rates of neutral particles. The apparent growth rates (dashed-dotted) and the growth rates calculated from vapor concentrations (dashed) differ less than 25 % from the real growth rates (solid) in this example.

In most simulations the apparent growth rate could be determined for both charged and neutral particles and these two growth rates were usually relatively close to each other. Thus the simulations would lead to a conclusion that the apparent growth rates of the charged particles could be used to estimate the real growth rates of the neutral particles.

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RESPIRATORY TRACT DEPOSITION OF NANO-PARTICLES FROM BIOMASS COMBUSTION AND TRAFFIC; IMPACT OF SIZE-DISTRIBUTION AND HYGROSCOPICITY ON THE DEPOSITED DOSE

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Keywords: ULTRAFINE PARTICLES, RESPIRATORY DEPOSITION, HEALTH EFFECTS

INTRODUCTION

There is still an ongoing discussion about the relative importance of particle number, surface and mass concentration in health effects of an aerosol. Air quality guidelines usually regulate the mass concentration. However, several studies show a better correlation for dose-response when comparing with particle surface area. Furthermore, some studies indicate more severe effects for aerosols with small particles and thus a high number concentration per unit mass.

It is possible that the differences in health effects of various aerosols could be partly explained by a potentially large variation in the respiratory tract deposited dose of the particles. In this study the dose has been measured and calculated for particles from traffic and biomass combustion.

METHODS

The respiratory tract deposition of particles from traffic in a street canyon in Copenhagen, two types of biomass combustion and a hydrophobic reference aerosol was measured for healthy human subjects with a novel instrument named RESPI (Löndahl et al. 2006). Data which fulfilled our quality assurance protocol was obtained for 9 subjects (4f/5m) for the traffic aerosol and 10 subjects (4f/6m) for the two biomass combustion aerosols.

Hygroscopic growth at 90% relative humidity (RH) was measured with an H-TDMA. Based on these data and on the measured chemical composition, the particle hygroscopic growth factors at the RH prevailing in the lung (99.5%) were estimated. Thereby, the well-established ICRP dose model could be adjusted for particle water absorption. This was done in order to show consistency between measured deposition and theory. Finally, the total deposited dose was calculated based on the ICRP model for a normal healthy adult during relaxed breathing, exposed for 1 hour to 100 $\mu g/m^3$ of biomass combustion and traffic aerosols. The size distribution of the traffic aerosol is described by Kristensson et al. (2004) and was assumed to have a density according to Park et al. (2003).

RESULTS AND CONCLUSIONS

Figure 1 shows the measured size-resolved deposition fractions of the aerosols. Note that two different groups of subjects were exposed to the biomass combustion and traffic aerosols respectively. However, the lower deposition of the ultrafine (<100 nm) biomass combustion particles is due to their high hygroscopic growth factors. The ICRP model, adjusted for hygroscopic growth, and the experimental values yielded similar results.

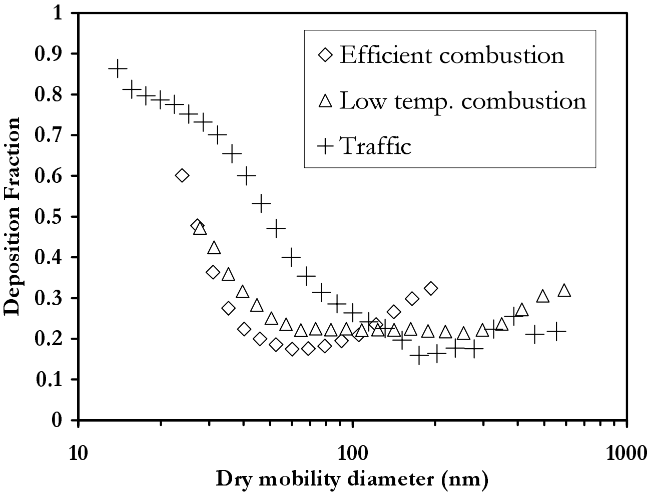

Figure 1. Measured deposited fraction of the aerosols.

Table 1 shows the calculated deposited dose of the aerosol particles. The number concentration of the traffic aerosol per unit mass was substantially higher than for the biomass combustion particles. This, in combination with the higher probability of deposition resulted in a considerable difference in dose.

Table 1. Deposited dose for a healthy adult exposed to 100 µg/m^3 during 1 hour. The calculations are based on the ICRP model and adjusted for hygroscopicity.

	Number ***(x10^9)***	***Surface*** ***(mm^2)***	***Mass*** ***(µg)***
Efficient combustion	7.2	170	3.0
Low temperature combustion	2.4	180	6.7
Traffic	6200	18800	14.3

This study represents the first experimental verification that hygroscopicity alters the respiratory tract deposition of real-world aerosols. It also shows the first measurements of respiratory tract deposition of biomass combustion and traffic aerosols. The findings demonstrate; a) that the respiratory tract deposition of biomass combustion aerosols is low compared to traffic, b) that it is essential to include particle water absorption in dose models and c) that the deposited dose has to be carefully calculated when estimating the toxicological potential of air pollution particles for a given exposure.

ACKNOWLEDGEMENTS

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A COLOURING PROCESS FOR ART GLASS ITEMS USING LIQUID FLAME SPRAY GENERATED NANOPARTICLES

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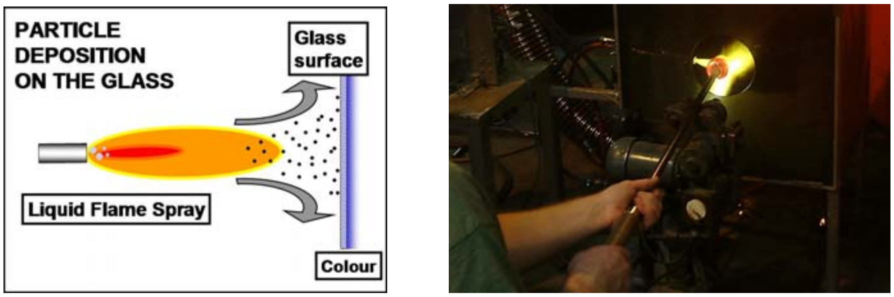
Keywords: NANOPARTICLES, FLAME SPRAY PYROLYSIS, COATING

INTRODUCTION

Presently, glass material is seen as a challenging target for modern research (Lehmann, 2006). Nanotechnology, on the other hand, offers convenient tools for adding value of items made of glass. Especially, flame techniques offer a way for controlled large-scale production of nanoparticles (Pratsinis, 1998; Gutsch, 2004). Compared to other methods for nanoparticle generation, the cost efficiency of flame processes is relatively high. Here, Liquid Flame Spray (LFS) technique has been applied for colouring of art glass items. Based on our earlier experience (Tikkanen et al 1994, Tikkanen et al 1997, Gross et al 1999), blue and yellow colour can be applied for the art glass items (see Table 1). Recently, red colour has been an issue, since previously used Cd is unfavourable due to toxicity. Alternatives are Au and Cu, both being challenging due to sensitivity on thermal conditions. Here, we apply gold to obtain red.

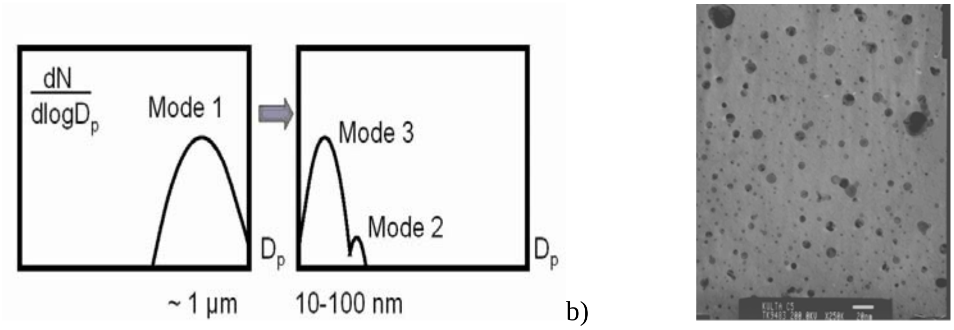
METHODS

LFS was developed in Finland (Tikkanen et al. 1994; Tikkanen et al.1997). The precursor liquid is sprayed into the H_2-O_2 flame. In glass colouring, the coloured item is exposed to flame (Figure 1) The spray mixes with the flame, and nanoparticles are formed in the gas phase via droplet evaporation, chemical reactions and nucleation, resulting in nearly monodispersed nanoparticle material (Mäkelä et al. 2004, Keskinen et al. 2007). The additional heat from the flame is useful in the glass surface processing. The advantage of the method is obtaining the coloured layer to glass object via a one-step process, carried out immediately after gathering glass out of glass furnace, being fast compared with the conventional colouring processes. A corresponding layer that would be as thin as this, cannot be produced with other glass colouring methods. Colour intensity can be controlled by varying solution concentration, feed rate, and spray time. In ionic colouring (CoO_3) the concentration of material in the glass counts. In colloidal colouring, the effect is strongly particle size dependent, with larger Ag-nanoparticles one obtains white, with smaller nanoparticles yellow. Using gold for red, one needs final size of 5-40 nm.



a) b)

Figure 1. a) A schematic of applying Liquid Flame Spray process for nanoparticle deposition on surface, b) in-situ photograph of a glass colouring session in studio.



a) b) c)

Figure 2. a) Schematic overall droplet size distribution (Mode 1) in the spray, b) size distribution of nanoparticles in the flame. Mode 2: evaporated residual droplets, Mode 3: actual nanoparticles. c) TEM graph of gold nanoparticles collected from the flame, prior to deposition on the glass (scale bar = 20 nm).

Colour	Precursor used	Compound	Particle size in glass matrix
Blue	$CoNO_3$ in methanol	CoO_3	(-) Ionic
Yellow	$AgNO_3$ in H_2O	Ag	5-10 nm
White	$AgNO_3$ in H_2O	Ag	~100 nm
Red	Au in HCl-HNO_3	Au	5-40 nm

Table 1. List of colours, precursors, colouring compounds and required particle sizes inside the glass.

CONCLUSIONS

We have shown, that in addition to producing the conventional ionic blue and colloidal yellow colours on the surface of the glass, LFS method succeeds also in obtaining red colour using gold nanoparticles.

ACKNOWLEDGEMENTS

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DISPLACEMENT BARRIER HEIGHTS FROM EXPERIMENTAL NUCLEATION RATES

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Keywords: homogeneous nucleation, nucleation theorem, nucleation experiments, scaling.

INTRODUCTION

Nucleation phenomena are ubiquitous in the Nature: In the atmosphere they are manifested by formation of new aerosol particles (Kulmala, 2003) and formation of ice in cloud droplets (Cantrell and Heymsfield, 2005). Both of these processes are subject to anthropogenic disturbances and have a remarkable effect to the radiative forcing. The basic tool to analyse nucleation phenomena is the classical nucleation theory (CNT) (Becker and Döring, 1935), which has been applied to describe the nucleation behaviour in different fields of science more or less successfully. However, while CNT in some cases predicts the nucleation rate correctly, it has its own shortcomings. Here we present results of a nucleation theorem based analysis of experimental nucleation rate data of a variety of substances, and discuss the general nature of corrections needed to bring CNT unison with experiments.

THEORY AND DATA ANALYSIS

The observable quantity in nucleation experiments is the nucleation rate, J, giving the number of new stable clusters appearing per time and volume as a function of partial vapour pressure and temperature. This experimental nucleation rate is compared to the classical Becker–Döring (1935) nucleation rate expression, $J_{\mathrm{CNT}} = K\mathrm{e}^{-W/kT}$. Here $K = K(m,p,S,\sigma,T,v)$ is the kinetic prefactor and S is the saturation ratio, v the molecular volume in the (bulk) liquid, m mass of the molecule, p the saturation vapour pressure, and $W_{\mathrm{CNT}} = 4\sigma R^2/3$ the work of formation, with σ the (planar) surface tension and R the radius of the critical cluster (assumed spherical). Also, the $1/S$-correction (Courtney, 1961) that makes the cluster distribution to satisfy the law of mass action is used, and it is assumed that the mass accommodation coefficient is 1.

Based on the model independent nucleation theorem and the Kelvin equation, McGraw and Laaksonen (1996) proposed the following scaling for the W:

$$-D(T) = W - W_{\mathrm{CNT}}\,. \tag{1}$$

Here $D(T)$, which is a function of temperature only, is the correction between the 'true' free energy of formation and the CNT prediction and is known as the displacement barrier height. As the kinetic prefactor in Eq. (1) is a slowly varying function of S and T when compared to the exponential Boltzmann-factor, $D(T)$ is very nearly given as $\ln(J/J_{\mathrm{CNT}})$. Inspired by computational studies of simple compounds (McGraw and Laaksonen, 1996), a linear model was chosen for $D(T)$:

$$D(T)/kT = a + bt, \tag{2}$$

where $t = T/T_c$ is the reduced temperature and T_c the critical temperature.

In data analysis, only measurements reporting actual measured nucleation rates (approximately since mid-1980's) instead of on-set saturation ratios and temperatures, were used. Also, only data from over-pressures (in case of diffusion based devices) and normal or underpressures (in case of expansion based devices) were used to avoid pressure effects (e.g. Brus et al., 200x). In evaluation of J_{CNT}, the best available thermodynamic data from literature was used. Also, published saturation ratios were reevaluated using more accurate expression for saturation vapour pressures when necessary. Some datasets that did not agreed with the other ones of the same substance were disregarded.

RESULTS AND CONCLUSIONS

Published data from nucleation experiments of normal and heavy water, *n*-alkanols, and *n*-alkanes (+ *i*-octane) were analysed. All studied substances showed reasonable agreement with the scaling relation (2). The parameter *b* seems to have quite universal value, approximately -160 for n-alkanes and and n-alkanols form ethanol to octanol, and -120 for waters and methanol, which is remarkable when considering the differences in molecular interactions between strongly hydrogen bonded substances as water and non-polar substances as longer alkanes. Furthermore, most of the variation in parameter *b* seems to be caused by differences in experimental techniques, which also have a more pronounced effect on parameter *a*. In Fig. 1., an example of analysed data (waters) is given. In future, simple physically motivated corrections to the CNT seem to be possible by using Eqs. (1) and (2).

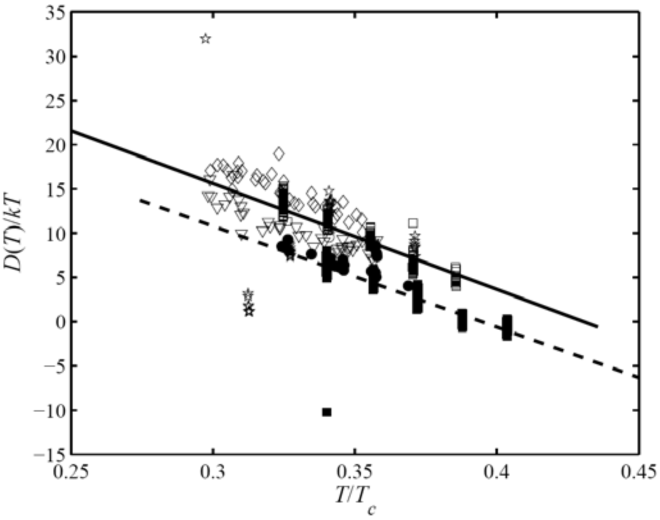

Figure 1. Analysed experimental data and linear fits for water (open symbols and solid line; $D(T)/kT = 51.5 - 120t$) and heavy water (filled symbols and dashed line; $D(T)/kT = 45.0 - 114t$).

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This work was supported by the Academy of Finland. All the researchers who provided us with their experimental data in electronic form or helped to determine the most accurate thermodynamic data are warmly acknowledged.

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A LABORATORY COMPARISON OF SIX CUSTOM BUILT H-TDMA SYTEMS

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Keywords: PARTICLE HYGROSCOPIC GROWTH, DMA, H-TDMA.

INTRODUCTION

The determination of the hygroscopic properties of atmospheric aerosol particles is crucial to evaluate their impact on global climate, since they influence the ability to form cloud droplets. A method used to investigate these properties of individual particles is the application of the H-TDMA (Hygroscopicity-Tandem Differential Mobility Analyzer) technique.

This principle has been used for more than twenty years to investigate hygroscopic properties of submicrometer aerosol particles with high temporal resolution. Up to now, H-TDMA systems are not commercially available, but all existing systems are based on a custom built setup. The H-TDMA system was firstly introduced by Liu et al. (1978). In this study, six European H-TDMA systems were compared within a workshop held in February 2006 at the Leibniz Institute for Tropospheric Research in Leipzig, Germany.

OVERVIEW OF USED INSTRUMENTS

The H-TDMA consists of two Differential Mobility Analyzers (DMA) in series and an aerosol humidifier in between. The first DMA selects a narrow particle size fraction from the aerosol (I). This fraction is then humidified in the aerosol conditioner to a well defined relative humidity (II) and the altered, humidified size distribution is determined by a size spectrometer (III) consisting of a second DMA in combination with a Condensation Particle Counter (CPC).

In general, custom built H-TDMA systems show substantial differences in technical details, used quality criteria, and applied data evaluation. Systems vary in used DMA, CPC, conditioning section, etc. In Figure 1, a schematic of a custom built H-TDMA system is shown.

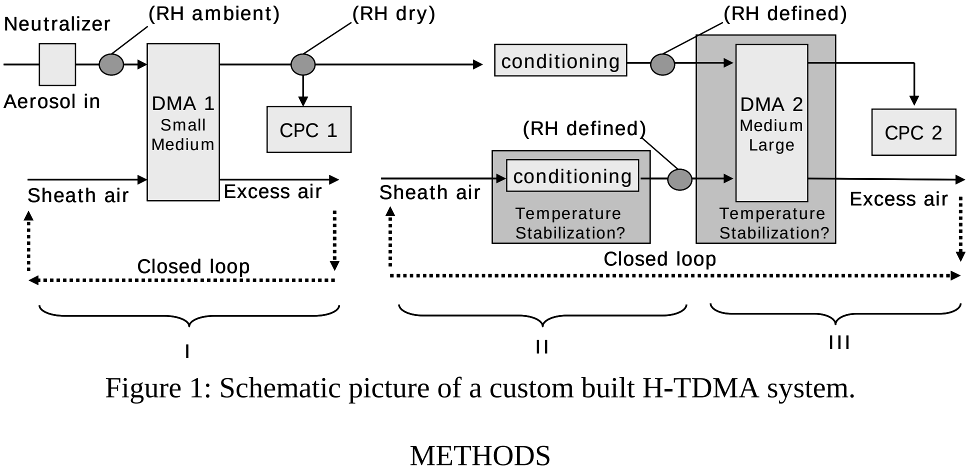

Figure 1: Schematic picture of a custom built H-TDMA system.

