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Organic compounds in atmospheric aerosols from a Finnish coniferous forest

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Atmospheric aerosol particles were collected with a high-volume sampler in a Finnish coniferous forest during the field campaign Quantification of Aerosol Nucleation in the European Boundary Layer (QUEST) in March–April 2003. Four chromatographic techniques were applied to characterise the organic composition of the samples, and to study variations in the concentrations of identified compounds. Among the nearly 160 organic compounds identified were *n*-alkanes, *n*-alkanals, *n*-alkan-2-ones, *n*-alkanols, *n*-alkanoic acids, *n*-alkenoic acids, dicarboxylic acids, polyaromatic hydrocarbons, hopanes, streranes, terpenes and terpenoids. The observed variations in the concentrations of certain compounds were mostly explained by ambient temperature. Comparison of days when atmospheric new particle formation took place with days when the formation did not occur, however, revealed higher concentrations of long-chain *n*-alkanes ($> C_{22}$) and $< C_{18}$ *n*-alkanoic acids on the particle formation days.

Introduction

The formation of secondary aerosol particles in the forest atmosphere is of considerable interest now that it is clear that atmospheric new particle formation plays an important role in determining the global aerosol load (Kulmala *et al.* 2004). It has been suggested that formation and growth of aerosol particles over forests are driven by condensable organic vapours emitted by the vegetation (O'Dowd *et al.* 2002). Data on the chemical content of aerosol particles produced over forested areas are scarce, however, and the compounds that drive the formation are unknown.

Atmospheric aerosol particles comprise a complex mixture of inorganic and organic compounds. Depending on the site and the degree of pollution, organic compounds may represent up to 70% of the total dry fine particle mass in the lower troposphere, and the number of organic compounds in aerosol particles may be several hundreds (Jacobson *et al.* 2000, Turpin *et al.* 2000, Alves *et al.* 2001, Kubátová *et al.* 2002). The compositional complexity of atmospheric aerosols requires several analytical techniques to be used if comprehensive information is to be obtained about their chemical composition and formation processes. Although numerous analytical techniques are available for the analysis

of bulk aerosol samples, and many of them provide selectivity and high resolution, there is still a great need for novel techniques.

Gas-chromatography mass-spectrometry (GC-MS) is still the most widely applied technique to the determination of organic aerosol composition. Straightforward on-line coupling of GC with MS makes the identification of compounds relatively easy because of the large amount of library reference spectra available. GC-MS is especially useful for the screening and quantification of non-polar and relatively volatile compounds and enables fast analysis of large sample series. A drawback in the case of highly polar and non-volatile compounds is the requirement for chemical derivatisation before analysis. The derivatisation tends to be time-consuming and may reduce the repeatability of the analysis. Additionally, residues of the derivatisation reagents in the sample may interfere with the analysis and complicate the identification of unknown compounds.

Recently, liquid chromatography coupled with mass spectrometry (LC-MS) has gained interest in the determination of polar compounds in aerosol particles (Glasius *et al*. 1999, Winterhalter *et al*. 2003). Electrospray ionisation (ESI) in negative ionisation mode enables a selective and efficient ionisation of anionic compounds such as organic acids. The combination of LC-ESI ion-trap-MS (ITMS) for structural characterisation and LC-ESI time-of-flight-MS (TOFMS) for accurate mass measurement provides a powerful tool for the identification of unknown compounds in complex sample matrices.

Multidimensional chromatographic techniques, involving the combination of two or more chromatographic techniques, offer attractive alternatives for aerosol analysis. These techniques provide the high peak capacity essential for the analysis of complex mixtures with numerous components. Limits of determination of the final analysis are usually improved as well. The reliability of the analytical method can be further improved by combining the sample pretreatment with the final separation and detection in a closed system to minimise risk of analyte loss and contamination from external sources.

In this study, aerosol particles were collected in a Finnish Scots pine forest during the field campaign Quantification of Aerosol Nucleation in the European Boundary Layer (QUEST) carried out in March–April 2003. We applied GC-MS and LC-MS to determine the organic aerosol composition and to study variations in the concentrations of the identified compounds. The compositions of samples collected during atmospheric new particle formation events (referred to as event days) and on days when formation did not occur (referred to as non-event days) were compared. Additionally, we tested the suitability for aerosol analysis of two novel multidimensional chromatographic techniques: on-line coupled supercritical-fluid-extraction liquid-chromatography gas-chromatography mass-spectrometry (SFE-LC-GC-MS) and comprehensive two-dimensional gas chromatography (GC×GC).

Experimental

Sampling and sample preparation

Sampling was carried out at the Station for Measuring Forest Ecosystem–Atmosphere Relations (SMEAR II) at Hyytiälä in southern Finland (61°51´N, 24°17´E, 180 m above sea level) during the period 16 March–10 April 2003. The stand at the site consists mostly of Scots pine (*Pinus sylvestris*) together with some Norway spruce (*Picea abies*) and deciduous trees. The submicron aerosol number size distribution, the meteorological data and the concentrations of inorganic gases (H_2O, CO_2, NO_x, SO_2 and O_3) were continuously monitored at various heights. For a more detailed description of the SMEAR II station, *see* Kulmala *et al*. (2001).

Total aerosol samples were collected with a high-volume sampler fitted with 240-mm quartz filters (Munktell, Grycksbo, Sweden). High-volume sampling was necessary to collect enough material for detailed organic speciation. A flow rate of 80–90 $m^3\ h^{-1}$ was applied and samples were collected continuously in periods of 2, 4, 12, 24 or 48 hours. The main focus was on samples collected in 2-hour and 4-hour sampling periods in the morning and afternoon (08:00–16:00 EET), during the initial stages of the new aerosol particle formation. Before sampling the quartz fiber filters were annealed at 880 °C for 5 h to remove any organic impurities, and packed in

clean aluminium foil until sampling. After sampling, each filter was stored in a clean glass jar in a freezer at –25 °C. No special devices were used for removal of gaseous oxidants or other gas phase compounds or for post-filter collection of particulate components volatilised during the sampling, because of the difficulty in applying such devices in high-volume sampling.

A dynamic sonication-assisted solvent extraction system was developed and used as an off-line sample preparation technique for GC-MS, LC-MS and GC×GC analysis. For GC-MS and GC×GC analysis, a part of the filter (6.25 cm^2) was sonicated in *n*-hexane–acetone mixture (1:1 v/v) for 40 min with a flow rate of 0.5 ml min^{-1}, and the extract was concentrated to 500 μl under a gentle stream of nitrogen. For LC-MS analysis and for GC-MS analysis of more polar compounds, the extraction was carried out in methanol. For LC-MS analysis, the methanol extract was concentrated to 200 μl. For GC-MS analysis, the extract was evaporated to near dryness and then dissolved in 100 μl dichloromethane. No manual sample pretreatment was required for SFE-LC-GC-MS analysis.

Instrumentation and analysis

Gas-chromatography mass-spectrometry

GC-MS was applied to the determination of relatively volatile and non-polar compounds. The GC-MS instrument consisted of an Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with an on-column injector and Agilent 5973 mass selective detector. The GC column was an HP5-MS capillary column (15 m × 0.18 mm inner diameter (i.d.), film thickness 0.18 μm) which was preceded by diphenyltetramethyldisilazane-deactivated retention gap (3 m × 0.53 mm i.d.). The GC oven was temperature programmed as follows: 60 °C for 5 min, then the temperature was raised by 25 °C per min to 300 °C, and it was kept at 300 °C for 5 min. Electron ionisation (EI) was applied at 70 eV, and mass spectra were recorded in the m/z 50–550 range. Agilent Enhanced ChemStation D.00.01.27 software was used for the data analysis. The compounds were identified by their retention times and comparison of their mass spectra with spectra of the NIST mass spectral library (ver. 2.0a). Quantification was performed with use of a five-point calibration based on mass chromatograms and relative peak areas of the characteristic ions.

For the identification of more polar compounds, GC-MS analysis of the samples was performed using splitless injection and a fused silica capillary column with a bonded cyano stationary phase (tailor-made CP-Select CB for FAME, 20 m × 0.25 mm i.d., film thickness 0.25 μm; Varian, Middelburg, The Netherlands). The temperature program was as follows: 60 °C for 6 min, then the temperature was raised by 10 °C per min to 275 °C, and then it was kept at 275 °C for 10 min.

Liquid-chromatography mass-spectrometry

For the determination of organic acids, the samples were analysed with a Hewlett-Packard 1100 HPLC system (Agilent Technologies, Palo Alto, CA, USA) coupled with an Esquire-LC ITMS (Bruker Daltonics, Bremen, Germany). An electrospray ionisation (ESI) interface was used in negative ionisation mode. The HPLC instrument was equipped with an Atlantis C_{18} column (150 mm × 2.1 mm i.d.) packed with 3 μm particles (Waters, Milford, MA, USA). Gradient elution with 17.5 mM acetic acid (pH 3.5) in ultrapure water and methanol (B) was applied. The gradient was programmed as follows: 2 min: B 0%, 25 min: B 40%, 40 min: B 60% and 50 min: B 100%. The scanned mass range was m/z 100–700. Quantification was done with use of a five-point calibration based on mass chromatograms and relative peak areas of the deprotonated molecules $[M–H]^-$.

A MicroTOF-LC TOFMS (Bruker Daltonics, Bremen, Germany) was used to determine the accurate molecular masses of the unknown compounds. The HPLC method was identical with the one used in LC-ESI-ITMS. At the beginning of the analysis, sodium formate solution was added post column to allow internal mass calibration. On the basis of the accurate masses, the (probable) elemental composition of the compounds of interest was calculated

using the molecular formula tool included in the Bruker Daltonics DataAnalysis 3.2 software. For detailed descriptions of the LC-MS methods, *see* Anttila *et al*. (2005).

Supercritical-fluid-extraction liquid-chromatography gas-chromatography mass-spectrometry

The SFE-LC-GC-MS system was constructed in the laboratory (Shimmo *et al*. 2002). The system is suitable for the determination of relatively volatile and non-polar compounds. Carbon dioxide was the extraction fluid in SFE. The extracts were trapped in a solid-phase trap packed with octadecylsilane particles and eluted with *n*-pentane–ethyl acetate mixture (95:5 v/v) to the LC column. The LC column, 150 mm × 2.1 mm i.d. LUNA silica column packed with 5 μm particles (Phenomex, Torrance, CA, USA), was coupled on-line with the gas chromatograph (HEGC5300, Instrumentation, Milano, Italy) with an on-column interface. Partially concurrent solvent evaporation technique with use of a solvent vapour exit was preferred to eluent evaporation through the analytical column because a much larger sample fraction could then be transferred to the gas chromatograph.