METHODS

The main goal of this study was to compare the performance of six H-TDMA systems in terms of particle dry sizing, relative humidity (RH) control and RH stability (certainty of growth factor determination), and determination in observed number fractions in case of external mixtures.

In a first set of experiments, dry ammonium sulfate particles were generated and conducted to a mixing chamber. In a second set of experiments dry ammonium sulfate particles were conducted to the chamber together with soot particles generated in a parallel process so that an externally mixed aerosol was present. All systems were measuring simultaneously from the mixing chamber and were operated for all experiments at the same parameters in terms of selected dry size and controlled RH. All data were evaluated using two different evaluation procedures, the individual evaluation procedure of the operated system and a second procedure being the individual evaluation procedure for the H-TDMA systems operated by the Leibniz Institute for Tropospheric Research.
In a first experiment, the particles were dried by system-individual drying sections before entering the first DMA. The systems were operated at dry conditions yielding the deviation in DMA dry sizing between DMA 1 and DMA 2 (theoretically 1.0) for selected sizes, here Dp = 30, 50, 70, and 100 nm. For this experiment the individual evaluation procedure of the operated system was applied to the obtained data.

RESULTS

Overall, shifts in DMA dry sizing between the two DMAs of individual systems were smaller than 4% in relative deviation as shown in Figure 2. In general it was found that that the shift in dry sizing behaved nearly linear for individual systems in dependence on examined size.

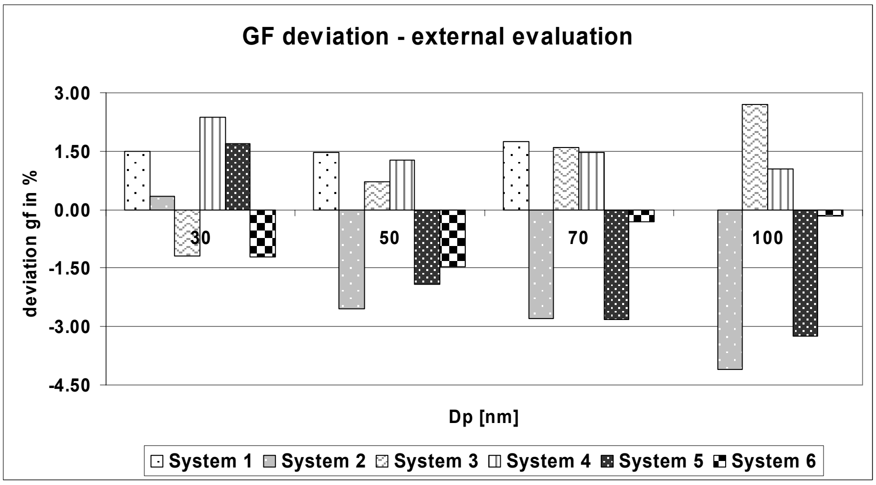

Figure 2: Size-dependent deviation in DMA dry sizing for all systems operated during the workshop.

Because shifts in dry sizing between the two DMAs of individual systems were about 1 to 4 % in relative deviation, we propose to correct the measured hygroscopic growth factors for the individual shifts based on dry ammonium sulfate scans taken during each field campaign from time to time. The dry scans can be measured at the same dry diameters as the H-TDMA is operated during the individual study. Thus, an internal dry growth factor can be calculated for each dry size and be applied to all data measured at that size.

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Elimination of Combustion Generated Nanoparticles – Why and How

Andreas C.R. Mayer / TTM

Solid nanoparticles are emitted in a very critical size range by all internal combustion engines and other technical combustions by nucleation from the gas phase. They mainly consist of soot which might be coated by PAH and other toxic combustion products but also oxides of heavy metals are included originating from lubrication oil packages and engine wear. These substances are highly toxic and they become very dangerous due to their size and their low solubility. The average size of these particles is so small that they can penetrate alveoli membranes, reaching the blood system, penetrate the blood/brain barrier and reach cell cores. They can trigger deceases like cancer, infarcts, Parkinson and even Alzheimer.

Filtration of these nanoparticles is possible and reaches efficiencies exceeding 99 % if the principles of diffusion filtration are carefully applied. Appropriate filter systems are available for all combustion engines and all applications for fit and retrofit of new engines and engines which are already in use on-road and off-road. Filter systems will be described and experience in many retrofit areas will be presented.

A technical standard, called the VERT-standard has been developed, which is based on particle size, number concentration and secondary emission control and targets to introduce best available technology BAT. The basic philosophy of this standard and the testing protocol acc. to SNR 277205 will be described and the application of this standard in low emission zones in Europe, US and Latin America will be presented.

PM10-Toxicity-Equivalent – New Approach to a Health-Oriented PM-Characterization

Andreas C.R. Mayer / TTM

Airborne Particulate Matter PM is widely accepted to be a very powerful health effecting pollutant but its definition for tailpipe emissions, ambient air pollution and occupational health are different, different metrics are used and none of them is clearly correlated to health effecting parameters like lung penetration properties, bioavailability, solubility and toxicity. Overall Mass is usually used as a metric and neither chemical composition nor particle size are respected. Comparison between PM-data collected according to legally accepted procedures in ambient air, at the tailpipe or at the working place is not possible and even PM10-samples taken at different times and having the same mass might represent an entirely different toxicity. Frustrating enough, this overall mass parameter used as a uniform metric suffers from the inability to distinguish particles of different toxicity, such as mineral dust, salt from sea spray, secondary atmospheric particles, or combustion soot. Since all captured particles are collected in the same bin, it is very difficult to reasonably link air pollution mass data to observed health effects.

A new approach tries to use the Toxicity-Equivalent TEQ model as it is used in similar cases where a multitude of substances is present in a sample the composition of which might vary from case to case. Examples are the Dioxin-TEQ and PAH-TEQ. The target is to assign a toxicity index to each substance contained in the mix, a number which increases with the assumed (or known) toxicity of the substance. In order to estimate the total toxicity of a PM sample, the contribution of each particle class is weighted by its toxicity index before calculating the sum. Using this approach, "PM10-TEQ", the toxicity of a PM10 sample consisting entirely of sodium chloride is close to zero, while the toxicity of a PM10 diesel soot sample reaches (an arbitrary) 100%.

Currently the approach is based on few classes of particle material, and on a limited number of toxicity criteria such as solubility, bio-availability and "toxicity". Further research is planned into refining these parameters; at the same time, the number of particle classes is to remain limited so as to facilitate differentiated measurement of the PM10 constituents with a reasonable extent of equipment. And following this approach it finally should become possible to conclude on improved and unified measurement principles in all application areas and supply data which find scientific support to be correlated to biological effects.

CLASSIFYING THE DMPS NPF DATA: A SCHEME FOR PREVIOUSLY UNDEFINED DAYS

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Keywords: atmospheric aerosols, new particle formation, nucleation event.

INTRODUCTION

Aerosol research has been investigating the phenomena of new particle formation (NPF) in the atmosphere, evolving with new techniques to detect and visualize the nano-particle process (Kulmala et al. 2004). The climatic importance of newly formed aerosols as potential cloud condensation nuclei propels the field to understand the mechanisms that increase the concentration of these in the atmosphere. A revision of the classification guidelines for new particle formation event days was devised by Dal Maso et al. (2005) and has been used to classify the last eleven years of continuous data from the Hyytiälä Forestry Field Station, Finland. While almost a third of the days have been labeled as 'event days', approximately 40% of the data is termed "undefined". This study proposes three alternative categories under which most of the 'undefined days' can be classified. The eleven years of undefined particle size distribution data, from 1996 to 2006, was analyzed and classified.

METHODS

The aerosol size distribution measurements were carried out in SMEAR II (System for Measuring Forest Ecosystem-Atmosphere Relationships II, 2006), a pine forest station in Hyytiälä, Finland (61º51' N, 24º17'E) dedicated to the investigation of the atmosphere-biosphere system. Particle size distribution measurements are taken using a twin DMPS system with a detection range from 3-500nm, and 10-min averaged values. Continuous gas and meteorological data is recorded via the station's 73-meter mast, including NOx, SO_2, O_3, temperature, global radiation and relative humidity. In addition, the Smart-SMEAR tool (http://www.atm.helsinki.fi/~junninen), the station's online database catalogue displaying daily gas and meteorological data, back trajectories, and particle size distribution measurements, was used extensively.

A preliminary study was done with the use of Smart-SMEAR, to identify possible recurring characteristics in the undefined days pool. Following a positive indication, the review of the undefined days for one randomly chosen year resulted in a detailed classification system described in Table 1. The DMPS data was plotted as 48hr time series, and each undefined day was accordingly classified.

Class	**Characteristics**
Failed Particle Formation Events	
Tail Events	Apparent 'tail' of a formation event, advected to Hyytiälä.
Quasi-Events	Particles appearing in the smallest size classes but showing unclear growth or/and persisting for less than 1 hour
Pollution Concentration Peaks	
Vertical pollution peaks	Peaks correlated in time to a high pollution peak, i.e. [SO2]> 1ppb, and [NOx]> 5ppb
Concentration Peaks	
Aitken-mode peaks	Max size at 100nm, but no less than 10nm
Nucleation-mode peaks	Minimum size at 3nm, and not surpassing 30 nm.
Missing Data	Gas and/or DMPS data missing
Unclassified	Not suitable for any of the above classes

Table 1. Classification system for the previously 'undefined' days

RESULTS

From 1996 to 2006, the undefined days measured at SMEAR II station account for a total 1543 days. After subjected to the proposed classification scheme, 110 days remained undefined, lowering the fraction of unclassified data to 7%. The failed events category accumulated 588 days, from which 332 were tail events and 256 quasi events: a comparable number to the 970 event days. The annual distribution of the failed events presents a clear maximum during summer the months, between the spring and fall peak of event days (Fig. 1). The peaks, both pollution and nucleation/Aitken mode peaks, showed greater abundance during the winter months. Furthermore, a plot of relative humidity versus condensation sink has placed the failed events at intermediate conditions between event and non-event days, while the peaks classes concentrate on the same range as the non-event days. This supports the validity of the proposed classification for undefined days, and suggests the importance that the failed event class could have in shedding more light into the conditions needed for a successful particle formation event, and the related physical processes.

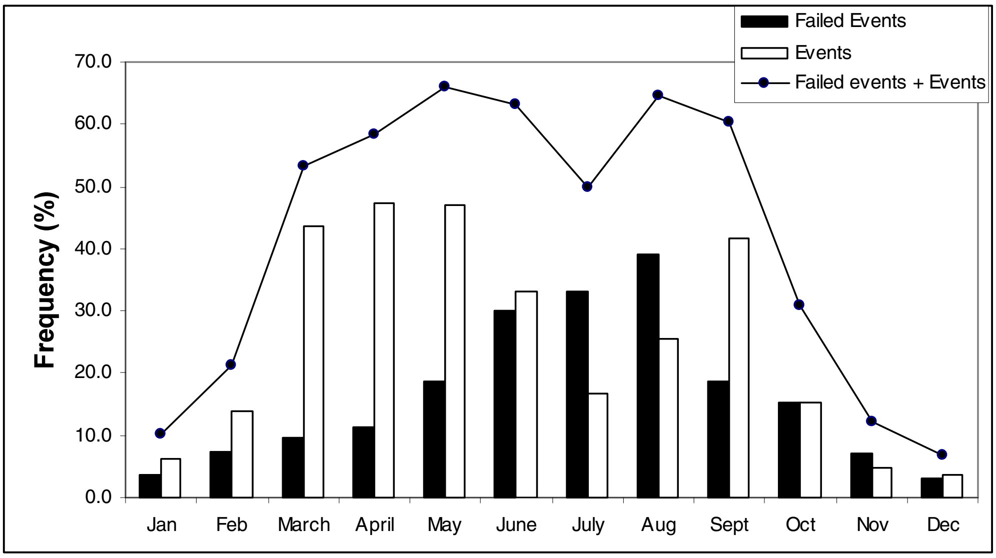

Figure 1.Annual distribution of event days, failed events, and the sum of failed events and event days in Hyytiala,Finland 1996-2006. Days with missing data are excluded from the total of days in a month.

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Smart –SMEAR tool (2007): http://www.atm.helsinki.fi/~junninen/

NUCLEATION AND GROWTH OF ATMOSPHERIC AEROSOLS

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Keywords: New Particle Formation, Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS), New Particle Formation Rates, Nanoparticle Growth Rates

INTRODUCTION

It is now well established that new particles are produced photochemically throughout the troposphere (Kulmala et al, 2004). These nucleated particles can grow to sizes that are large enough to serve as cloud condensation nuclei (CCN) during the course of a day or two. There is a need for microphysical models that predict both the rates at which new particles are formed by homogeneous nucleation and the rates at which they grow. This presentation summarizes the recent work of our research team on understanding production and growth rates of atmospheric particles.

METHODS

New Particle Formation Rates. In previous studies, classical nucleation theory has been used to calculate rates of new particle formation (NPF) in the atmosphere. However, empirically observed rates of particle production are usually much higher than are predicted by classical theories and have a much weaker dependence on sulfuric acid concentrations (Weber et al., 1996; Sihto, 2006; Riipinen, 2007). In this lecture we summarize empirical observations on new particle formation rates in the atmosphere from studies in diverse locations including Mauna Loa, Macquarie Island (Southern Ocean), Idaho Hill (Rocky Mountains), Atlanta, Mexico City, and Boulder (Colorado). From our data we directly estimate the rate at which 3 nm particles are produced ($J_{3\ nm}$). From this, by extrapolation, we estimate the rate at which 1 nm particles are produced ($J_{1\ nm}$). Because the critical size of freshly nucleated particles is probably in the vicinity of 1 nm, $J_{1\ nm}$ should be a reasonable estimate of the nucleation rate. In recent work, Kuang et al. (2007) found that for all of our studies, $J_{1\ nm}$ can be expressed as:

$$J_{1\ nm} = K[H_2SO_4]^2.$$

The quadratic dependence of $J_{1\ nm}$ on $[H_2SO_4]$ is remarkably consistent for all locations. The prefactor, K, varies significantly with location, and ranges from about 10^{-1} to 10^{-4} of the calculated $[H_2SO_4]$ collision rate. Factors that likely influence the value of K include concentrations of species other than sulfuric acid that participate in the formation of the nucleating clusters, and the collision accommodation coefficient.

We are in the process of developing a new scanning mobility particle sizer that will measure size distributions down to about 1 nm and a Cluster-Chemical Ionization Mass Spectrometer (Cluster-CIMS) that will detect neutral molecular clusters smaller than that. From these measurements we hope to measure $J_{1\ nm}$ directly and to obtain information on species and reaction rates that lead to new particle formation. The status of that work will be discussed.

Nanoparticle growth rates. The rate at which freshly nucleated particles grow determines the time required for them to grow to sizes that can serve as CCN. Because of its exceedingly low vapor pressure, sulfuric acid is one species that will contribute to growth. Stolzenburg et al. (2005) reviewed data from studies where growth rates and sulfuric acid concentrations were both measured and found that sulfuric acid condensation often accounts for only a fraction of the observed growth rate (typically between 5% and 100%). Thus, species other than sulfuric acid contribute significantly and their contributions must be taken into account when modeling the impact of new particle formation on CCN concentrations.

Dr. James Smith and coworkers have developed the thermal desorption chemical ionization mass spectrometer (TDCIMS) to measure the composition of sub-10 nm particles (Smith et al, 2005). Smith and coworkers have successfully quantified sulfates and nitrates in these very small particles, and have recently made significant progress in measuring certain organic compounds as well. They have carried out measurements in Atlanta, Boulder, Mexico City and Hyytiälä (Finland). Consistent with parallel measurements of growth rates and sulfuric acid concentrations, they have found that sulfates are often only a minor constituent of nanoparticles. Other important compounds include nitrates and organics. There is a need to understand the chemical processes that lead to the accumulation of these compounds on nanoparticles.

CONCLUSIONS

Rates of particle production observed at diverse locations including remote continental and marine sites, a suburban site, an urban site, and a megacity show that nucleation rates vary in proportion to $[H_2SO_4]^2$. This suggests a kinetic process, where nucleation rates are determined by the collision rate sulfuric acid. This is similar to results that were previously obtained in smog chamber experiments (McMurry, 1980).

Growth rates of freshly nucleated nanoparticles can be as much as 20 times greater than rates that can be explained by the condensation of sulfuric acid alone. This suggests that species in addition to sulfuric acid contribute to growth. Measurements of nanoparticle composition with the TDCIMS show that those species include nitrates and organics. These high growth rates enhance the impact of NPF on the formation of CCN. There is a need to understand the chemical processes that are responsible for these high growth rates.

ACKNOWLEDGEMENTS

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NOVEL APPROACHES FOR MEASURING PHYSICAL AND CHEMICAL PROPERTIES OF PARTICULATE ORGANICS

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Keywords: Tandem Measurement Methods, Particle Mass, Particle Mobility, TDMA, ATOFMS, Multiangle Light Scattering, Refractive Index, Water Content, Volatility,

INTRODUCTION

Our understanding of particulate organic compounds is primitive relative to our understanding of the major inorganics. This is because the organics include many species with a broad spectrum of chemical and physical properties, many of which cannot be readily quantified using existing analytical methods. In this presentation, techniques that have been developed in our laboratory to study the physical and chemical properties of atmospheric particles, with an emphasis on organics, will be discussed. Some of these measurements were made using several instruments in tandem to determine multiple properties of the same particle. Information on hygroscopicity, refractive index, density, volatility, and composition has been obtained. Measurements have been carried out on atmospheric aerosols and on aerosols produced by combustion, including emissions from engines.

METHODS

Figure 1 schematically summarizes the various tandem techniques that we have developed to obtain information about the chemical and physical properties of atmospheric aerosol particles. The use of these methods to obtain information on the organic constituents is emphasized in this lecture. Table 1 summaries properties that have been measured along with references that provide further details.