The GC pre-column consisted of a 10 m × 0.53 mm i.d. deactivated fused silica column that was connected to a 3 m × 0.32 mm i.d. retaining precolumn (HP-5, 0.25 μm film thickness) and further to the solvent vapour exit and the analytical column (HP-5, 20 m × 0.25 mm i.d., 0.25 μm film thickness). The following temperature program was used: 80 °C for 1 min, then the temperature was raised by 15 °C per min to 150 °C, then it was raised by 5 °C per min to 200 °C, then it was raised by 10 °C per min to 300 °C, and then it was kept at 300 °C for 30 min. A quadrupole (Automass Solo, Thermoquest, Argenteuil Cedex, France) was used as for mass analysis. Electron ionisation was performed at 70 eV, and mass spectra were recorded in the m/z 50–550 range. The organic acids were derivatised *in situ* with 2,3,4,5,6-pentafluorobenzylbromide (PFBBr) in static SFE, and the derivatised acids were extracted in dynamic SFE. The EI voltage was lowered to 20 eV to maximize the intensity of the molecular ion signal of the derivatised acids. For a detailed description of the analytical procedure, *see* Shimmo *et al*. (2002) and Shimmo *et al*. (2004b).

Comprehensive two-dimensional gas chromatography

The GC×GC system was built into an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA). A non-polar first column (ZB-5, 20 m × 0.25 mm i.d., film thickness 0.25 μm; Phenomenex, Torrance, CA, USA) was connected to a semi-polar second column (BGB-1701, 0.7 m × 0.1 mm i.d., film thickness 0.10 μm; BGB-Analytik, Zürich, Switzerland), and between the columns there was a modified version of the laboratory-built semi-rotating cryogenic modulator (Kallio *et al*. 2003). Samples were injected in splitless mode, and a flame ionisation detector (Agilent Technologies, Palo Alto, CA, USA) was used.

Results and discussion

About 60 atmospheric aerosol samples were collected in a Finnish coniferous forest during the field campaign Quantification of Aerosol Nucleation in the European Boundary Layer (QUEST) in March–April 2003. Four chromatographic techniques, GC-MS, LC-MS, SFE-LC-GC-MS and GC×GC, were applied to characterisation of the organic composition of the samples. After discussing the applicability and performance of the techniques, we present the results with a separate discussion for each compound group.

Instrumental techniques

GC-MS was applied to the identification and quantification of relatively non-polar compounds in the aerosol samples. The target compounds were even numbered *n*-alkanes (C_{10}–C_{28}), polyaromatic hydrocarbons (PAH), oxygen-containing polyaromatic hydrocarbons (oxy-PAH), sesquiterpenes copaene and longifolene, and an oxidised monoterpene, verbenone. Additionally,

odd numbered *n*-alkanes (C_{11}–C_{31}) were quantified for several samples. The external calibration curves of the target compounds were linear (R^2 = 0.949–1.000) from the limits of detection to 2.5 μg ml^{-1}. The limits of detection (LOD) were at the level of 0.01–0.05 μg ml^{-1}, depending on the compound. The limits of quantification were set to 3 × LOD. The relative standard deviation (RSD) of the total analysis (incl. extraction) calculated from the peak areas of 12 PAH compounds was on average 18% (n = 3). In addition to the target compounds, a variety of other compounds were identified by comparison of their mass spectra with spectra of the NIST library.

LC-ESI-ITMS and LC-ESI-TOFMS were applied to the screening and identification of organic acids and for the quantification of two abundant monoterpene oxidation products, pinonic acid and pinic acid. Since internal mass calibration was used with LC-ESI-TOFMS, the molecular masses of several compounds could be determined within an accuracy of 5 ppm, which is a commonly accepted level for verification of the elemental composition. The external calibration curves for pinonic acid and pinic acid were linear (R^2 = 0.995 and R^2 = 0.994, respectively). The detection limit for pinonic acid was 0.03 μg ml^{-1}, and that for pinic acid 0.04 μg ml^{-1}. The RSD of the total analysis was 20%, calculated as an average of the peak areas of ten carboxylic acids (n = 3).

Two multidimensional chromatographic techniques, on-line coupled SFE-LC-GC-MS and GC×GC, were also applied to determine organic compounds in the samples. In SFE-LC-GC-MS, after extraction of the sample, normal-phase LC was used to separate the extract into three fractions based on the polarity of the analytes. The LC-GC interface with partially concurrent solvent evaporation allowed the large-volume injection needed to concentrate the fractions, and GC-MS was employed for the final separation, identification and quantification of the analytes. The first fraction contained aliphatic hydrocarbons such as *n*-alkanes, hopanes and steranes. The second fraction contained mainly PAH compounds, while the third fraction consisted of more polar compounds such as oxygenated PAH compounds, *n*-alkanals, *n*-alkan-2-ones and terpenoids.

SFE-LC-GC-MS enabled analysis of the aerosol samples in a closed system without manual sample pretreatment. The most significant advantage of the system was that because of the efficient fractionation by LC, the GC chromatograms consisted of fewer compounds than in conventional GC-MS. Therefore, the mass spectra were relatively clean, which made the identification more straightforward. The drawback of our prototype SFE-LC-GC-MS system was the long analysis time needed for large sample series. Thus, the system was mainly used for identification of compounds in selected samples, and these results could then be utilised in the identification and quantification with the simple GC-MS system.

Comprehensive two-dimensional gas chromatography (GC×GC) with high resolution was applied to characterise the entire complex aerosol samples. The technique allows an efficient two-dimensional separation, in which the analytes are separated in the first dimension mainly according to their volatility and in the second dimension according to their polarity. In addition to enhanced separation efficiency also sensitivity is improved due to the concentrative modulation. Typically, the modulation is based on cold-trapping with liquid CO_2 or N_2. As result, very sharp peaks are obtained with substantially increased peak heights. A further feature of the GC×GC technique is that an ordered structure can often be seen in the chromatograms, which simplifies the identification. Screening of the aerosol samples by GC×GC made it easy to observe, in the two-dimensional chromatogram, the large number of compounds and their wide volatility–polarity range. Even a part of a two-dimensional GC×GC plot shows that there are many compounds in the sample that would overlap in one-dimensional separation (Fig. 1).

Qualitative and quantitative analysis

n-Alkanes

The most abundant compounds identified in the samples were *n*-alkanes (C_{11}–C_{42}). The concentrations of the quantified even *n*-alkanes (C_{12}–C_{28}) varied between 0.13 and 14 ng m^{-3} for individual compounds, while the total concentration ranged from 1.7 to 55 ng m^{-3}, except for the morning

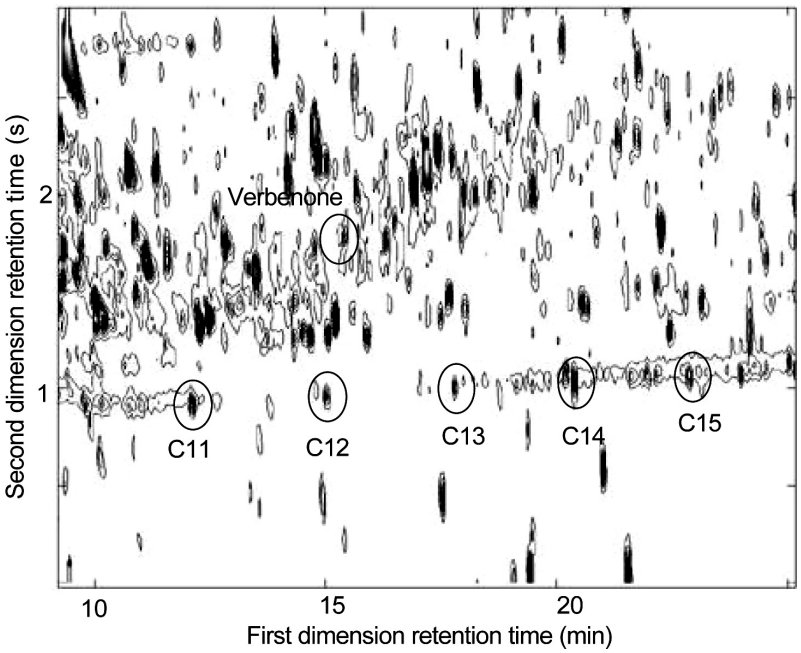

Fig. 1. Part of the GC×GC contour plot of an aerosol sample collected at Hyytiälä, Finland, on 10 April, 2003. In the first dimension, the compounds are separated mainly according to their volatility (decreasing to the right) and in the second dimension according to their polarity (increasing upwards). The intensity of the dots increases with the concentration of the compounds. *n*-Alkanes (C_{11}–C_{15}) and verbenone are marked on the plot.

sample (08:00–12:00 EET) of 7 April when the concentrations of long-chain *n*-alkanes (> C_{22}) were exceptionally high (Fig. 2). The concentrations of *n*-alkanes in the 24-hour samples were 10 to 100 times lower than in the 24-hour samples collected in the city of Helsinki with the same sampler in July 2002 (Shimmo *et al.* 2004a). The present concentrations agree reasonably well with the data obtained from other rural areas (Azevedo *et al.* 2002, Fraser *et al.* 2002). Concentrations were clearly higher in the 2-hour and 4-hour samples, however, indicating a strong influence of the duration of the sampling on the results (*see* 'Concentration variations' below).

For most of the samples, the maximum concentration (C_{max}) of *n*-alkanes was observed at C_{27} or C_{29}. The *n*-alkane distribution in forest environment typically shows C_{max} at C_{27}, C_{29} or C_{31} attributable to natural plant wax (Abas and Simoneit 1996). Other sources of *n*-alkanes include e.g. vehicle emissions (Rogge *et al.* 1993a), wood combustion (Rogge *et al.* 1998) and road dust (Rogge *et al.* 1993b). The carbon preference index (CPI), which is defined as the sum of the concentrations of the odd carbon number *n*-alkanes divided by the sum of the concentrations of the even carbon number *n*-alkanes, can be used as an indicator of the biogenic and anthropogenic contributions of *n*-alkanes (Simoneit 1986). The CPI typically ranges from 1.1 to 2.0 in urban environments, while a CPI above 2.0 is typical of rural environments, where the biogenic influence is more significant. The CPI values in our study ranged from 0.9 to 1.9, which are low values for forest environment. This may be partially due to the weak emission of plant waxes at the low temperatures (–10 °C to +10 °C) prevailing during the sampling.