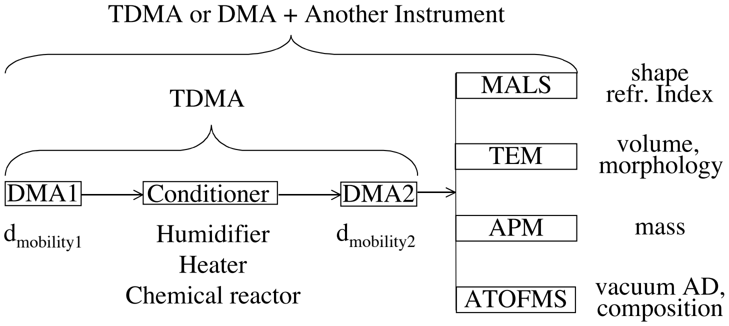

Figure 1

In this lecture we will discuss techniques for the measurement of:

- *water uptake* for particulate atmospheric organic matter obtained from impactor measurements of composition and HTDMA measurements of total water uptake (Dick et al, 2000);
- the *refractive index* of particulate organic matter inferred through measurements of multiple angle light scattering (MALS) from mobility-classified particles (Dick et al, 2007);
- the *density* of the volatile organic fraction on diesel exhaust particles, obtained from tandem measurements of mobility (DMA), mass (APM) and sometimes morphology (TEM) (Park et al, 2004);
- the *composition* of mobility classified particles, including the effect of volatility on composition, measured using the aerosol time of flight mass spectrometer (ATOFMS) (Park et al., 2007);
- the *composition* of particulate organics emitted from engines operated with blends of bio and fossil fuels (Dutcher, 2008);
- direct, in-situ measurements of *mass concentrations* that avoid errors due to adsorption of semivolatile organics on filter media (Park et al, 2003).

Table 1. Methods developed at UMN to measure various aerosol chemical and physical properties.

Instrument System	**Properties Measured**	**Reference**
DMA	Diffusivity $D=kTB$	Einstein Equation
DMA + APM	Sedimentation Speed $V_s=mgB$	Hinds (1999)
DMA + APM	Aerodynamic diameter	McMurry et al (2002)
DMA + APM	Effective density	McMurry et al (2002)
AMD + APM	Total Mass Concentration	Park et al. (2003)
DMA + APM + TEM	Material density	Park et al (2004a)
DMA + APM + TEM	Dynamic shape factor	Park et al. (2004b)
HTDMA + [Composition]	Water Uptake (esp organics)	Dick et al. (2000)
HTDMA + MALS	Refractive index (inc. organics)	Dick et al. (2007)
HTDMA + APM	Density (RH); Effects of Processing on Shape Volatile Mass Fraction	Park et al. (2007) Pagels et al. (2007) Sakurai et al. (2003)
HTDMA + ATOFMS	Composition (Hygroscopicity)	Park et al. (2007)
VTDMA + APM	Density (T)	Park et al. (2007)
VTDMA + ATOFMS	Composition (Volatility)	Dutcher (2008)

CONCLUSIONS

By measuring multiple properties of the same particles it is possible to obtain detailed information about their chemical and physical properties. Such measurements show that environmental aerosols typically include multiple types of particles that differ chemically and physically.

ACKNOWLEDGEMENTS

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GENERATION OF NANOMETER-SIZED GOLD PARTICLES BY SPARK DISCHARGE – FOR GROWTH OF GaP NANOWIRES

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Keywords: nanoparticles, spark discharge, nanowires.

INTRODUCTION

Nanowires are one dimensional (1-D) rod shaped nanostructures with two dimensions in the size range of tens of nanometers or less and a much longer third dimension, typically in the range of micrometers. Due to this specific 1-D structure, nanowires possess unique properties such as a large surface-to-volume ratio and the ability to laterally quantum confine electrons in discrete energy levels. These properties, combined with a nearly perfect crystalline structure, make the nanowires highly promising as building blocks for the next generation of electronic and optoelectronic devices. Several applications utilizing nanowires, such as light emitting diods, a single electron transistor, and nanobiosensors have already been demonstrated.

In order to produce highly perfect nanowires, which can be used for construction of different devices, the knowledge and skills on how to manufacture the wires are of major importance. The most common approach for fabrication of perfect nanowires, the bottom up method, mimic nature and uses self assembly to build up the structure atom by atom. To initiate the epitaxial growth of a highly perfect ordered nanowire a nanometer-sized metal seed particle, in general gold, is often used. Growth of nanowires has been initiated by both colloid and aerosol gold particles, with aerosol particles being the preferred particle type. The advantages of the aerosol particles compared to the colloid particles include a higher particle purity as well as simpler methods for deposition of particles of a known size and given surface density. Benefits that are highly desirable for the application of nanometer-sized gold particles as seed particles for epitaxial growth of nanowires.

The setup of a simple and delicate technique to generate nanometer-sized aerosol gold particles by spark discharge is described. Size-distributions of the produced agglomerate particles, as well as morphological investigations of particle shape are presented. In addition, the reshaping behavior of the generated agglomerate particles following heating in a special compaction furnace is reported on. Finally the ability of the particles to successfully function as seed particles for growth of epitaxial GaP nanowires is demonstrated.

METHODS

A commercially available aerosol generator (Palas, model GFG 1000), mainly constructed for production of carbon soot particles (Helsper et al., 1993), was used to produce nanometer-sized agglomerate gold particles by spark discharge between two electrodes. Two parameters can be adjusted to affect the particle generation, namely the spark discharge frequency over the electrodes and the gas flow through the gap between the electrodes transporting away the generated particles. In order to enable size distribution measurements, reshaping of the agglomerate particles, and controlled depositions of the produced particles, the spark generator was connected to an aerosol nanoparticle system. Apart from the spark generator, this system includes a neutralizer to achieve mostly single charged particles, a tandem differential mobility analyzer (DMA) setup for size selection and size distribution measurements, a special compaction furnace for reshaping of the particles and an electrostatic precipitator (ESP) to provide controlled deposition of the particles. Transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (XEDS) were used to investigate the morphology and confirm the composition of the particles. Nanowires seeded with the generated gold particles were grown by metal organic vapor phase epitaxy (MOVPE).

RESULTS & DISCUSSION

The production of nanometer-sized gold particles by spark discharge appeared to be a reliable and simple method. It was possible to produce particles with fixed characteristics during several hours, indicating the ability of the spark generator to operate in a stable manner during continuous operation. In good agreement with previous results, the use of different spark discharge frequencies during generation of particles was observed to affect both particle number concentration and particle size. With an increase of spark discharge frequency the concentration of particles increased and a shift to larger particle diameters was observed. The second adjustable parameter for nanoparticle generation, the gas flow, was observed to influence particle number concentration with a trend towards an increased concentration upon a decrease in gas flow but showed almost no affect on particle size. XEDS measurements and measurements of lattice fringes confirmed that the generated particles were indeed pure gold particles. From TEM investigations it was clear that the produced agglomerate gold particles consisted of collections of almost spherical, fairly compact primary particles of sizes between 1 and 8 nm.

In order for the agglomerate particles produced by the spark generator to properly function as seed particles for nanowire growth, a reshaping step might be necessary, to yield compact spherical particles. Monodisperse particles of a known diameter are often required and the tandem DMA setup is utilized to achieve a narrow size distribution of particles of almost identical size. A DMA, however, is constructed for size selection of spherical particles and hence a less monodisperse distribution is achieved for non-spherical agglomerate particles. In addition, previous experiments on nanowire growth from uncompacted agglomerate gold particles have shown poor results. By pre-selecting agglomerate particles of a known size with the first DMA prior to compaction, scanning the compaction temperature and measure the peak value of the respective size distribution with the second DMA, the reshaping behavior of the particles was obtained. The compaction temperature, i.e. the temperature were no more shrinking of particle diameter occur, was observed to be approximately 523 K. According to Karlsson et al. (2005), the compaction temperature for metal particles should be in the range between 1/3 and 1/2 of the bulk melting point. Since the gold bulk melting point is 1337 K, the compaction temperature of around 523 K agrees well with that prediction. TEM micrographs of the compacted particles confirmed that the particles had become almost compact at 300°C, but also showed that they become more spherical and less polycrystalline at even higher compaction temperatures.

Generated gold particles reshaped at four different compaction temperatures between 300°C and 1200°C were observed to work excellent as seed particles for growth of epitaxial GaP nanowires. Nanowire characteristics such as surface density and growth rate corresponded well with what was expected from previous growth of GaP nanowires seeded by aerosol gold particles (Dick et al., 2004), for all particles except the once reshaped at 300°C. For these particles the surface density of nanowires was slightly lower than expected from measurements of the surface density of deposited particles. This might be due to partial compaction of a small amount of the particles, which hence made them unusable as seed particles for nanowires.

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CONTROLLED SYNTHESIS OF NANOPARTICLES FOR INHALATION EXPOSURE STUDIES

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Keywords: NANOPARTICLES, INHALATION EXPOSURE, HEALTH EFFECTS.

INTRODUCTION

Nanomaterials are already a part of our everyday life and there are growing demands in the society for reliable information on their possible health effects. In the previous toxicity studies of nanoparticles, the problem has often been nanoparticle synthesis and controlled production. The focus of our project is to build up a highly controlled nanoparticle generator for inhalation exposure studies with mice. Titanium dioxide (TiO_2) was selected as the primary substance because it is widely used e.g. in cosmetics, catalysts and electrical applications. TiO_2 particle generation is also extensively studied.

METHODS

We have constructed a flow reactor for long term (over 5 hours) production of nanoparticles with high yield based on setup of Backman *et al.* (2004) with some modifications (Figure 1.). In inhalation exposure experiments the exposure chamber will be in the place of the filter holder and the SMPS and TEM measurements will be done directly from the chamber.

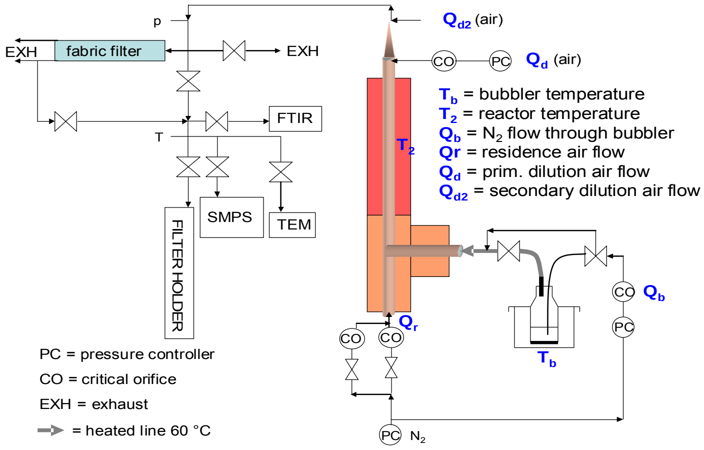

Figure 1. Experimental setup

TiO_2 nanoparticles have been generated using titanium tetraisopropoxide (TTIP) as a precursor. Liquid TTIP is vaporized in a bubbler and carried with nitrogen into the reactor, where it decomposes thermally according to equation $Ti(C_3H_7O)_4 \rightarrow TiO_2 + 4C_3H_6 + 2H_2O$ (Okuyama *et al.*, 1986). Right after the reactor, the sample is diluted with humidified air and extra oxygen is added when needed. Size distributions of generated TiO_2 agglomerates have been measured with Scanning Mobility Particle Sizer

(SMPS). Reaction byproducts, moisture and oxygen content of the sample flow have been measured with the Fourier Transform Infrared Spectroscope (FTIR). Mass concentrations have been verified with filter samples. Transmission Electron Microscope (TEM) samples have been taken for morphology studies. TiO_2 powder has been collected on fabric filter for x-ray diffraction (XRD) and BET analyses.

RESULTS

Mass concentrations up to 35 mg/Nm^3 with narrow size distribution (GSD = 1.6) and geometric mean diameter (GMD) below 130 nm were observed. Dilution rate (DR) affected the GMD of the agglomerates at high mass concentrations (Figure 2.). Higher reactor or bubbler temperatures lead to larger agglomerates, as well as longer residence time in the reactor. The primary particle size in the agglomerates was ca. 10 nm. The XRD and BET analyses combined to morphology analysis will give us exact information on agglomerate properties (e.g. crystal phase, specific surface area and effective density).

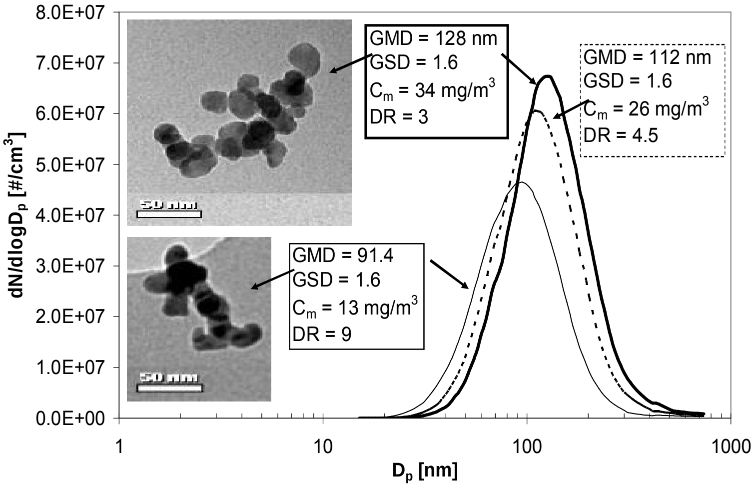

Figure 2. Particle size distributions [#/cm^3] and TEM micrographs of TiO_2 agglomerates. Average mass concentrations determined from filters and dilution rates are also marked. Reactor parameters: T_b = 50 °C, Q_b = 1 Nl/min (20 °C and 101325 Pa), Q_r = 1.8 Nl/min, Q_d = 5.6 Nl/min, T_2 = 500 °C.

CONCLUSIONS

This nanoparticle generator is a highly controlled device for inhalation exposure studies. It will be used to expose mice that inhale the particles exiting the reactor. The properties and the concentration of the agglomerates can be controlled via changing the reactor parameters. When the system is qualified with the TiO_2, we will continue with other nanoparticles such as copper and cobalt.

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MULTIVARIATE MIXED EFFECTS REGRESSION MODEL IN THE ANALYSIS OF NUMBER CONCENTRATION OF 50NM PARTICLES

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Keywords: Atmospheric aerosols, particle concentration, multivariate analysis, mixed effects model.

INTRODUCTION

It is well known, that atmospheric aerosols have a great effect on radiation budget, formation of clouds, climate change and to human health. Despite of several years of research, many of the factors affecting the new particle formation and the growth of new formed particles remain unclear. Kulmala et al. (2004) studied several physical and chemical properties affecting particle growth and suggested that the factors affecting new particle formation and growth vary between locations. The purpose of this study is to use statistical data analysis methods to find factors that affect the growth of the particles to detectable sizes in Po Valley area, Italy and predict the number concentration of 50nm particles for air quality research purposes.

METHODS

Most of our models were combinations from hourly averages of gas and meteorological parameters measured at SPC, including temperature, relative humidity, radiation, O3, SO2, NO2, condensation sink, wind speed and -direction and the probability that the day is a nonevent day i.e. a day when significant new particle formation cannot be seen. The probability of a nonevent day (PrNE) was calculated with discriminant analysis, details of the method can be found from Mikkonen et al. (2006). PrNE was favoured instead of probability of event day due to better predicting ability. The calculated nonevent probability was used instead of observed event classification because otherwise we would have had to exclude the unclassified days, which would have reduced the number of data points drastically. In addition, the probabilities of a nonevent day can be estimated also for those days where the visual event classification has not been made at all which enables the use of the model in predictive purposes.
Due to complex structure of processes affecting to concentration of small particles it is not reasonable to use general linear effect models in the analysis. We chose to use generalized linear models with logarithmic link function and combine it with mixed model structure (McCulloch and Searle, 2001). The main idea of a mixed model is to estimate, not only the mean of the measured response variable y, but also the variance-covariance structure of the data.

RESULTS

We found out that RH, PrNE and the concentration of SO2 caused significant additional variance to the estimates of the model. Magnitude of the additional variance was estimated by adding individual variance components to the model for each of the above-mentioned variables for different times of year. When the additional variance is taken into account, the model suggests that the effect of RH is negative in January, July and December and positive for the rest of the year. The decreasing effect of PrNE is on its highest in January, June and July, and the effect of SO2 concentration is negative in winter months and positive for the rest of the year.

Significant weekend effects have been reported for several pollutants (e.g. Marr and Harley, 2002). This reflects also to particle concentrations: Tuesday, Wednesday and Thursday seem to have the highest effects on the concentration of 50nm particles. Effect varies slightly between months.

Wind direction showed out to have a significant effect on the behaviour of some of the predictor variables. The effect of local wind speed is mainly positive, i.e. the particle number is higher when the wind speed is higher, except for the winds coming from northeast, south and southwest. The effect of Condensation Sink is on its lowest on north, northwest and west, respectively. These are the directions to the highly populated areas but also the directions to the mountains.

Effect of Ozone varies within the day; positive effect can be detected on daytime and negative effect on night. The coefficient of determination R2 for the model is 0.61 which indicates that the model explains roughly 61% of the total variation of the particle concentration.

The other significant fixed parameters of the model were relative humidity, which has negative effect on the particle concentration; the growth of the condensation sink, i.e. the difference of two consecutive CS values, which had a positive effect, and the yearly intercept terms.

It is also possible to separate high concentrations which are not caused by nucleation events from the results for air quality research purposes.

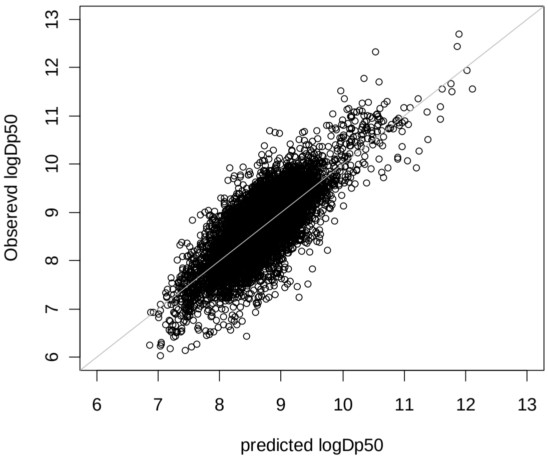

Figure 1. Observed vs. predicted number concentrations. Grey diagonal line represents the perfect fit

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Pressure controlled gas to gas humidification of HTDMA:s

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Keywords: HTDMA , Aerosol instrumentation

INTRODUCTION

EUSAAR is an infrastructure project within FP6, and one of the aims is to develop future tools for aerosol monitoring (www.eusaar.net). The HTDMA is one of the instruments which are included in the project and one specific goal is to come up with a set of recommendations for the new generation HTDMA hardware. The aim of this work was to investigate the efficiency of a humidification system based on nafion dryers previously used by Don Collins (2004).