Straight-chain carbonyls and carboxylic acids

The homologue series of carbonyl compounds and carboxylic acids identified in the samples were *n*-alkanals (C_{24}–C_{32}), *n*-alkan-2-ones (C_{19}–C_{31}), *n*-alkanoic acids (C_6–C_{30}), *n*-alkenoic acids ($C_{10:1}$–$C_{18:1}$) and aliphatic dicarboxylic acids (C_9–C_{14}). Additionally, we identified two *n*-alkanols (C_{16} and C_{18}) and one diunsaturated monocarboxylic acid, linolic acid ($C_{18:2}$). The identification of *n*-alkanals and *n*-alkan-2-ones was based on the mass chromatograms at m/z 82 and m/z 59, respectively, and comparison of their GC retention times with those of *n*-alkanes (Abas and Simoneit 1996). The carboxylic acids

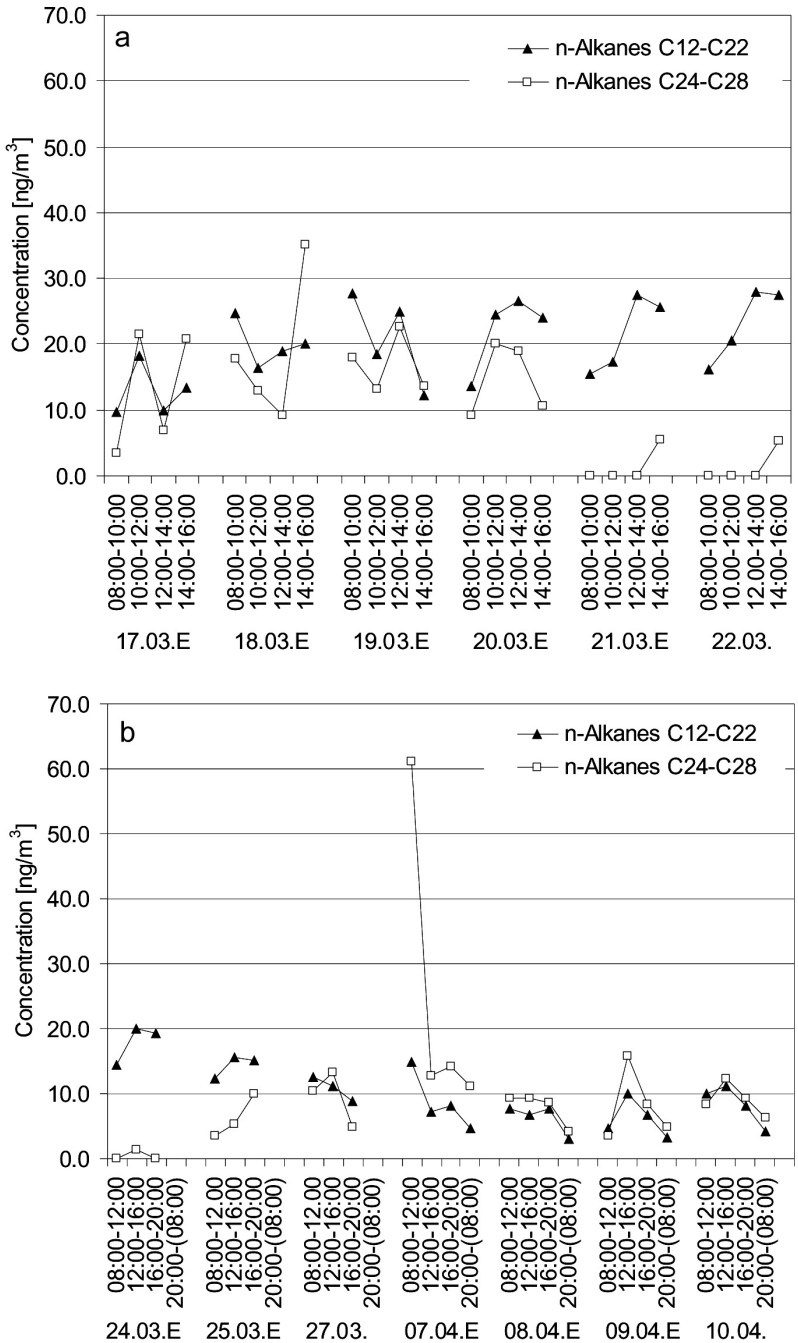

Fig. 2. *n*-Alkane concentrations in aerosol samples collected (**a**) in 2-hour periods and (**b**) in 4-hour periods (night samples in 12 h periods) at Hyytiälä, Finland, in March–April 2003. "E" after the date indicates a day when an atmospheric new particle formation event was observed.

were tentatively identified on the basis of their accurate molecular masses (elemental composition) determined by TOFMS and their retention times in LC.

The homologous compound distribution of *n*-alkanoic acids (C_6–C_{30}) in the samples exhibited a strong even carbon number predominance, indicating a biogenic origin. The most abundant homologues were C_{16} and C_{18}. *n*-Alkanoic acid homologues with the carbon number smaller than C_{20} are considered to derive mostly from microbial activity and the larger homologues (> C_{22}) likely

Table 1. Organic compounds identified in the aerosol samples collected with a high-volume sampler at Hyytiälä, Finland in March–April 2003.