MATERIALS AND METHODS

For long term measurements, simplicity of a measurement system is important, and for this purpose a closed loop system is preferred, giving the possibility of only humidifying the aerosol line. RH control with a dew point sensor implies that both the dew point temperature and the temperature of the second DMA is needed to obtain the DMA RH. RH fluctuations corresponding to double the precision of the temperature sensors is therefore acceptable (this corresponds to ~ ± 0.5% for Ammonium Sulphate at RH = 90%).

For this study, the response time and stability of the humidification system presented in Fig 1 was investigated. The principle is to control the RH by controlling the pressure of the purge flow of the second nafion dryer (Permapure MD-110 series) with a mass flow controller between bubbled air with an RH close to 100% and a vacuum source. The humidification is done in two steps, allowing both deliquescence and hysteresis measurements of the aerosol. The DMA tested in this study was a 50 cm Vienna type, and a small (pulse free) lamell pump for a minimal dead volume was used in the loop. There was no temperature stabilisation except the lab air conditioning system.

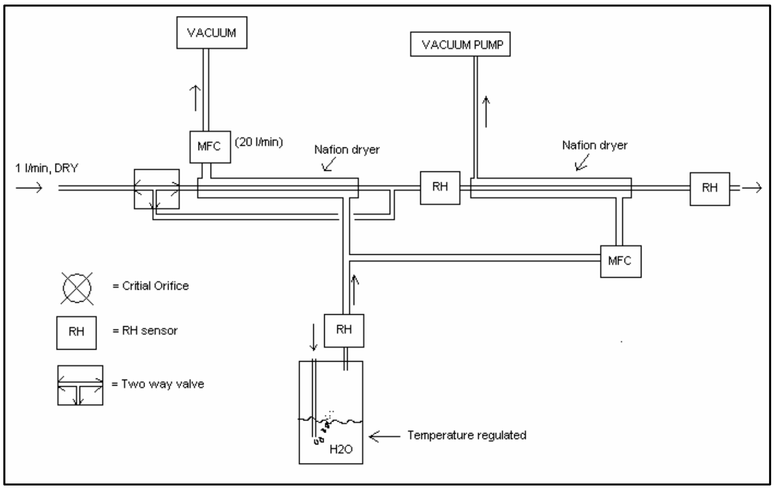

Figure 1. Setup of humidification system.

RESULTS AND CONCLUSIONS

Figure 2 shows the response time in the aerosol line and of the DMA, The response time is ~ 6 minutes for *RH* values between 35% and 90% and around 20 minutes from 90% to 25%. The long term stability of the aerosol *RH* before the DMA is well within ± 0.5%. In addition to this, the dead volume in the closed loop gives a significant buffering effect for the *RH* experienced by the particles passing through the DMA, adding further stabilization of the *RH*. The stability of the *RH* in the DMA is also within ± 0.5%, even though temperature fluctuations of the surrounding air temperature could be expected to decrease the stability.

Hence, for a closed loop system working in field measurements, temperature control of the second DMA is most likely a prerequisite for high quality measurements.

It was concluded that the system is capable of keeping the *RH* within the desired ± 0.5%, even without rigorous temperature stabilization, and the response time is acceptable for most long-term HTDMA measurement applications.

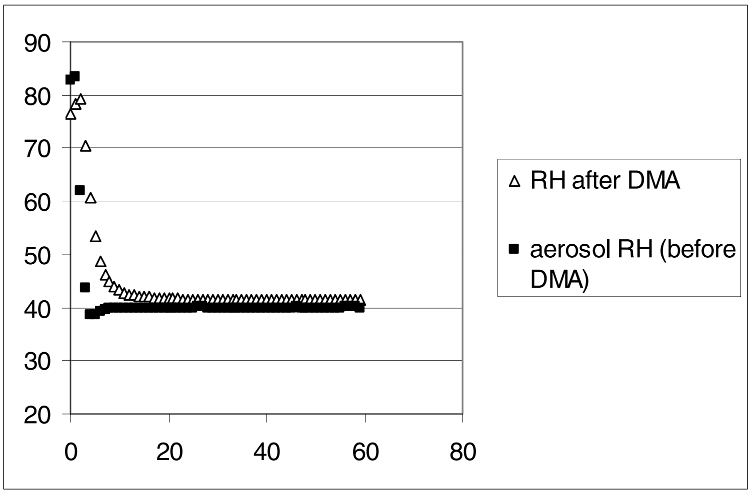

Figure 2. Response time of aerosol before and after DMA.

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PROCESSING OF SOOT BY CONTROLLED SULPHURIC ACID AND WATER CONDENSATION – GROWTH AND MASS TRANSFER TO AGGREGATES AND SPHERES

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Keywords: Soot Aggregates, Ageing, Mass Transfer, Sulphur Particles, Fractals,

INTRODUCTION

Soot particles are ubiquitous in the atmosphere and are of interest in studies related to climate forcing and adverse effects on human health. The hygroscopicity and CCN efficiency of soot will increase upon processing through condensation of for example sulphuric acid-water mixtures in the atmosphere. The optical properties may also be significantly altered upon processing. The complexity and alterations in soot particle morphology (aggregate structure) upon processing makes hygroscopic growth measurements based on particle mobility (e.g. H-TDMA) troublesome and model predictions of the optical properties complex. The morphology and mass-mobility relationship of fresh soot, such as particles in diesel exhaust has been studied previously (e.g. Park et al. 2003). However, the morphology of processed soot has received less attention. There is also a need to establish in-situ methods to directly determine the mass transfer and growth of soot aggregates upon processing. A better knowledge of the processes which control aged soot particle hygroscopicity and optical properties will improve the precision in modelling of cloud formation and the global radiation balance. The aim of this work was to investigate: 1) The influence of particle morphology on the mass transfer rate (from the gas phase to the particle phase) of sulphuric acid and water vapour *and* 2) The influence of processing on particle morphology and the mass-mobility relationship.

METHODS

The main components of the experimental set-up were: 1. A Santoro burner, using propane as fuel to generate soot; 2. A Differential Mobility Analyzer (DMA) for selecting particles with given mobility size; 3. An "aerosol conditioner," which simulates processing similar to that which may occur in the atmosphere; 4. Either a second DMA or an APM (Aerosol Particle Mass Analyzer) to measure the altered mobility size or mass, respectively. This information also enabled us to determine the effective density and fractal dimension of fresh and processed soot. In the aerosol conditioner sulfuric acid was condensed onto the soot particles as described by Zhang and Zhang (2005). A heater (200° C) could be used to evaporate condensed material. A few experiments involved high RH cycling (a humidifier to increase the RH to 90% and a drier to reduce the RH to 5% before measurement).

RESULTS AND CONCLUSION

Using the DMA-APM technique, size-resolved mass increments (Δm) of soot particles and spherical model particles (Polystyrene latex; PSL) which had passed the aerosol conditioner could be determined (Figure 1). It can be seen that the sulphuric acid uptake is similar for PSL spheres and soot aggregates with the same equivalent mobility diameter. This indicates that sulphuric acid condensation was independent of the chemical makeup or microphysical structure of the particles. Our data represent the first direct measurements of mass transfer of sulphuric acid to aggregates and spheres in the transition regime. We suggest that coating by sulphuric acid likely represents a common aging process for most tropospheric aerosol types, e.g., soot, mineral dust, and organic aerosols.

(1), $$\rho_{eff} = \frac{6m}{d_B^3 \pi}$$ (2), $$m \propto d_B^{Df}$$

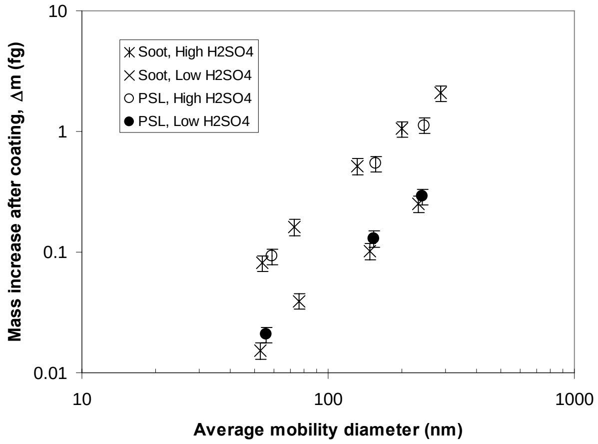

Figure 1. Absolute mass coating of sulphuric acid on soot aggregates and PSL spheres after H_2SO_4 exposure. High and low corresponds to sulphuric acid vapour concentrations of 1.4×10^{10} and 2.5×10^{9} molecules cm^{-3}, respectively. Estimated uncertainties of mass measurements are given as ± 1 std. dev.

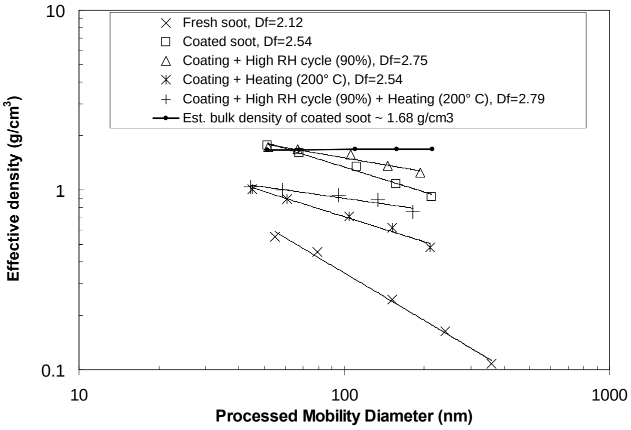

Figure 2. Effective density and fractal dimension of fresh and processed soot.

The morphology and mass-mobility relationship of fresh and processed soot was studied with the DMA-APM technique and Transmission Electron Microscopy (TEM). Typically the mass (m) increased and the mobility diameter (d_B) decreased as sulphuric acid was condensed onto the particles. The combined effects lead to compaction of the soot aggregates represented as an increased effective density (ρ_{eff}; Eq. 1) and fractal dimension (Df; Eq. 2). Coating the particles with a low sulphuric acid mass fraction (~20%) resulted in a moderate influence on ρ_{eff} and Df. Results for a higher H_2SO_4 mass fraction (~55%) are given in Figure 2. The fractal dimension increased from 2.11 to 2.54 upon coating with sulphuric acid. An additional high RH cycling caused further compaction. For sizes below 100 nm, effective densities approached the estimated bulk density and dynamic shape factors approached 1, indicating a transformation from highly agglomerated to compact, nearly spherical particles in agreement with TEM analysis. Increased ρ_{eff} and Df were also observed when sulphuric acid was condensed on agglomerates and then removed by heating, indicating restructuring of the soot core. Soot with a hydrophilic coating, but not fresh hydrophobic soot, experienced restructuring upon RH cycling.

The atmospheric implication is that fresh (hydrophobic) soot will remain agglomerated when exposed to high RH cycles at subsaturation or upon low amounts of condensation. However as more mass condenses a gradual compaction takes place. Our data suggested a full compaction to spheres at a mass ratio ($m_{proc.}/m_{fresh}$) of 2-3. Extrapolating our data to a typical daytime H_2SO_4 concentration of 10^7 molecules cm^{-3}, we estimated that less than 5 hours would be required to transform aggregated hydrophobic fresh soot to compact sulphuric acid droplets with embedded soot core. Hence, the composition, mass, and morphology of soot aerosols will be considerably altered during their typical atmospheric lifetimes of about one week.

The CCN efficiency and optical properties of the well-characterised fresh and processed soot has been investigated experimentally (Zhang et al. 2007). It was found that the critical supersaturation required to activate processed soot could be well predicted using Köhler theory. The light scattering efficiency increased strongly for processed soot (especially at elevated RH) compared to fresh soot.

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Zhang RY, Khalizov AF, Pagels J, Zhang D, Xue H, Chen J., McMurry PH. (2007) *Submitted*

FINE PARTICLE EMISSIONS FROM SOLID BIOFUEL COMBUSTION STUDIED WITH SINGLE PARTICLE MASS SPECTROMETRY – IDENTIFICATION OF MARKERS FOR ORGANICS, SOOT AND ASH COMPONENTS

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Keywords: Biofuels, Single Particle Analysis, ATOFMS, Combustion

INTRODUCTION

An increased use of biofuels in residential heating is desired to decrease net emissions of green house gases, such as CO_2 to the atmosphere. This includes conventional woody biofuels, as well as novel crop fuels such as corn. It is well established that the particle emissions during less optimised combustion in small scale wood combustion are most often dominated by products of incomplete combustion, i.e. organic and elemental carbon (OC/EC), McDonald et al. (2006). In contrast during optimised combustion in modern domestic pellet combustion systems, the aerosol can be dominated by ash compounds, especially KCl and K_2SO_4 formed via heterogeneous reactions in the gas-phase. However, little research has focused on the variations in physical and chemical particle properties over the combustion cycle. This is partly due to the lack of experimental methods with sufficient time resolution to follow the inherently transient nature of batch wise wood log combustion. Further, little information is available on emissions from novel fuels such as corn. For example, corn has higher ash content than conventional wood fuels. In this work we used single particle mass spectrometry to investigate chemical signatures from three wood log fuels (oak, pine and birch) and corn.

METHODS

The wood fuels were combusted in a conventional wood stove, while the corn was combusted in a commercially available corn stove, which operates similarly to modern wood pellet stoves. Each wood-combustion experiment involved start-up from a cold stove with a full load of fuel. Fuel was then added once and experiments were conducted until only glowing embers remained. Particles were sampled and diluted with particle free air using a three stage dilution system which allowed dilution ratios between 1:10 and 1:10000. An Aerosol Time-of-Flight Mass Spectrometer (ATOFMS; TSI Inc., Shoreview, MN, USA) was used to study chemical signatures from single particles in the range 100-500 nm. In a few experiments a Differential Mobility Analyzer was applied upstream of the ATOFMS to determine the particle effective density. A Scanning Mobility Particle Sizer was used to determine the particle size distribution (20-800 nm). A Tapered Element Oscillating Microbalance was used to determine the total mass concentration (PM2.5) and a gas analyzer (TSI CA-6215) was used to determine the flue gas composition (O_2, NO_x, CO).

RESULTS AND CONCLUSION

The emission factors of $PM_{2.5}$, CO and NO_x varied strongly between corn and wood combustion. For corn the average $PM_{2.5}$, CO and NO_x emission factors were 28, 120 and 297 mg/MJ, respectively, while for wood combustion it was 102, 3100 and 97 mg/MJ. The emission factors were similar for the three wood fuels studied.

During the start-up phase and during throttling of the supply air in wood combustion, strong organic markers were present. Several of these, for example *m/z* =-45 ($C_3H_3O_2^-$), -59 ($C_3H_3O_2^-$) and -71 ($C_3H_3O_2^-$) have previously been detected from pure levoglucosan (Silva et al. 1999), a dominant organic component from low temperature wood combustion. Signatures of Poly Aromatic Hydrocarbons (PAHs) were also strongly enhanced during the start-up phase (Figure 1).

In the efficient combustion phase, many markers for organic compounds diminished, while $^{113}K_2Cl^+$ - $^{24}(C_2)^-$, $^{36}(C_3)^-$, $^{48}(C_4)^-$ were strongly enhanced (Figure 1). We interpreted this to mean that emissions during the start up phase were rich in organics while emissions during the efficient combustion phase were dominated by ash compounds such as KCl and soot. Signatures of particles from Oak, Birch and Pine showed strong similarities.

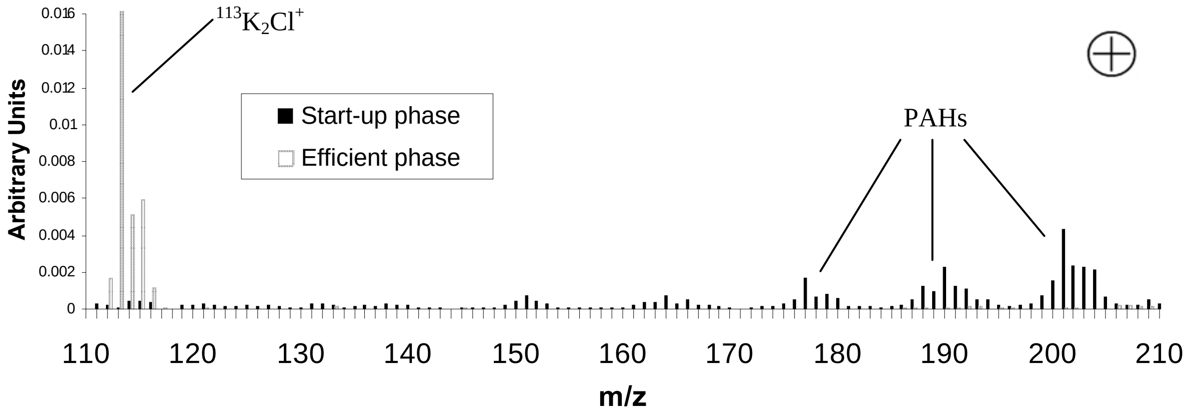

Figure 1. Average positive mass spectrum from ATOFMS measurements during the start-up phase and efficient phase in birch combustion.

When the corn stove was operating optimally, markers for inorganic ash components were dominant. These included $^{39}K^+$, $^{113}K_2Cl^+$, $^{97}HSO_4^-$ and $^{79}PO_3^-$. The largest difference between the composition of corn compared to wood emissions was the strong signature for phosphates and the generally weaker signatures for organics and soot. Note that the corn combustion process is semi-continuous as opposed to batch-wise log combustion, where distinct combustion phases can be identified.

Overall the laser-desorption ionization approach used in the ATOFMS instrument enabled us to detect signatures from organic compounds, soot and low volatility alkali salts, such as KCl. It is a promising tool to investigate the variations in particle chemical composition during the inherently transient nature of batch-wise wood log combustion. The combination of these three classes of signatures is promising for source receptor studies.

ACKNOWLEDGEMENTS

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CLOUD DROPLET ACTIVATION OF AMINOACIDS

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Keywords: Amino Acid, CCN, WSOC, WSON.

INTRODUCTION

Water soluble organic nitrogen (WSON) has been found to contribute about 18% to the total fine aerosol mass in California (Zhang *et al*., 2002). A later study in California by Zhang and Anastasio (2003) showed that WSON comprised about 13 and 10 % of the water soluble organic carbon (WSOC) PM2.5 mass in the fog droplets and aerosol particles respectively. WSON has also been found in biomass combustion particles over the Amazonian Basin (Mace *et al*., 2003). Despite its abundance in the atmosphere, the sources of amino acids and WSON remain poorly characterized.

The critical supersaturations needed to activate 7 different amino acids and peptides into cloud droplets have been measured. Mixtures with ammonium sulphate (AS) were also investigated. The results were compared with a modified Köhler theory that accounts for the limited solubility of the amino compounds.

METHODS

The amino acids and AS were dissolved in commercial high purity MilliQ-water and the solution was thereafter atomized with a TSI 3076 atomizer. The liquid particles produced were dried in a diffusion drier before passing through a Kr-85 bipolar ion source to obtain a known charge distribution of the dry particle. Then, the aerosol was diluted and the particles were selected in a narrow size distribution using a differential mobility analyzer (DMA) of type TSI model 3081. Finally, the aerosol flow was divided between a condensation particle counter (CPC TSI model 3010) to calculate the particle number concentration and a static thermal gradient diffusion Wyoming type cloud condensation nucleus counter to measure the critical supersaturation of activation (Snider *et al*., 2006).

The critical activation supersaturation of 7 different amino acids was measured using pure compounds and mixtures with AS with varying mass fractions.

CONCLUSIONS

The critical supersaturation obtained for 2 different amino acids is shown in Table 1 for an 80 nm dry particle diameter. The results show that the amino acids as pure compounds are relatively active as cloud condensation nuclei (CCN), except for L-Tyrosine and L-methionine which have very low solubility (L-Tyrosine and L-methionine results are not shown). However, with an addition of inorganic salts, these amino acid mixtures again become relatively active as CCN. Table 1 shows the critical supersaturation as function of a 75 nm dry particle diameter in a mixture of 60 and 40% L-Tyrosine and AS by mass respectively. In Figure 1, the same mass fraction is plotted, although with a variable dry particle diameter.

The experimental activation lies somewhere between the modified Köhler model accounting for a limited solubility (Schulman et al., 1996, Laaksonen et al., 1998, and Kulmala *et al*., 1997) and the Köhler model assuming full solubility (Köhler 1936).

Compound	Solubility (kg m^{-3})	Critical supersaturation (%)
AS	760	0.30
L-aspartic acid	5.0	0.53
L-glutamic acid	8.6	0.60
L-Tyrosine 60% and AS 40%	0.479 (L-Tyrosine)	0.39

Table 1. The measured critical supersaturation of activation of 2 different aminoacids with a dry diameter of 80 nm, and the measured critical supersaturation of 60% and 40% by mass of L-Tyrosine and AS respectively with a dry diameter of 75 nm.

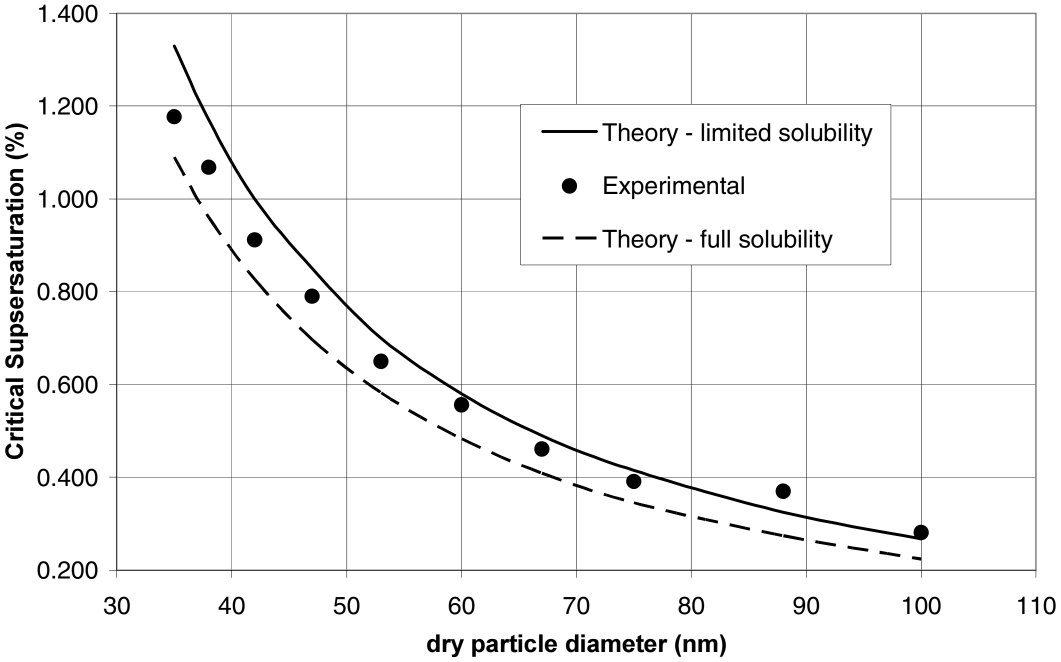

Figure 1. Measured critical activation supersaturation as function of dry particle diameter (experimental) versus theoretical critical supersaturation using traditional Köhler theory (Theory – full solubility) and modified Köhler theory (Theory – limited solubility).

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CLUSTER ION REACTIONS

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Keywords: Cluster ion, Water Clusters, Time-of-Flight

INTRODUCTION

We want to better understand the various mechanisms occurring inside molecular clusters of atmospheric relevance. This is done by experiments where we observe interactions and reactions between charged molecular clusters and different gases, in a modified quadrupole time-of-flight unit.

METHODS

Clusters studied include pure water clusters, ammonia-water clusters, sulphuric acid, sulphuric acid-water, sulphuric acid-water-ammonia clusters, salt, salt-water clusters, and various organic solvent clusters. The collision gases most commonly used are D_2O and argon.

An example of experimental results is shown in Fig. 1, where the cluster size dependence for producing HDO by reaction of charged pure water and ammonia water clusters with D_2O is shown. Upon collision with the gas molecule, the cluster and gas molecule forms an excited intermediate with short lifetime. The intermediate then decay by sending out a molecule and the excess energy is thereby reduced. During the lifetime of the intermediate complex, rearrangement of atoms takes place; hence the leaving molecule may differ from the original colliding gas molecule. The ordinate in Fig. 1 gives the relation between different reaction channels, detected as mass increase in the cluster.

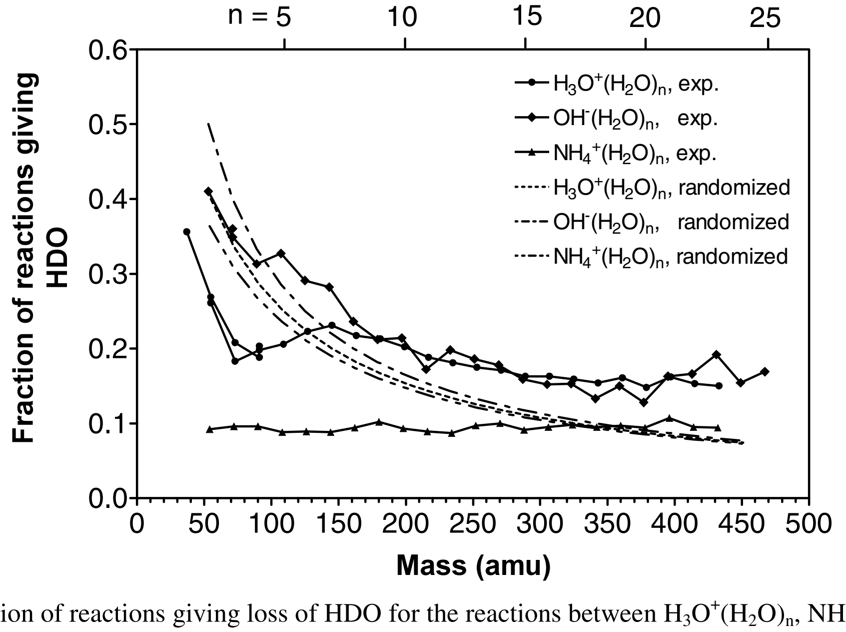

Figure 1. Fraction of reactions giving loss of HDO for the reactions between $H_3O^+(H_2O)_n$, $NH_4^+(H_2O)_n$, and $OH^-(H_2O)_n$ and D_2O.

This experiment have been extended by using ^{18}O isotopes in the water clusters, *i.e.* the reaction becomes $H_3{}^{18}O^+(H_2{}^{18}O)_n$ + $D_2{}^{16}O$. This way, even more information can be obtained about the mechanism taking place during the reactions between cluster ions and gases, as we now can detect some exchange of oxygen atoms as well.

In addition, experiments on cluster fragmentation (mainly with argon as collision gas) are conducted. In order to evaluate our results, we also make use of some computational methods, *e.g.* RRKM to calculate reaction rates.

ACKNOWLEDGEMENTS

This work is supported by the Swedish Research Council.

FILTER AND ON-LINE MEASUREMENTS OF FINE PARTICLE ORGANIC CARBON IN HELSINKI, FINLAND

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Keywords: Organic carbon, levoglucosan, biomass burning.

INTRODUCTION

Urban aerosol is a complex mixture of primary particulate emissions (from industry, transportation, power generation and natural sources) and secondary material formed by gas-to-particle conversion. Urban aerosol contains a substantial amount of carbonaceous material (20–80%; Rogge et al., 1993; Nunes and Pio, 1993) that is composed of elemental carbon (EC) and organic carbon (OC). EC is a primary pollutant formed in combustion processes whereas OC is a complex mixture of different groups of compounds originating from a large variety of sources. In this study the sources of OC were investigated in Helsinki using the data from the year-round measurements carried out using both on-line instruments and filter/impactor measurements.

METHODS

The measurements were conducted in Helsinki (Finland) at an urban background station (SMEAR III, 60°20’N, 24°97’E, 26 m above sea level). The measurement site is located in the university campus area, 4 km northeast from the Helsinki city center. The most important local source of fine particulate matter is vehicular traffic since there is a densely trafficked major road (60 000 cars/day) at a distance of less than 200 m from the station. However, the contribution of biomass combustion may be substantial, especially in winter. OC, EC, BC (black carbon) and water-soluble ions were measured continuously at SMEAR III. In addition to those, also $PM_{2.5}$ mass concentration data was available from the station. From the daily PM_1 filter samples OC, EC, water-soluble organic carbon (WSOC), levoglucosan and major ions were determined. All the measurements are summarized in Table 1.

Instrument	Component	Time-resolution	Size fraction
Semicontinuous OCEC	OC, EC	3 h	<1 µm
PILS-IC	Ions	15 min	<1 µm
Aethalometer	BC	5 min	<2.5 µm
FDMS-TEOM	$PM_{2.5}$	30 min	<2.5 µm
Filter casette	OC, EC, WSOC, ions, levoglucosan	24(–72) h	<1 µm
MOUDI	WSOC, ions, mass	72 h	0.056–10 µm

Table 1. Instruments, aerosol components analyzed and the time-resolution of each measurement.

RESULTS

The concentration of OC from February 2006 to February 2007 is shown in Figure 1. OC concentration ranged from 0.3 to 16 µg/m^3 with a yearly-mean value of 2.5 µg/m^3. No clear seasonal variation was found for OC. The concentration was slightly lower in the period from October 2006 to January 2007 than in the other months studied. This period was warmer than usually, which might have an effect on OC concentration. In contrast the highest OC concentrations were measured during the episodes of long-range transported smokes emitted from wildfires in Russia.

A tracer for biomass burning, levoglucosan, was analyzed from filter samples in order to investigate the impact of biomass burning on OC concentrations (Figure 1). Levoglucosan concentrations showed a strong correlation with ambient temperature. However, similarly to OC the highest concentrations were obtained during the long-range transport episodes. This finding suggest the significant contribution of biomass burning to OC concentrations in Helsinki in cold season whereas in summer OC seems to be related to secondary sources, shown by the annual trend of oxalate. The impact of local traffic on OC concentration was studied using the semicontinuous OCEC instrument, but the impact was found to be small. Only in few days the diurnal cycle of OC correlated with that of EC which was considered as traffic-related component. This is in agreement with a recent study of Robinson et al. (2007), where it was found that OC from traffic has mostly more regional than local contribution to urban fine particulate matter.

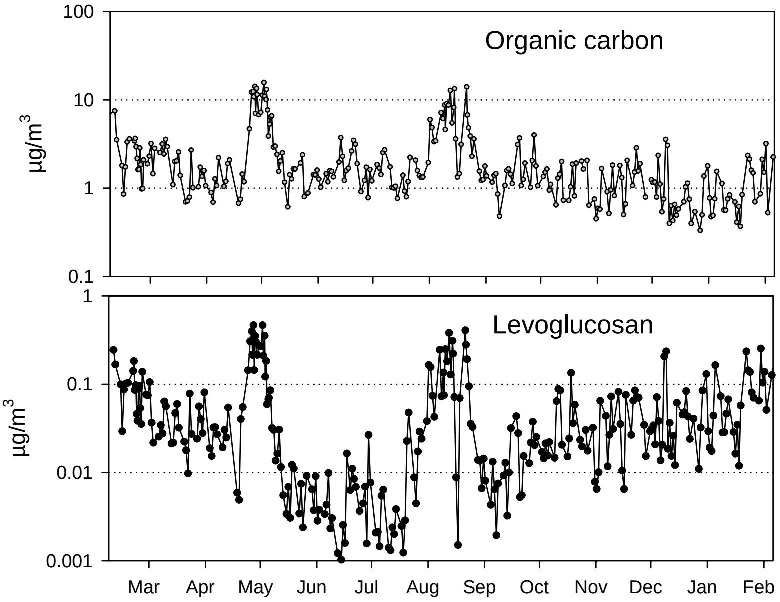

Figure 1. One-year data of organic carbon and levoglucosan measured in Helsinki, Finland. Note logarithmic y-axis.

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VOLATILITY MEASUREMENTS ON ORGANIC AEROSOLS USING A VTDMA SYSTEM

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Keywords: Volatility, Secondary organic aerosol, Monoterpenes

INTRODUCTION

Aerosol particles in the atmosphere can affect our lives in many different ways, possessing both environmental and health effects. Particles can origin from numerous sources, both natural and anthropogenic and their size can range from few nm up to 100 µm. A considerable fraction of aerosol particles is formed from oxidation of volatile organic compounds (VOCs). When oxidised the organic compounds are transformed via atmospheric radical and photochemical processes to less volatile compounds that can condense or nucleate to form secondary organic aerosols (SOA). The biogenic contribution to VOCs producing SOA is large on a global scale, where compounds such the terpenes dominate.

METHODS

The actual mechanistic pathways forming low volatile products that originate from oxidation of terpenes are not firmly established. However, a typical class of products from atmospheric oxidation processes yielding SOA is carboxylic acids, *e.g.* pinonic and pinic acids from α-pinene oxidation. The volatility of organic aerosols is an important characteristic for gas-to-particle partitioning that originates from fundamental properties such as vapour pressure of its constituents and their concentration. To quantify the volatility of aerosol particles one can *e.g.* use a Volatility Tandem-DMA (VTDMA) system. This paper describes the initial tests and the performance of our newly developed VTDMA system. The main focus has been on dicarboxylic acids with the general chemical formula $HOOC(CH_2)_{n-2}COOH$, where n is the number of carbon atoms, which in this study ranged between 4 and 10. The results are presented and discussed in relation to previous studies on vapour pressure determinations. An example of results from the VTDMA measurements is shown in Fig. 1.

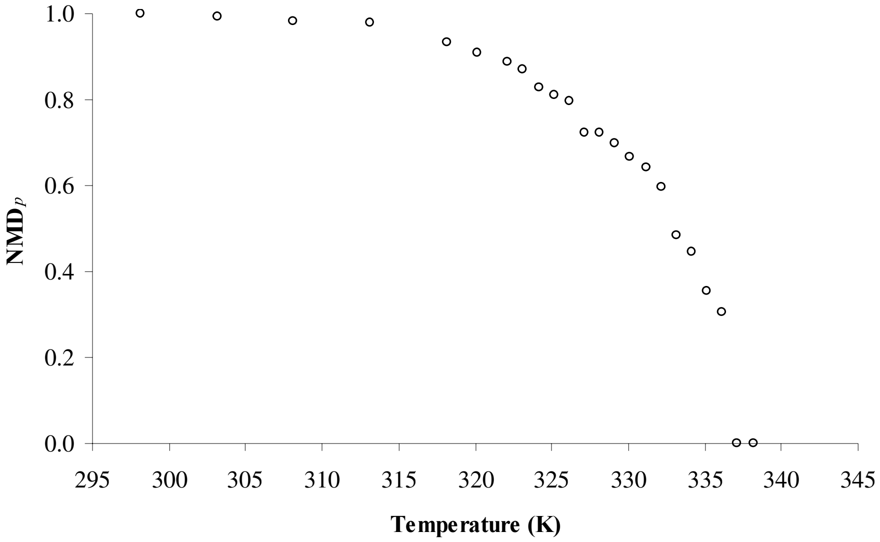

Fig. 1. Change in Normalised Modal particle Diameter (NMD_p) with evaporative temperature for succinic acid

CONCLUSIONS

We will in this presentation demonstrate that the VTDMA is a suitable instrument for determination of heat of vaporization for pure compounds and in addition can be used for mechanistic studies of SOA formation with examples from oxidation of selected monoterpenes.

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MODELLING OF ORGANIC AEROSOL IN EUROPE

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Keywords: Modelling, Organic Aerosol, SOA.

The EMEP MSC-W model is used to assess our understanding of the sources of carbonaceous aerosol in Europe (organic carbon, OC, elemental carbon, EC, or their sum, total carbon, TC). The modelling work makes use of new data from two extensive measurement campaigns in Europe, those of the CARBOSOL project, and of the EMEP EC/OC campaign (see Simpson et al., 2007 and refs therein). As well as EC and OC measurements, we are able to compare with levoglucosan, a tracer of wood-burning emissions, and show that discrepancies between modelled and observed wintertime OC at several, but not all, sites can be accounted for in terms of missing wood-burning contributions. Further, the CARBOSOL project included tracers such as 14C and cellulose, which allowed Gelencser et al. (2007) to generate a source-apportionment (SA) of TC into primary versus secondary, and fossil-fuel versus biogenic origin. We use estimates of the primary, secondary, fossil-fuel and biogenic components of TC from the CARBOSOL project to evaluate the performance of the EMEP model and as a basis for a discussion of the accuracy of emission inventories and the uncertainties in modelling carbonaceous aerosols. Two schemes for secondary organic aerosol (SOA) contribution are included in the model, and we show that model results for TC are very sensitive to the choice of scheme.