Compound	Method	Identification	Concentration (ng m^{-3})
n-Alkanes (C_{11}–C_{42})	1, 4	STD	1.66–76.1 (C_{12}–C_{30})
n-Alkanals (C_{24}–C_{32})	1, 4	EI	
n-Alkan-2-ones (C_{19}–C_{31})	4	EI	
n-Alkanols (C_{16}, C_{18})	2	EI	
n-Alkanoic acids (C_6–C_{30})	2, 3	EI, TOFMS	
n-Alkenoic acids (C_{10}–C_{18})	3	TOFMS	
n-Alkanedioc acids (C_9–C_{14})	3	TOFMS	
Hopanes (C_{28}–C_{35})	4	EI	
Steranes (C_{27}–C_{29})	4	EI	
PAH compounds			
Naphthalene	1	STD	LOQ–0.60
Naphthalene, methylphenyl	1	EI	
Acenaphthylene	1	STD	LOQ
Acenaphthene	1	STD	
Fluorene	1, 4	STD	LOQ
Phenanthrene	1, 4	STD	LOQ–0.84
Phenanthrene, dimethyl	4	EI	
Phenanthrene, trimethyl	4	EI	
Anthracene	1, 4	STD	LOQ–0.28
Anthracene, trimethyl	4	EI	
Carbazole	1, 4	STD	LOQ
Fluoranthene	1, 4	STD	LOQ–0.98
Pyrene	1, 4	STD	0.09–1.95
Pyrene, dimethyl	4	EI	
Benzo(a)anthracene	1, 4	STD	LOQ–0.38
Chrysene	1, 4	STD	LOQ–0.44
Benzo(k)fluoranthene	1, 4	STD	LOQ–0.95
Benzo(b)fluoranthene	1, 4	STD	LOQ–0.44
Benzo(a)pyrene	1, 4	STD	LOQ–0.51
Indeno(123-cd)pyrene	1, 4	STD	LOQ–0.67
Dibenzo(ah)anthracene	1	STD	LOQ–0.14
Benzo(ghi)perylene	1, 4	STD	LOQ–0.79
Oxy-PAH compounds			
9H-Fluorenone	1, 4	STD	LOQ–1.94
Xanthone	1	STD	LOQ
9,10-Anthracenedione	1, 4	STD	LOQ–1.95
9-Phenanthrenecarboxaldehyde	1	STD	LOQ–0.21
7H-Benz(de)anthracen-7-one	1, 4	STD	LOQ–0.95
Terpenes and terpenoids			
Verbenone + 2 isomers ($C_{10}H_{14}O$)	1, 4	STD, EI	LOQ–7.39 (Verbenone)
Campholenal + 2 isomers ($C_{10}H_{16}O$)	4	EI	
Borneol + 2 isomers ($C_{10}H_{18}O$)	1, 4	EI	
Pinonaldehyde ($C_{10}H_{16}O_2$)	1, 2, 3	EI	
Bornyl acetate ($C_{12}H_{20}O_2$)	1, 4	EI	
Pinonic acid + 2 isomers ($C_{10}H_{16}O_3$)	2, 3, 4	STD, EI	0.51–3.69 (Pinonic acid)
Pinic acid ($C_9H_{14}O_4$)	2, 3	STD	0.18–1.48
Norpinonic acid + 3 isomers ($C_9H_{14}O_3$)	3, 4	TOFMS, EI	
Norpinic acid ($C_8H_{12}O_4$)	3	TOFMS	
10-Oxo-pinonic acid ($C_{10}H_{14}O_4$)	4	EI	
Copaene ($C_{15}H_{24}$)	1	STD	LOQ
Longifolene ($C_{15}H_{24}$)	1	STD	LOQ–1.73
Cubenol + several isomers ($C_{15}H_{26}O$)	1, 4	EI	
Manool ($C_{20}H_{34}O$)	4	EI	
Manoyloxide ($C_{20}H_{34}O$)	4	EI	
Squalene ($C_{30}H_{50}$)	1, 2	EI	

continued

Table 1. Continued.

Compound	Method	Identification	Concentration (ng m^{-3})
Other			
2,4-Dimethylpentanol	1	EI	
2,6-Dimethyl-2,5-heptadien-4-one	1	EI	
2,6-Dimethyl-6-nitro-2-hepten-4-one	1	EI	
6,10,14-Trimethylpentadecan-2-one	4	EI	
Dodecanoic acid, methyl ester	1	EI	
Hexadecanoic acid, butyl ester	1	EI	
Octadecanoic acid, butyl ester	1	EI	
Octadecadienoic acid	3	TOFMS	
2,6-Di-tert-butyl-4-methylphenol	4	EI	
2,6-Di-tert-butyl-4-ethylphenol	4	EI	
6-Tert-butyl-3-methylphenol	4	EI	
Trichloroacetic acid, dodecyl ester	1	EI	
4-Nonylphenol	4	EI	
2,6-Di-tert-butyl-*p*-benzoquinone	4	EI	

1 = GC-MS (extraction with *n*-hexane–acetone (1:1 v/v)); 2 = GC-MS (extraction with methanol, polar column); 3 = LC-MS; 4 = SFE-LC-GC-MS; STD = Confirmed reference to authentic standard; EI = Tentatively identified on the basis of the electron ionisation mass fragmentation pattern and retention time in GC; TOFMS = Tentatively identified on the basis of the accurate molecular mass (elemental composition) and retention time in LC; LOQ = Concentration below the limit of quantification.

have a biogenic origin (Simoneit 1982, Limbeck and Puxbaum 1999). Other sources proposed for *n*-alkanoic acids include vehicle emissions for short-chain homologues ($< C_{20}$) and wood combustion for longer chain-length homologues ($> C_{20}$) (Rogge *et al*. 1993a, Fine *et al*. 2002).