The model results have been reported in detail in Simpson et al. (2007). They suggest that emissions of primary EC and OC from fossil-fuel sources are probably captured to better than a factor of two at most sites. In Northern Europe the model seems to capture TC levels rather well with either SOA scheme, but in southern Europe the model strongly underpredicts TC. Comparison against the results of Gelencser et al (2007) shows severe underprediction of the SOA components. This modelling work confirms the difficulties of modelling SOA in Europe, but shows that primary emissions constitute a significant fraction of ambient TC.

Finally, the science of SOA formation is still undergoing rapid change. The state of SOA modelling will be discussed, and priorities for future work highlighted.

ACKNOWLEDGEMENTS

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MEASUREMENT OF PRIMARY MARINE AEROSOLS USING HE DISSIPATION TECHNIQUE

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Keywords: MARINE AEROSOLS, PARTICLE FLUX

INTRODUCTION

It is widely recognised that interactions between oceans and the atmosphere play a major role in climate, via exchanges of heat, CO2, trace gases and particles. The atmospheric aerosol particle concentration is affected by the production of primary marine aerosols, particle deposition and air sea exchange of gases that can produce secondary particles. The atmospheric aerosol particles can affect climate directly by scattering and absorbing solar and terrestrial radiation and indirectly by acting as cloud condensation nuclei (CCN).

Parameterizations of production of primary marine aerosols are improving (Mårtensson, E.M., et al., 2003), however there is still a need for validation using data of sea spray fluxes from field measurements. Data of fluxes from open sea can only be obtained from platforms or ships.

It is not an easy task to obtain fluxes of sea spray from a ship due to the motion of the ship, which is influencing the spectra of vertical velocity.

METHODS

The Galathea 3 was a worldwide Danish research cruise carried out from August 2006 to April 2007. Continuous measurements of particle concentrations were carried out during the cruise using a WCPC 3785 sampling at 20 Hz. Turbulence was measured using 2 ultrasonic anemometers.

The particle flux can be calculated using the covariance method if the measured turbulence can be corrected for ship movements - which isn't always an easy task. Here we present the dissipation technique to measure fluxes using the higher frequency area of the spectra, which is not disturbed by the motion of the ship. We present data of fluxes estimated by this technique and compare to filtered covariance fluxes.

CONCLUSIONS

The dissipation technique used to calculate fluxes seem to be a very powerful tool and a very good alternative to the covariance method – especially when measurements are carried out from ships.

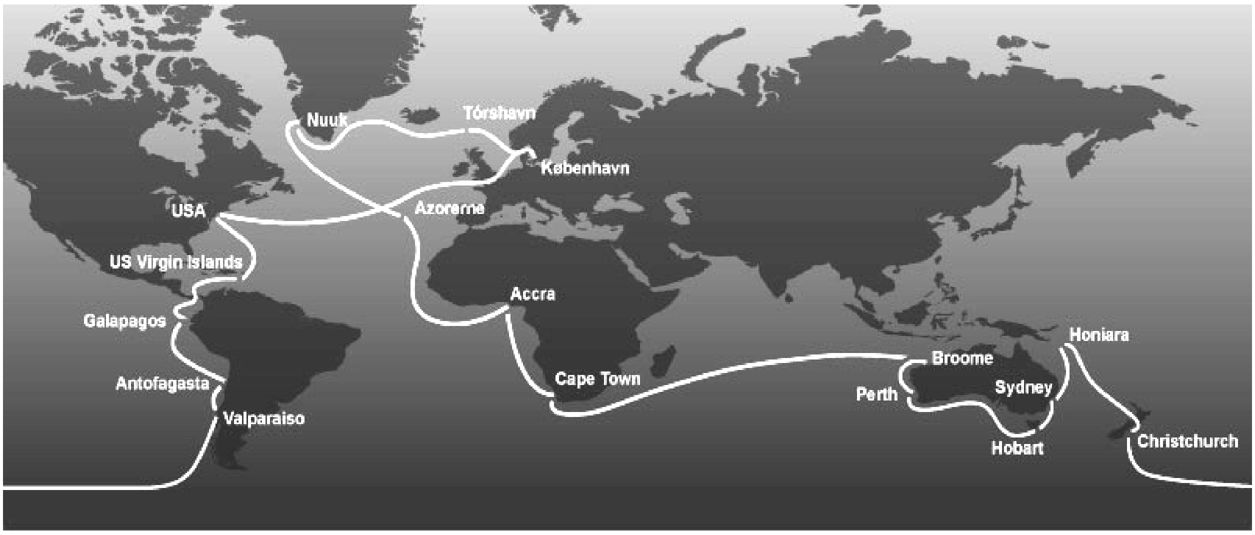

Figure 1. The route of the Galathea 3

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AIR POLLUTION FROM DOMESTIC WOOD COMBUSTION

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Keywords: Wood combustion, domestic heating, particulate matter, soot.

INTRODUCTION

Air pollution from domestic wood combustion is a growing problem in the Nordic countries, since rising prices on fossil fuels lead to an increase in the use of wood stoves for domestic heating. The amount of people affected by the pollution may be rising accordingly, leading to potential negative health effects in the population (e.g. Boman et al., 2003). Previous studies have shown increased levels of $PM_{2.5}$ and other air pollutants in Danish as well as Swedish residential areas, where wood stoves were used (Glasius et al., 2007; Glasius et al., 2006; Johansson et al., 2004). In the ongoing interdisciplinary study WOODUSE a broad approach is applied, as the study investigates emissions, ambient and indoor pollution levels, human exposure, health effects, social aspects and abatement options.

METHODS

Measurements of ambient $PM_{2.5}$, particle size distribution (10-700nm), soot, PAH, CO and NOx were conducted from December 2006 to March 2007 in the small village Slagslunde (approx. 350 houses) 30 km. northwest of Copenhagen. Simultaneous background measurements were conducted 500 meters west of the village (i.e. upwind in the predominant wind direction). In addition indoor measurements of soot were conducted for one week in a house where a wood stove was used every day. Simultaneous measurements were carried out outside the house (from the village monitoring station located 50 meters away) and at the rural monitoring station outside the village. Only $PM_{2.5}$ and soot measurements will be presented here.

RESULTS

Local contributions of the measured air pollutants are obtained by subtracting the background level (rural) from the level in the village. In the case of $PM_{2.5}$ and soot, the local contribution is solely attributable to emissions from wood stoves in the village, and the contribution was approximately 1.7 $\mu g/m^3$ $PM_{2.5}$ and 0.16 $\mu g/m^3$ soot as an average over the three month campaign (Table 1). The contribution to $PM_{2.5}$ falls between the values observed in two previous Danish studies, which showed 4.5 $\mu g/m^3$ in the village Gundsømagle (Glasius et al., 2006) and 1.2 $\mu g/m^3$ in the village Vindinge (Glasius et al., 2007). This is in good agreement with the expected outcome, since the amount of active wood stoves in proximity of the sampling location was higher than in Vindinge and lower than in Gundsømagle.

Table 1: $PM_{2.5}$ and soot in the village Slagslunde and at a rural location outside the village. The local contribution is obtained by subtracting the rural level from the level in the village. Measurements were done with a TEOM Series 1400a, where some particle mass is lost due to heating of the airflow to about 50°C. This means that the $PM_{2.5}$ levels at the two stations would be higher than shown here when measured according to the reference method.

	$PM_{2.5}$	Soot
Slagslunde village	10.35 $\mu g/m^3$	0.51 $\mu g/m^3$
Rural	8.62 $\mu g/m^3$	0.35 $\mu g/m^3$
Local contribution (from wood burning)	1.74 $\mu g/m^3$	0.16 $\mu g/m^3$

The average daily variation in $PM_{2.5}$ and soot levels showed a distinct rise in the local contribution from late afternoon (approx. 15:00) to after midnight (Figure 1). This rise is a result of the wood stoves in the area being used mainly in the late afternoon and evening, when people are neither at work nor sleeping. The local contribution that is observed during the remaining hours of the day (from 02:00 to 14:00) indicates that some wood burning takes place during all hours of the day.

The indoor soot measurements revealed that the wood stove was a source of indoor air pollution. This is obvious in Figure 2, where the high peaks in the indoor level all occur at times when the stove was open for lighting the fire or for putting on additional wood logs. Due to ventilation in the house, the indoor levels dropped down to the initial level after a few hours. The average outdoor level of soot was however higher than the average indoor level, so the removal of particles at passage from outdoors to indoors apparently on average exceeded the indoor emissions from the wood stove.

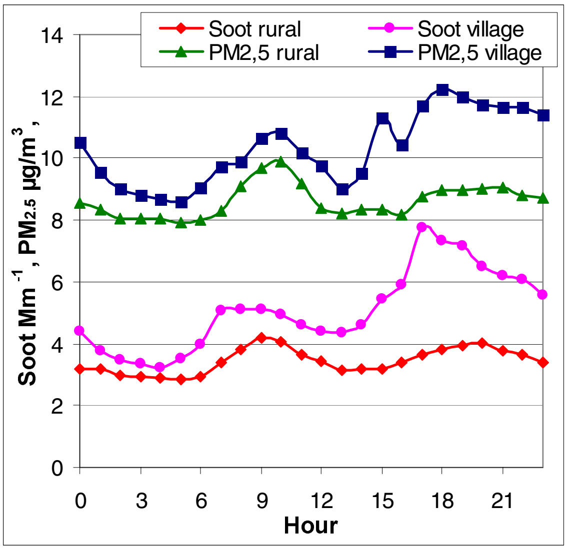

Figure 1: Average daily variation in $PM_{2.5}$ *and soot levels in the village and at the rural location.*

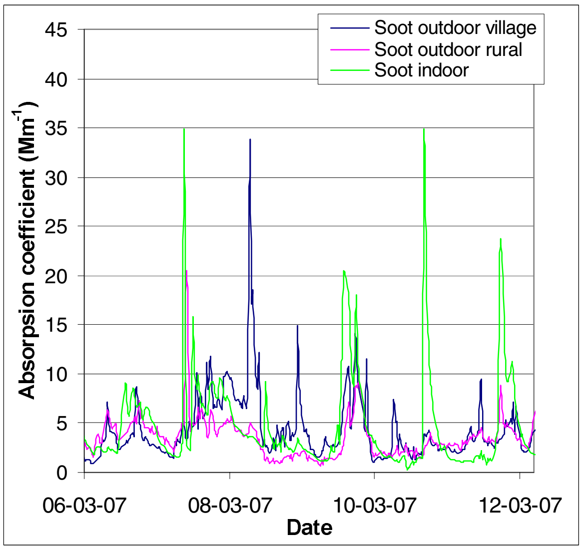

Figure 2: Soot levels indoors in a house with a wood stove, outside the house and at the rural location.

ACKNOWLEDGEMENTS

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The gratefully acknowledge the skilled work of technical staff at NERI during the campaign.

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THERMODYNAMIC STABILITY OF CHARGED WATER CLUSTERS

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Keywords: water clusters, fragmentation, early droplet-formation

INTRODUCTION

Water is one of the most important substances for humankind, both for our technology as well as our very own existence. Despite this there are many properties of water which are not yet understood. The study of small clusters of water molecules offers a possibility to study the transition from the isolated molecule to the "infinite" solid or liquid "bulk"-water. Water clusters are also interesting for a number of other reasons, such as the study of hydrogen bonding, aqueous phase solution, and insight into phenomena of importance in atmospheric science. The amount and stability of subcritical water droplets is an important parameter for the formation of clouds, since this stage acts as a bottleneck in the drop formation. The increased stability of small charged particles relative to neutral species reduces the critical size and hence enhances the aggregation strongly. The presence of atmospheric ions may therefore have a large impact on the rate with which clouds are formed (Yu and Turco, 2001).

GOAL

The goal of the project is to measure the thermodynamic properties of pure and lightly contaminated charged water clusters. The contaminations will be chosen from atmospheric relevant substances such as NH_3 and SO_2. The experiments will ideally provide binding energies of the least bound molecule without any need for modelling of the decay process, which will allow quantitatively realistic modelling of the first stage of nucleation in the atmosphere.

METHOD

By measuring the energy needed to induce fragmentation in a water cluster, one can get information about the binding energies between the molecules and thus get information of the stability and reactivity of the cluster. We intend to use a method previously used on Au-clusters (Vogel *et al.* 2001) in which the absolute dissociation energies can be measured by recording the amount of metastable loss vs. photon energy when irradiating the clusters with a laser of tuneable photon energy. The main advantage of this method is that it allows for a direct measurement of dissociation energies without any assumptions on how the decay proceeds. The idea is to compare the excitation energy E_A of a sequential decay

$$A \rightarrow B \rightarrow C$$

with the corresponding energy E_B of the single decay

$$B \rightarrow C$$

leading to the same final product. The second process can be used as a uncalibrated thermometer for the last step of the sequential reaction, when it depends in a measurable way on the amount of excitation energy present. The dissociation energy of A can then be extracted by comparing the two excitation energies E_A and E_B.

For this experiment we use a Time-of-Flight (TOF) mass spectrometer equipped with a reflectron and a OPO-laser which has a pulse-length of tens of ns and a wavelength that can be varied between about 220-2000 nm. The water clusters are produced in a pulsed supersonic expansion, either in a neat expansion or seeded with a second gas, and then ionized with an electron gun. The electron gun has recently been rebuilt and gives a strong signal when tested on Ar.

ACKNOWLEDGEMENTS

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CHARACTERIZATION OF ORGANIC AEROSOL COMPONENTS AT A EUROPEAN AEROSOL SUPER-SITE IN SOUTHERN SWEDEN

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Keywords: organic aerosol, climate, closure studies.

INTRODUCTION

A number of studies have indicated that organic aerosols (OA) play an important role in both the direct and indirect aerosol forcing. However, the uncertainty related to this forcing is at least a factor of 3. Numerous epidemiological studies have shown that elevated outdoor particle concentrations measured as PM_{10} and $PM_{2.5}$ are associated with increased prevalence of respiratory and cardiovascular disease and mortality, both acute and chronic. Since ~40% of the Nordic background PM_{10} is OA, this implies that several thousands extra deaths annually might be attributable to OA in the Nordic countries, but the uncertainties in these estimates remain large.

Quantification of the effects of aerosols – including OA – on climate and European air quality is studied within the framework of two EU FP6 research projects. The Integrated Infrastructure Initiative EUSAAR (European Super-sites for Atmospheric Aerosol Research, April 2006 – March 2011, http://www.eusaar.net) will provide important aerosol research infrastructure in terms of a European network of aerosol super-sites and development of new climate-relevant aerosol instrumentation. The Integrated Project EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality interaction; http://www.atm.helsinki.fi/eucaari/; Jan. 2007 – Dec. 2011) aims to reduce the uncertainty in the impact of aerosols on climate by 50% and to quantify the relationship between aerosol loading and air quality. EUCAARI will make use of the aerosol research infrastructure developed in parallel within EUSAAR. Lund University (Div. of Nuclear Physics) is partner of both these EU FP6 projects.

We also aim to develop a methodology by which to determine the contribution to the Nordic background aerosol of various organic aerosol (OA) components of anthropogenic and biogenic origin, and to use the data to help further improve and validate the model for particulate matter (PM) and OA now being developed at EMEP/MSC-W.

METHODS

The ambition of EUSAAR is that, at the end of the project, aerosol parameters that are essential to the effect of aerosols on climate will be measured at the EUSAAR aerosol super-sites, supplementing the EMEP monitoring network (http://www.emep.int). The boundary layer aerosol properties to be measured are aerosol mass, aerosol inorganic and organic composition, light scattering coefficient and aerosol size distribution. In addition the aerosol optical depth (sun photometer) and vertical distribution (lidar) will be measured at several stations. Several EUSAAR stations will also operate HTDMA instruments (Hygroscopic Tandem Differential Mobility Analyzers) and CCN counters (Cloud Condensation Nuclei) to provide vital information regarding the aerosol indirect effect on climate.

One of the European aerosol super-sites within EUSAAR is Vavihill (56° 01' N, 13° 09' E, 172 m asl) in southern Sweden where intensive aerosol measurements will be performed during 2008 within EUCAARI. Here, size distribution measurements cover the size interval 0.5 nm – 10 µm, combining an Air Ion Spectrometer (AIS), a Differential Mobility Particle Sizer (DMPS), and an Aerodynamic Particle Sizer (APS).

Filter samples for analysis of organic and "elemental" carbon (OC/EC) will be taken with a sampling train (denuder - quartz filter - sorbent) that was constructed according to the recommendations agreed upon within EUSAAR (NA2: "Standardised measurement protocols, intercomparisons and quality assurance for carbonaceous aerosols compounds"). The samples are then analyzed with the Lund DRI Aerosol Carbon Analyzer using a new thermal-optical analytical protocol for OC/EC proposed within EUSAAR (NA2). The EC determined using the thermo-optical method (time resolution 12-48 h) will be compared with the light absorption (equivalent black carbon) determined with a soot photometer (design: Dr Johan Ström, Stockholm University, time resolution ~1h) and calibrated within EUSAAR (NA4: "Standardised measurement protocols, intercomparisons and quality assurance for optical properties of aerosols").

Further information regarding the organic aerosol fraction will be achieved using a high-resolution time-of-flight aerosol mass spectrometer (AMS) from Aerodyne Research Inc., USA. This instrument has been shown to be able to provide fully size-resolved and quantitative chemical information for sulphate, nitrate and ammonium ions as well as various classes of organics in different stages of aging and with high time resolution. This method enables a quantitative separation between the oxygenated (processed, secondary) organic aerosol and the hydrocarbon-like (freshly emitted) organics.

We intend to quantify and distinguish between anthropogenic and biogenic aerosol carbon, more precisely by separating fossil from modern carbon, and biogenic secondary organic aerosol from organic aerosol originating from biomass combustion. This will be achieved by analyzing the aerosol samples for ^{14}C (using Accelerator Mass Spectrometry at Lund University) in both the total sample and in various organic/elemental carbon (OC/EC) fractions based on a thermal-optical separation. A complementary elemental analysis (using Particle Induced X-ray Emission at Lund University) will enhance the capability of a source-receptor model to apportion the various carbon fractions to their sources.

The particle soluble volume fraction as a function of the dry particle size – and thereby also the number of water-soluble entities in each particle – can be determined with an HTDMA (Hygroscopic Tandem Differential Analyzer). We have shown that the CCN concentrations can be accurately predicted with high time resolution (minutes) solely on the basis of measurements of the dry particle size distribution (DMPS: Differential Mobility Particle Sizer) and the hygroscopic properties (HTDMA), even for aerosols containing very high organic mass fractions. A new generation of HTDMA instruments is now being constructed to meet the demands of unattended long-term operation at the EUSAAR sites, including Vavihill. This is coordinated with EUSAAR (Joint Research Activity 2: "Building a new generation of humidity-controlled aerosol monitors"). CCN concentrations will be measured at Vavihill for water vapour supersaturations between 0.1% and 1% using a continuous air-flow CCN counter (Droplet Measurement Technologies, USA).

Note that several essential instruments (DMPS, APS, HTDMA, CCNC, AMS) provide data that are highly resolved in both time and particle size. The hygroscopic growth model and the CCN prediction model can therefore be validated with similarly high time and size resolution in the planned closure studies (Hygroscopic closure study; DMPS+AMS → Hygroscopic growth model → HTDMA; CCN closure study; DMPS + HTDMA → CCN prediction model → CCNC). Recent work has shown that excellent agreement can be achieved between observed (HTDMA) and predicted hygroscopic properties (hygroscopic closure), including also the organic fraction determined using and Aerodyne AMS.

ACKNOWLEDGEMENTS

This work is carried out within the frameworks of the EU FP6 Infrastructure Project EUSAAR, the EU FP6 Integrated Project EUCAARI, the NOS-N Nordic Centre of Excellence BACCI, the Swedish research program SCARP (Swedish Clean Air Research Program, 2008-2011) and a Swedish FORMAS project ("Development of a methodology for apportionment of primary and secondary organic aerosols for European-scale model validation", 2007-2009).

ROAD-SIDE MEASUREMENTS OF AIR IONS

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Keywords: ROAD-SIDE, IONS, CLUSTERS

INTRODUCTION

In addition to electrically neutral aerosol particles, charged particles from small cluster ions to charged larger aerosols are observed in ambient air. High energy radiation (such as alpha and beta particles or gamma radiation) ionises air molecules into pairs of a positive ion and a free electron. New ions react with other air molecules and form cluster ions within microseconds. Larger charged particles can form via ion-induced nucleation, in collisions between neutral and charged particles or cluster ions, or by water droplet splitting (e.g. Israel, 1970).

Because reliable instruments for measuring ion size distributions are quite novel, not many experimental studies have been conducted so far in urban environments

METHODS

We introduce the ion number concentrations and number size distributions measured with the AIS (air ion spectrometer) next to a road in Kuopio. At the same time we measured ion size distributions also with the AIS at SMEAR II station at rural site in Southern-Finland, Hyytiälä. The nature of the environments as well as the sources of particles and their precursors is very different at these two sites, and we hope that comparison of the two datasets will add to the understanding of the influences of these factors on air ions (see Tiitta et al., 2007).

For detailed analysis, two different wind sectors were separated; downwind sector (DW), when the wind blows from the Savilahti road to the measurements site (270 ° < WD < 360 °) and upwind sector (UW) when the wind blows from the VT5 motorway towards the measurements site (90 ° < WD < 180 °).

The time dependence of cluster ion concentration *dn/dt* is determined by the simplified equation (Israel 1970)

$$\frac{dn}{dt} = Q - \alpha n^2 - S \cdot n \qquad (1)$$

where Q denotes the ion production rate due to ionisation process of air molecules and their further reactions with other air molecules, α is the ion-ion recombination coefficient, n is concentration of positive or negative ions, S describes the sink due to pre-existing aerosol particles Thus clusters concentration is connected to condensation sink by the balance equation (Eq.1).

CONCLUSIONS

The cluster ion concentrations are connected to sink due to pre-existing aerosol particles by the balance equation (Eq.1). Condensation sink (CS) describes the removal rate of vapour molecules by the aerosol particles (see e.g. Dal Maso et al. 2005) . We utilised the CS as an indicator of the aerosol sink for cluster ions, although it is not exactly the sink *S* in Eq. 1. When the condensation sink increased (e.g. because of local emissions) cluster ion concentrations decreased (Fig. 1), whereas the ratio of negative to positive cluster ions was almost independent of CS. The average ratios of negative to positive cluster ion concentrations were 1.2 in Kuopio with a maximum ratio of 8.7 and 0.9 in Hyytiälä with a maximum ratio of 2.0. Additionally, the average ratios were equal during upwind (1.1) and downwind conditions (1.1), but they varied significantly between 0.5 and 4.3 during upwind condition and between 0.2 and 3.9 during downwind conditions.

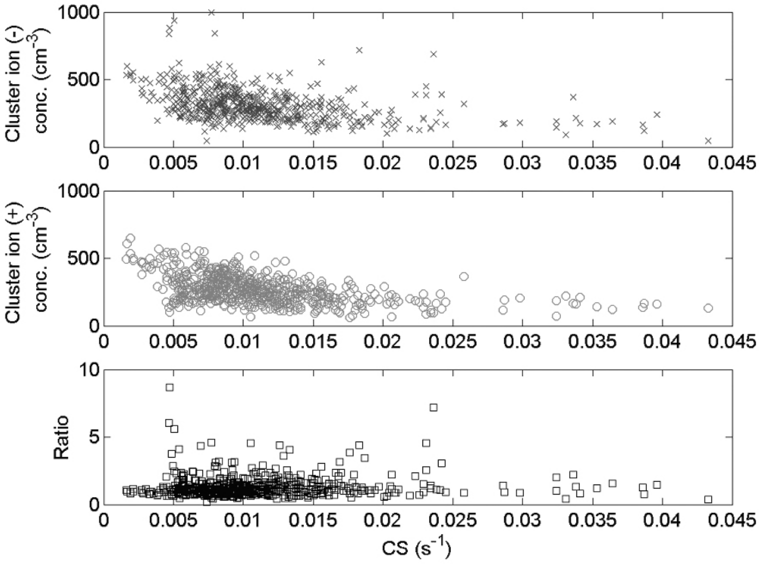

Figure 1: Cluster ion concentrations as a function of condensation sink (CS) for total dataset (16.6.--2.7.2004) at Savilahti measurement site.

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INFLUENCE OF SURFACE TENSION ON CLOUD DROPLET ACTIVATION: A MODEL STUDY

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Keywords: Surface tension, CCN, Succinic acid, Sodium chloride

INTRODUCTION

Köhler theory takes into account the surface tension of the droplet (Köhler 1936). Usually the surface tension of multicomponent mixtures is not known and surface tension of pure water is used in cloud models. Clouds are an important factor in the radiative balance of the Earth and that is why proper knowledge of their properties is crucial especially when studying the indirect forcing of aerosol particles (Hegg *et al.* 2007). In this study the influence of surface tension of ternary solution containing sodium chloride, succinic acid and water on cloud droplet activation was examined by using a cloud model (Anttila *et al*. 2002).

METHODS AND RESULTS

Surface tensions of ternary solutions containing sodium chloride, succinic acid and water were previously measured (Vanhanen *et al.* 2007). An equation by Chunxi *et al.* (2000) was fitted to the data. Sodium chloride is an abundant hygroscopic compound in aerosols of marine origin (O´Down *et al.* 1999) and succinic acid is a typical dicarboxylic acid also found in aerosol phase (Legrand *et al.* 2007). In figure 1 the surface tension of the ternary solution is presented as a function of mole fractions of sodium chloride and succinic acid at 25°C. Sodium chloride increases and succinic acid decreases the surface tension of water. Succinic acid can lower surface tension of the solution even though sodium chloride is added. This is because succinic acid as a surface active compound tends to concentrate to the surface.

The model used in this study is a box model that simulates interaction of aerosol particles and water vapour inside an adiabatically rising air parcel (Anttila *et al.* 2002). The model uses a sectional representation to model the aerosol size distribution inside the air parcel. The bimodal aerosol size distribution used in the simulations is shown in table 1. The distribution represents a typical size distribution measured in marine environment (Heintzenberg *et al.* 2000).

Table 1. Modes of the particle size distribution used in the cloud model simulations.

Mode	Geometric mean diameter [nm]	Geometric standard deviation	Number of particles [cm^{-3}]
Aitken	45	1.5	300
Accumulation	170	1.5	200

Cloud model simulations were made using three different updraft velocities; 0.1, 0.5 and 1.0 m/s. In figure 2 the ratio of the number of cloud droplets to the total number of particles is presented as a function of succinic acid mass fraction of the initial aerosol particles. It can be seen that there is a difference in the amount of activated particles between the simulations made using surface tension of pure water and those made using the surface tension parameterization. The difference increases with increasing mass fraction of succinic acid and with increasing updraft velocity. By using the surface tension parameterization more particles are activated at higher mass fractions of succinic acid. When there is very little or no succinic acid in the particles the difference is the opposite. This is because as sodium chloride increases the surface tension of the solution, it hinders the cloud droplet activation. Succinic acid enhances the activation by decreasing the surface tension. The effect of updraft velocity can be explained by larger activation diameter of a particle as the updraft velocity, and thereby the supersaturation, is lower. When a particle is larger it contains more water and is therefore more dilute having surface tension closer to the surface tension of pure water. The ratio of the number of cloud droplets to the total number of particles decreases as the mass fraction of succinic acid increases. This is because succinic acid has lower density than sodium chloride and the critical supersaturation increases with decreasing solute mass.

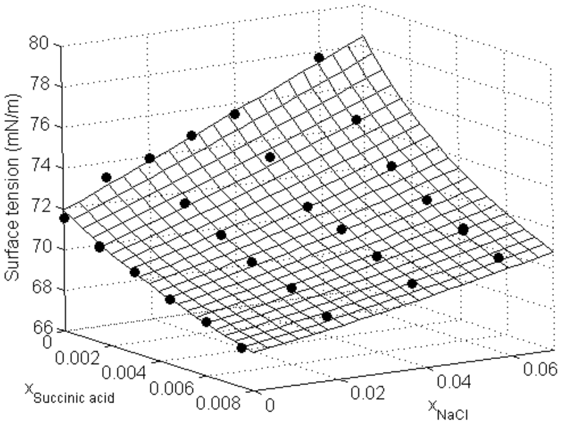

Figure 1. The surface tension of ternary solution of sodium chloride, succinic acid and water at 25°C as a function of mole fractions of the solutes. Dots represent the measurement data and lines are the fit by Vanhanen *et al.* 2007.

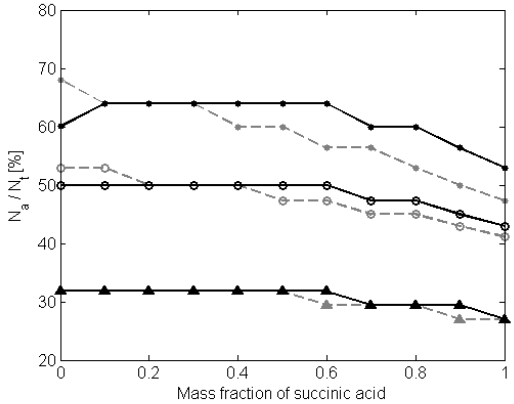

Figure 2. Ratio of activated to total particle concentration as a function of the mass fraction of succinic acid. Updraft velocities 1.0, 0.5 and 0.1 m/s is presented with symbols ●, ○ and ▲ respectively. Solid black lines are simulations made using surface tension of sodium chloride/succinic acid/water mixture and dashed grey are those made with surface tension of pure water.

CONCLUSIONS

There is a clear difference in the number of cloud droplets in model simulations made using surface tension of pure water and those made using the measured surface tension of the ternary mixture. An increase up to 8% in number of cloud droplets was observed by using surface tension of the ternary mixture for particle size distributions containing succinic acid and a decrease up to 8% for particle size distributions containing almost only sodium chloride. This kind of difference in cloud droplet number concentration can perceptibly change the properties of the cloud by increasing the albedo (Hegg *et al.* 2007) and also the lifetime of the cloud.

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SOURCE APPORTIONMENT OF PM10 IN COPENHAGEN URBAN BACKGROUND

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Keywords: Mass closure problem, COPREM, health effects.

INTRODUCTION

PM in urban background is a mixture of many different components originating from various sources, with local and regional variation, affecting its toxicity. Knowledge about which sources of PM are most relevant in determining health effects remains limited. For targeted prevention of PM associated health effects, identification of the most relevant sources is required and data are urgently needed.

METHODS

Particle data were measured by the Danish National Environmental Research Institute (NERI) at the fixed roof (20 m above the ground) urban background monitoring station (HCOE) located in the centre of Copenhagen. Daily (24 h, midnight-to-midnight) mean concentrations were available for PM10, measured by SM200 monitor. Data from HCOE station were not sufficiently comprehensive for a complete source apportionment of PM10. This is due to monitoring networks in Denmark focusing on the local sources at urban sites, and on the long-range sources at the rural site, resulting in inorganic ions being measured only at the rural monitoring station. Thus additional data consisting of daily samples for total suspended particulates (TSP) from a forest rural station (Frederiksborg, 3 m above the ground) 35 km NNW of central Copenhagen were necessary for a source apportionment of PM10. These samples from HCOE and Frederiksborg (03.05.2002-22.12.2003) were analyzed for elements and ions using proton induced x-ray emission (PIXE), ion chromatography, automated colorimatry, and atomic absorption spectrophotometry encompassing the elements Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Sn, Sb and Pb, and ion analyses encompassed Na+, Mg2+, NH4+, Cl-, SO42-, and NO3-. The chemical analysis was performed at Department of Atmospheric Environment at NERI.

We used the constrained physical receptor model (COPREM) to apportion PM10 between different sources. COPREM is a hybrid model unifying Chemical Mass Balance (CMB) modelling and non-negative factor analysis. The details of COPREM software are published previously (Wåhlin, 2003). The initial fixed source profiles included road dust, direct vehicle emissions (exhaust and brake dust), sea salt, converted sea salt ($NaNO_3$), two soil profiles, NH_4NO_3, $(NH_4)HSO4$, and $(NH_4)_2SO_4$. The road dust profile (including dust due to tyre wear) and direct vehicle profile were determined from a study of PM10 road increments at a busy street in Copenhagen (Wåhlin *et al.*, 2006), and the profiles were used under the assumption that the road increments measured in the street are representative for the general traffic emissions in the city background. The soil contributions (beyond what can be explained by the road dust source) were fitted using two representative profiles, one with the composition of igneous rock, the other with the composition of limestone. The COPREM profiles for the ammonium sources were calculated according to the stoichiometric content, while the sea salt source profiles were calculated according to the average composition of sea water. Only about the half of the PM10 could be explained by well-defined initial source profiles in COPREM. Unexplained enriched concentrations of some elements were considered tracers for different combustion sources not accounted for initially. These included biomass combustion (K), fuel oil combustion (V and Ni), and coal combustion/incineration (Zn, Se, and Pb), which represented probably several sources, but without additional measurements of organic compounds it was not possible to make better differentiation. Therefore, in COPREM, elements K, V and Se were chosen as tracers for the ‘Biomass’, ‘Oil’ and ‘Coal’ in the following way: V and Se were not allowed in ‘Biomass’, K and Se were not allowed in ‘Oil’, and K and V were not allowed in ‘Coal’. The PM and the other elements in the ‘Biomass’, ‘Oil’ and ‘Coal’ profiles were allowed to adapt freely to the data in the non-negative range.

RESULTS

Source	PM10 (μgm^{-3})
Road	1.2
Vehicle	0.8
Salt	1.3
Biomass	7.5
Oil	3.6
Coal	0.0
Rock	0.8
Lime	0.5
$NaNO_3$	0.9
NH_4NO_3	3.3
$(NH_4)_2SO_4$	2.6
$(NH_4)HSO_4$	0.9
Sum	23.3
Measured	23.9

Table 1. Result of source apportionment.

CONCLUSION

A large fraction of the measured PM10 in urban background can be explained by well-defined, mostly inorganic, sources. Nevertheless, almost 50% of the mass needs to be explained by other sources. Biomass burning seems to be the most important candidate for this.

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Measurements of heavy metals in particles in Nuuk, West Greenland

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Keywords: Atmosphere, heavy metals, particles, COPREM

INTRODUCTION

The Greenlandic population on the West Coast of Greenland is exposed to heavy metals depending on the fraction of their diet coming from sea animals. Long distance atmospheric transport of air pollution to western Greenland, possibly from Canada or USA and in episodes also from Eurasia, is suspected to be a main cause of the levels of heavy metals in the environment. The pollutants enter the environment and food chain via atmospheric deposition.

METHODS

Lille Malene Station is located at 345 m above sea level and at 64°11' N, and 51.°39' W and thus is a Subarctic station. The station is located at Lille Malene Mountain just outside Nuuk (Godthåb), the capital of Greenland with about 13,500 inhabitants.

Filter pack samples are collected on a weekly basis. The exposed particle filters are analysed for the content of SO_4^{--}, NO_3^-, NH_4^+, and elements from Al and above (with the exception of Hg and Cl) using proton induced x-ray emission (PIXE). The elements are the subject of this presentation.
The concentrations of the elements are analysed by the constrained physical receptor model ((Wahlin, 2003; Heidam, Christensen, Wåhlin et al., 2004; Skov, Wåhlin, Christensen et al., 2006). The results of the COPREM analysis is shown in Table 1.

CONCLUSIONS

The measured values of elements and SO_x were very low and the atmosphere at Nuuk can be considered to be a very pristine with respect to these species. The highest levels of SO_x were found during winter but the seasonal variation is much weaker than at e.g. at Station Nord. Lead had an even weaker seasonal variation. Comparison with historical data showed lower values of Pb than in mid 80's.

COPREM receptor analysis showed that 77% of the inorganic part of the particle mass originated from sea spray, 15% from soil erosion and less than 8% from anthropogenic sources.

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Table 1 The resulting source profiles shown as the source contributions to the average concentrations in ngm^{-3}. The inorganic PM contributions (in ngm^{-3}) are calculated using the PM factors in the right part of the table. The organic PM contributions cannot be estimated using these data.