The series of *n*-alkenoic acids ($C_{10:1}$–$C_{18:1}$) exhibited a strong predominance of $C_{16:1}$ and $C_{18:1}$ homologues. Rogge *et al*. (1993c) proposed that unsaturated carboxylic acids, among which palmitoleic acid ($C_{16:1}$) and oleic acid ($C_{18:1}$) are the most abundant homologues, are derived mainly from abraded fragments of leaf surface and other plant fragments. The series of aliphatic dicarboxylic acids (C_9–C_{14}) had a maximum at C_9, and may be oxidation products of unsaturated carboxylic acids, hydroxy acids and other unsaturated hydrocarbons. The most abundant C_9 homologue is considered to be a photo-oxidation product of long-chain unsaturated carboxylic acids such as oleic acid ($C_{18:1}$) (Stephanou and Stratigakis 1993).

Polyaromatic hydrocarbons

Several PAH compounds were identified in the samples (Table 1). The total concentrations of the quantified PAHs ranged from 0.8 to 3.4 ng m^{-3}, except on 10 April when the maximum concentration climbed to 6.3 ng m^{-3}. On that day, the airflow was from Russia and the Baltic countries (east and south) and presumably carried anthropogenic pollution. Even if the influence of the duration of the sampling is taken into consideration, the concentrations of the PAH compounds were almost as high as those we measured in the city of Helsinki in July 2002 (Shimmo *et al*. 2004a). However, this may be in part due to the higher ambient temperatures (16–20 °C) during the sampling in summer 2002. The most abundant PAHs identified in the samples were fluoranthene and pyrene.

Additionally, a few oxygen-containing PAH compounds (oxy-PAH) were identified. Oxy-PAHs are emitted directly from combustion processes (Rogge *et al*. 1993a), or they are generated in the atmosphere in oxidation reactions of the parent PAHs (Bunce *et al*. 1997). The oxy-PAH concentrations were low, often below the limit of quantification. The maximum concentration for individual compounds was 2.0 ng m^{-3}, and the maximum total concentration was 2.7 ng m^{-3}. The day-to-day concentration variation of oxy-PAH compounds followed that of the PAH

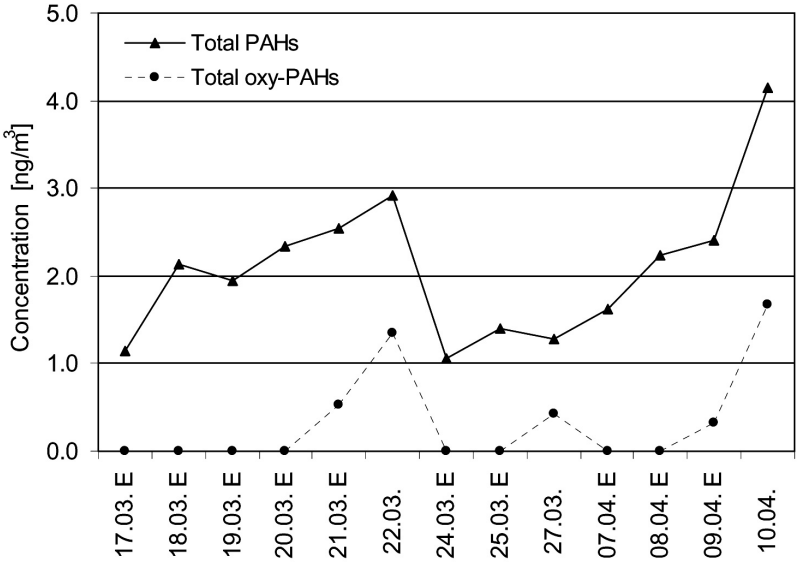

Fig. 3. Mean concentrations of PAH compounds (PAHs) and oxygen containing PAH compounds (oxy-PAHs) in aerosol samples collected at Hyytiälä, Finland, in March–April 2003. Sampling time 08:00–16:00 EET, sampling periods two hours (17 Mar.–22 Mar.) and four hours (24 Mar.–10 Apr.). "E" after the date indicates a day when an atmospheric new particle formation event was observed.

compounds (Fig. 3). The highest concentration was determined for 9,10-anthracenedione, but the most common oxy-PAH compound was 9H-fluorenone, which was detected in almost every sample.

Terpenoids

The most abundant terpene compounds identified in the samples were oxidation products of monoterpenes (Table 1). Typically, these compounds were present as several isomers with a similar mass fragmentation pattern. We identified verbenone, pinonic acid and pinic acid through reference to authentic standards and other compounds tentatively on the basis of their mass fragmentation patterns or accurate molecular masses (elemental composition) and the retention times in GC or LC.