	Soil	Sea	Combustion	Metal_1	Metal_2	Sum	Measured average	Estimated chemical composition	PM factor
Al	39.29	0.00	0.00	0.00	0.36	39.65	44.36	Al_2O_3	1.89
Si	109.72	0.12	0.00	0.55	6.14	116.53	143.46	SiO_2	2.14
S	0.21	56.04	60.64	0.00	0.00	116.88	119.31	H_2SO_4	3.06
Cl	0.19	1176.91	0.00	0.00	0.00	1177.10	519.43	NaCl	1.65
K	9.98	23.04	0.67	5.02	1.39	40.10	42.89	K_2CO_3	1.77
Ca	15.96	25.03	3.65	4.66	0.00	49.30	51.66	$CaCO_3$	2.50
Ti	2.90	0.00	0.11	0.00	0.03	3.05	3.09	TiO_2	1.67
V	0.11	0.00	0.03	0.00	0.02	0.16	0.17	V_2O_5	1.79
Cr	0.08	0.00	0.01	0.02	0.00	0.11	0.11	Cr_2O_3	1.46
Mn	0.51	0.00	0.07	0.00	0.01	0.60	0.60	MnO_2	1.58
Fe	31.05	0.00	1.49	0.02	0.39	32.94	33.42	Fe_2O_3	1.43
Ni	0.04	0.00	0.04	0.06	0.00	0.14	0.17	NiO	1.27
Cu	0.03	0.00	0.10	0.11	0.02	0.26	0.36	CuO	1.25
Zn	0.03	0.00	0.00	2.71	0.00	2.74	2.62	ZnO	1.24
Ga	0.01	0.00	0.00	0.00	0.00	0.01	0.02	Ga_2O_3	1.34
As	0.00	0.00	0.02	0.00	0.00	0.02	0.02	As_2O_5	1.53
Se	0.00	0.00	0.03	0.00	0.01	0.04	0.05	SeO_2	1.41
Br	0.00	4.05	0.00	0.00	0.00	4.05	0.72	NaBr	1.29
Rb	0.12	0.01	0.00	0.00	0.00	0.13	0.11	Rb_2CO_3	1.35
Sr	0.06	0.50	0.00	0.09	0.05	0.70	0.79	$SrCO_3$	1.69
Zr	0.10	0.00	0.00	0.00	0.00	0.10	0.10	ZrO_2	1.35
Pb	0.01	0.00	0.00	0.00	0.49	0.49	0.48	PbO_2	1.15
PM	418.29	2221.13	198.50	25.50	17.61	2881.03			

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PARTICLE FORMATION FROM GAS COOKERS

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Keywords: PARTICLES, AEROSOLS, GAS COOKERS, GAS BURNER

INTRODUCTION

A recent hypothesis on the associations between illness and nitrogen dioxide found in epidemiological studies (Seaton et al, 2003) is that it may be the consequence of confounding by particle numbers. According to Bang et al (2004), like many other phenomena in nature, the presence of carbon nano-tubes in blue combustion flames went virtually unrecognized because it was essentially unexpected.

When particles are measured as mass, the greatest contribution comes from the largest particles, but the greatest number of particles by far is the submicron ones. These ultrafine particles are generated, as is nitrogen oxides (Seaton et al, 2003; Dennekamp et al, 2001), by the combustion process, and therefore the two pollutants are likely to correlate closely. Bang et al (2004) and Murr et al (2004) reported aggregated multi-wall carbon nano-tubes with diameters ranging from 3 to 30 nm and related carbon nano-crystal forms ranging in size from 0.4 to 2μm (average diameter) in the combustion streams for methane/air, natural gas/air, and propane gas/air flames from domestic (kitchen) stoves. These observations suggests that the proliferation of so-called clean- burning gaseous fuel sources, particularly methane-series gases ($C_nH_{2(n+1)}$); n=1,2,3…etc) may, in fact, make a significant contribution of carbon nano-crystal forms to both the indoor and outdoor air environment. In this PhD study, the objective is to provide new results on particle generation from gas cookers together with their size distribution, nature and origin.

METHODS

The burner is installed in a compartment which is supplied with particle free air at its bottom; keeping the partial premixed flame structure of the burner unchanged. The compartment functions as a steady state reactor with no mechanical mixing. Natural gas from the city line is used as the fuel supply. Experiments are repeated with methane to observe the differences; as well as addition of minor amounts of hydrogen sulphide and acetylene to methane. Namely studied concentrations of hydrogen sulphide are <100ppm in the fuel and acetylene <1000 ppm. Excess air ratio is kept above 10. Particle concentrations, size distributions, gas concentrations (CO, CO_2, O_2, NO, NO_x) and temperatures are measured at the reactor outlet. Particle samples are collected using a gas ejector probe developed for particle analysis in a research program instigated to study fine particles (Johannessen et al, 2000). Particles are classified using a TSI Model 3080 Electrostatic

Classifier with a TSI Model 3081 LDMA (Long Differential Mobility Analyzer), and/or a TSI Model 3085 NDMA (Nano Differential Mobility Analyzer). Particle concentrations are measured with a TSI Model 3775 Condensation Particle Counter (CPC). Electron microscopy methods (SEM and TEM, coupled with EDA, EDX) are addressed to identify the nature of particles. A thermophoretic sampler is developed to collect the TEM samples. Chemical kinetic modelling will be addressed together with experimental measurements to determine the origin of the particles.

CONCLUSIONS

The present findings of this study concerning the particle concentrations and size distributions are partly in agreement with the ranges reported by Dennekamp et al (2001) in that UFP concentrations rise to ~10^5 UFP/cm^3; and with Bang et al (2004) and Murr et al (2004) that the average diameters of these particles are 3-30 nm. The size ranges detected in this study is 2-15 nm. Natural gas resulted in an order of magnitude higher particle concentration than methane. Addition of hydrogen sulphide to methane resulted in an increase in particle concentrations to the levels achieved from natural gas combustion. Acetylene addition did not create an effect in the concentrations studied, but an effect is expected if added in higher amounts.

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SORGA (SECONDARY ORGANIC AEROSOLS IN THE URBAN ENVIROMENT) - MODELLING AND MEASUREMENTS OF CARBONACEOUS AEROSOLS AT A RURAL AND AN URBAN SITE IN NORWAY

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Keywords: CARBONACEOUS AEROSOLS, LEVOGLUCOSAN, SUGARS, ^{14}C-ANALYSIS, ORGANIC CARBON

INTRODUCTION

The environmental relevance of the carbonaceous aerosol comprises a number of important topics, such as human health, direct and indirect climate forcing, and air-quality. In the future, carbonaceous material is likely to constitute an increasingly important fraction of the ambient aerosol, following from climatic changes. An increased frequency of forest fires (by drought/heat), changes in biogenic emissions of precursor gases and aerosols (controlled by temperature, radiation and snow cover), decreased deposition (less precipitation), increased radiation (less clouds) speeding up the photolysis rates and the photochemical formation, and enhanced photochemical formation due to higher temperatures, are mechanisms which all could increase the non-anthropogenic contribution of particulate carbonaceous material. Thus, it is ever more important to allocate the sources of the carbonaceous material.

In the ongoing project SORGA (Secondary Organic Aerosols in Urban Areas), we will quantify the non-anthropogenic sources of organic matter (OM) in both rural and urban areas, which is particularly important in order to sort out the policy of controlling man-made emissions. We attempt to reach this goal through chemical and dispersion modeling and with chemical analysis, involving ^{14}C-analysis and source specific organic tracers. There will be a particular focus on Biogenic Secondary Organic Aerosols (BSOA), formed by oxidation of volatile organic compounds (VOCs) emitted from the vegetation.

Here we present some preliminary results from the measurements performed, focusing on the organic speciation, whereas we will present and discuss results obtained by ^{14}C-analysis and modeling at the conference.

METHODS

Two measurement campaigns were conducted for a summer period (19 June - 5 July 2006) and a winter period (1 - 8 March 2007) at a rural background site (60°22N, 11°04E) and an urban background site (59°93N, 10°74E) in Norway.

Aerosol filter samples (PM_{10}, $PM_{2.5}$, PM_1) subjected to TOA (EC, OC, TC) and HPLC/HRMS (polyols) analysis were collected according to the QBQ approach (Quartz-fibre filter behind Quartz-fibre filter) (McDow and Huntzicker, 1990), with a 12-hour time resolution (night time and day time samples). Aerosol filter samples (PM_{10} and PM_1) subjected to ^{14}C-analysis were collected on single filters, with a sampling time of 1 week. The samples were separated into night time samples and day time samples. All aerosol filter samples were collected on pre baked (850 °C, 3.5 h) Quartz fibre filters (Whatman, QM-A, 47 mm). Day time (12 h) and night time (12 h) samples of selected terpenes and aromatic compounds (BTEX) (VOCs), were collected actively using a Tenax sorbent. In addition, one 12 hour daytime VOC sample were collected each week for a one year period (1 July 2006 - 1 July 2007). Concurrent measurements of NO_2, NO, NO_x and O_3 was performed using monitors.

The following meteorological parameters were monitored; temperature at 2 and 10 meters, wind speed, -direction, and gust, turbulence, net-radiation and relative humidity.

Two Eulerian models have been used: the urban-scale model EPISODE, and the EMEP model. The EPISODE model, used for dispersion calculations, is a combined Eulerian and Gaussian model designed for air quality assessment in urban areas (Slørdal et al., 2003). The EMEP model (Simpson et al., 2003) covers Europe with a resolution of 50x50km^2. In the SORGA project a SOA two-product model with the terpene classes, stoichiometric and partition coefficients proposed by Chung and Seinfeld (2002) has been used.

RESULTS

Particulate carbonaceous matter (PCM) was a major contributor to PM regardless of season, site and size fraction, accounting for more than 50% of PM_1 at the urban background site when corrected for the positive sampling artefact. As the QBQ-approach don't account for the negative artefact, this is even a conservative estimate.

The levels of source specific organic compounds varied substantially between the two sites; e.g. levoglucosan (tracer for biomass burning) concentrations were 2-3 times higher at the urban background site compared to the rural background site during winter and 3.5-4.5 times higher in summer. The mean concentration of levoglucosan increased by more than a factor of three at the urban background site when going from summer to winter, whereas at the rural background site the increase was even more pronounced (more than a factor of five). By assuming a levoglucosan-to-OC_{wood} ratio of 0.1, it was estimated that 25-30% of OC in PM_{10} could be attributed to wood burning during the wintertime sampling period at the two sites. The corresponding percentage for the summer period was only 3-7%.

A pronounced diurnal variation was observed for selected sugars and sugar-alcohols in the PM_{10} fraction (Figure 1). Sucrose was found to be increased during daytime sampling and could be attributed to daytime release of e.g. pollen and fern spores. Arabitol, mannitol, and trehalose were increased during the night, which could be attributed to the nighttime release of fungal spores. On average, nighttime concentrations of arabitol, mannitol, and trehalose were two times higher than those reported for daytime sampling. By adapting the assumptions made by Elbert et al. (2006), ambient aerosol concentrations of mannitol was used to estimate the relative contribution of fungal spores to PM. At the rural background site, fungal spores were found to account for 9% of the PM_{10-1} fraction during the day and 17% during the night.

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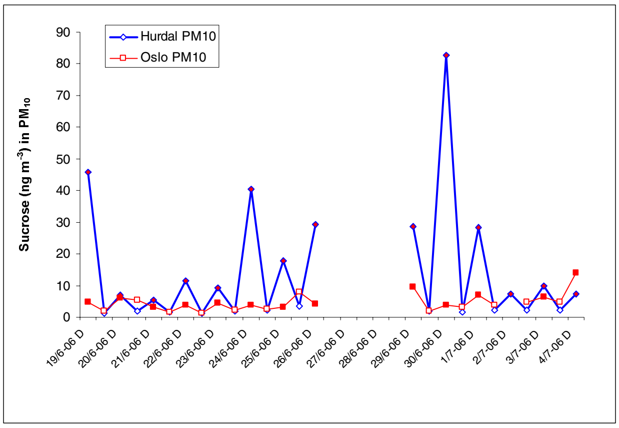

Figure 1: Diurnal variation of sucrose at the rural and the urban background site

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CARBONACEOUS AEOROSOLS IN THE NORWEGIAN ENVIROMENT

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Keywords: CARBONACEOUS AEROSOLS, ORGANIC TRACERS, NORWAY, HPLC/HRMS-TOF, ^{14}C-ANALYSIS

INTRODUCTION

The environmental relevance of the carbonaceous aerosol comprises a number of important topics, such as human health, direct and indirect climate forcing, and air-quality. In the future, carbonaceous material is likely to constitute an increasingly important fraction of the ambient aerosol, following from climatic changes. An increased frequency of forest fires (by drought/heat), changes in biogenic emissions of precursor gases and aerosols (controlled by temperature, radiation and snow cover), decreased deposition (less precipitation), increased radiation (less clouds) speeding up the photolysis rates and the photochemical formation, and enhanced photochemical formation due to higher temperatures, are mechanisms which all could increase the non-anthropogenic contribution of particulate carbonaceous material. Thus, it is ever more important to allocate the sources of the carbonaceous material.

There are only a few studies addressing carbonaceous aerosols in the Norwegian environment. Such studies have focused on bulk measurements of carbon in the ambient aerosol, speciation of the carbonaceous fraction on the molecular level, development of novel analytical methods for source specific organic molecules (tracers), and recently there has been an initiative to start modelling of carbonaceous aerosols in the urban environment, including the SOA fraction.

RESULTS

Analysis of EC/OC/TC using TOA

Bulk measurements of EC and OC using thermal-optical analysis (TOA) have shown that carbonaceous matter is a major fraction of the ambient aerosol both in rural and urban areas in Norway. At the rural background site Birkenes, measurements of EC and OC in PM_{10} and $PM_{2.5}$ have been conducted since 2001. The variation in the annual mean concentration of OC and TC at this site clearly follows that of PM_{10}, $PM_{2.5}$ and SIA (secondary inorganic aerosols). For the period 2001-2006 particulate carbonaceous matter (PCM = OC x 1.7 + EC x 1.1) is found to constitute 28±3% of PM_{10} and 36±6% of $PM_{2.5}$. Interestingly, the concentration of OC in $PM_{10-2.5}$ has increased stepwise year by year since the measurements started in 2001 and until 2006, and currently (2006) account for 20% of $PM_{10-2.5}$.

In urban areas, measurements of EC and OC have only been performed on a campaign basis and mainly in wintertime due to the higher aerosol loading experienced during this season (residential heating, resuspended road dust, unfavorable dispersion). The results reported from these studies show that PCM-to-PM range between 46-83% for PM_{10}, $PM_{2.5}$ and PM_1. Most of the studies conducted in the urban environment have used tandem filter set ups (QBQ and QBT) to account for the positive sampling artifact of OC. The magnitude of the positive artifact has been reported to range between 9-42% (Yttri et al., submitted). In rural background areas, the positive artifact is even more pronounced (>50%), underlining the importance of addressing this issue.

Speciation of the carbonaceous fraction

It is estimated that approximately 70% of the annual PM_{10} emissions in Norway could be attributed to residential wood burning, which is substantial for a source expected to be active in winter only. Thus, emission from residential wood burning is likely to be the major contributor of carbonaceous matter in the urban environment in winter. This has been underlined by high concentrations (~1 µg m^{-3}) of the source specific organic tracer levoglucosan reported for major Norwegian cities (e.g. Oslo) as well as in minor towns and villages (e.g. Elverum) (Yttri et al., 2005). Indeed, levoglucosan measurements have improved our understanding of the magnitude of PM emissions from residential wood burning and in particular the temporal and spatial resolution of such emissions.

While most studies argue for the importance of the secondary biogenic organic aerosols, less emphasis has been put on the primary biogenic aerosol; i.e. the primary biological aerosol particles (PBAP). In a recent study by Yttri et al. (2007a), it was shown that coarse ($PM_{10-2.5}$) OC occasionally might account for the majority of OC in PM_{10} during summer, even on a monthly basis, at the rural background site Birkenes. Further, coarse OC was found to have a seasonal variation closely resembling the vegetative season; coarse OC was almost absent when snow was covering the ground (November-April), and its concentration started to increase soon after the snow had melted in April. The highest concentration was observed from July-October. Coarse OC has typically been associated with PBAP (Matthias-Maser, 1998). At Birkenes, it has been shown that the aerosol content of sugars and sugar alcohols, which are tracers for certain PBAP (Graham *et al.*, 2003), has the same seasonal variation as coarse OC (Yttri *et al.*, 2007b), which corroborates the fact that the coarse OC at this site could be attributed to PBAP.

Effort has been made to develop novel HPLC/HRMS-TOF methods for quantitative measurements of the ambient aerosols content of source specific polar organic tracers, such as levoglucosan (Dye and Yttri, 2005) and sugars and sugar-alcohols (Yttri et al., 2007). Using LC/MS technique, several advantages is expected compared to the current GC-methodology applied. The first and most obvious advantage is that aqueous solutions can be injected onto a wide range of different columns without causing damage. This includes a wide range of polar solvents such as acetonitrile, methanol, tetrahydrofuran and 2-propanol. Secondly, it is expected to be less labour and less time consuming, as the sample preparation is less extensive because derivatization can be omitted. Thirdly, using HPLC/HRMS will extend the diversity of analytical methods available for determination of polar organic compounds. It should be emphasized that LC/MS methodology is complementary to the frequently used GC/MS methods, implying that there is a potential to extend the knowledge of the organic aerosol composition.

Currently, we attempt to combine the effort of ^{14}C-analysis and HPLC/HRMS-TOF analysis of source specific organic compounds to separate the anthropogenic and the biogenic sources of organic carbon. Such measurement will be highly useful for model validation.

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Evaporation of inorganic/organic aqueous solution droplets

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Biogenic sources as well as human activities contribute large amounts of volatile organic compounds to the atmosphere.

Upon oxidation, polyfunctional molecules such as dicarboxylic acids are formed. These molecules generally have lower vapor pressures than the parent molecules and are able to condense on existing particles or maybe even participate in formation of new particles in the atmosphere. Current knowledge about the thermodynamic properties governing this partitioning as well as the influence of the organic molecules on properties of aqueous solution droplets is poor. We have therefore developed a new method based on the HTDMA technique (Hygroscopicity Tandem differential Mobility Analyzer) for determining the subcooled liquid state vapor pressure as well as other thermodynamic properties of secondary organic aerosol components.

We have recently measured evaporation rates of aqueous solution droplets containing one dicarboxylic acid (C3 to C5) and water [1-2-3]. In this work we expand our studies to more complicated systems as dicarboxylic acid together with inorganic salts.

The first results from these studies will be presented.

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