Of the oxidised monoterpenes, verbenone, pinonic acid and pinic acid were quantitatively analysed. Particular interest was on the 2-hour and 4-hour samples collected in the morning and afternoon (08:00–16:00 EET), during the initial stages of the new aerosol particle formation. The concentrations of verbenone, pinonic acid and pinic acid in these samples were in the range 0.0–7.4 ng m^{-3}, 0.5–3.7 ng m^{-3} and 0.2–1.5 ng m^{-3}, respectively. The concentrations of pinonic acid and pinic acid are comparable with the results obtained in a previous campaign conducted at Hyytiälä in August 2001 (Boy *et al*. 2004). The maximum concentrations of the acids measured in August 2001 were somewhat higher than those measured in March–April 2003 in agreement with the higher precursor monoterpene concentrations in summer (Hakola *et al*. 2003). Exact comparison with previous results is not possible, however, because the sampling times in August 2001 were considerably longer.

In addition to monoterpene oxidation products, Kourtchev *et al*. (2005) detected several isoprene oxidation products in aerosol samples collected at Hyytiälä in July–August 2004. These compounds were not detected in the samples collected in March–April 2003, most probably due to the low isoprene emissions at Hyytiälä in early spring (Hakola *et al*. 2003).

Two target sesquiterpenes, longifolene and copaene, were present in some of the samples. The concentration of longifolene ranged from 0.04 to 1.7 ng m^{-3}, while the concentration of copaene was always below the limit of quantification. Since sesquiterpenes are highly reactive in the atmosphere, their concentrations are expected to be low (Hakola *et al*. 2003). In addition, the emission of these compounds can be expected to be weak at the low temperatures prevailing during the sampling. Additionally, several isomers of oxidised sesquiterpenes with molecular formula $C_{15}H_{26}O$ were identified in the

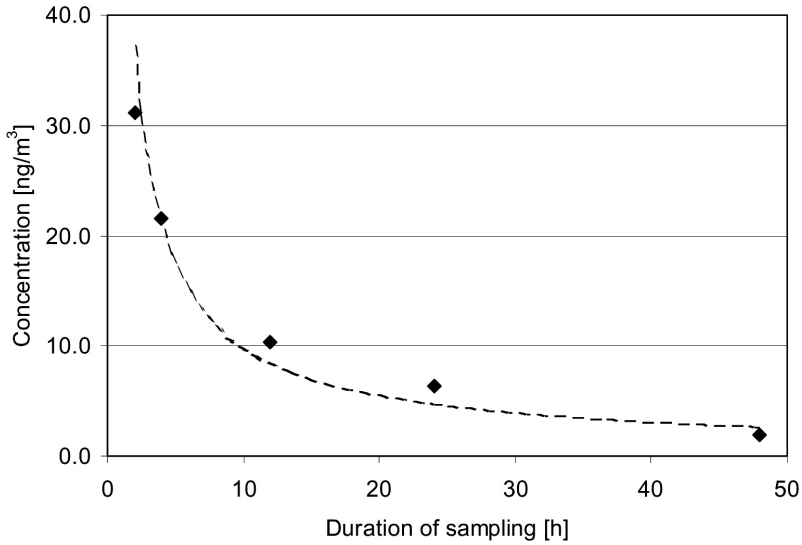

Fig. 4. Mean total concentration of even *n*-alkanes (C_{12}–C_{28}) measured in aerosol samples collected in 2, 4, 12, 24 and 48-hour periods at Hyytiälä, Finland, in March–April 2003.

samples. Two diterpenoids, manool and manoyloxide, and a triterpene, squalene, were identified in most samples.

Other compounds

The hopanes (C_{28}–C_{35}) and steranes (C_{27}–C_{29}) identified in the samples are molecular fossils found in crude petroleum and therefore indicative of vehicle emissions (Cass 1998). The presence of these compounds in forest aerosol underlines the significance of long-range transport of pollution. Other anthropogenic compounds identified were 4-nonylphenol, 2,6-di-tert-butyl-p-benzoquinone and dodecyl ester of trichloroacetic acid.

Additional biogenic compounds identified in the samples included 6,10,14-trimethylpentadecan-2-one, a degradation product of the phytol of chlorofyll (Alves *et al*. 2001). The phenolic compounds such as 2,6-di-tert-butyl-4-methylphenol; 2,6-di-tert-butyl-4-ethylphenol and 6-tert-butyl-3-methylphenol are reported to derive from vegetation cellular walls (Alves *et al*. 2001). However, these compounds are also used as additives in plastics and rubber (Castillo and Barceló 2001). Further compounds, likely of biogenic origin, were 2,6-dimethyl-2,5-heptadien-4-one; 2,6-dimethyl-6-nitro-2-hepten-4-one; 2,4-dimethylpentanol and a few esters of *n*-alkanoic acids (Table 1).

Concentration variations

Duration of sample collection

The concentrations of *n*-alkanes and PAH compounds were lower in the 24-hour and 48-hour samples than in the 2-hour and 4-hour samples, probably due to evaporation and/or degradation of the compounds on the filter over a long sampling period. In particular, the accumulation of *n*-alkanes decreased significantly when the duration of the sampling increased (Fig. 4). For pinonic and pinic acids, mean concentrations were somewhat higher in the 4-hour samples than the 2-hour samples. Because no provision was made to remove gaseous oxidants or other gas phase compounds during the sampling, oxidation of gas phase monoterpenes to the acids could have occurred on the filter, creating a positive error in the results, particularly for the 4-hour samples. These results are only indicative, however, because the concentrations of the compounds varied widely from one day to another.

Ambient temperature

The total concentration of *n*-alkanes showed a clear diurnal pattern following the temperature changes during the day, being highest in the daytime and lowest during the night. Concentration levels of *n*-alkanes and PAH compounds did not

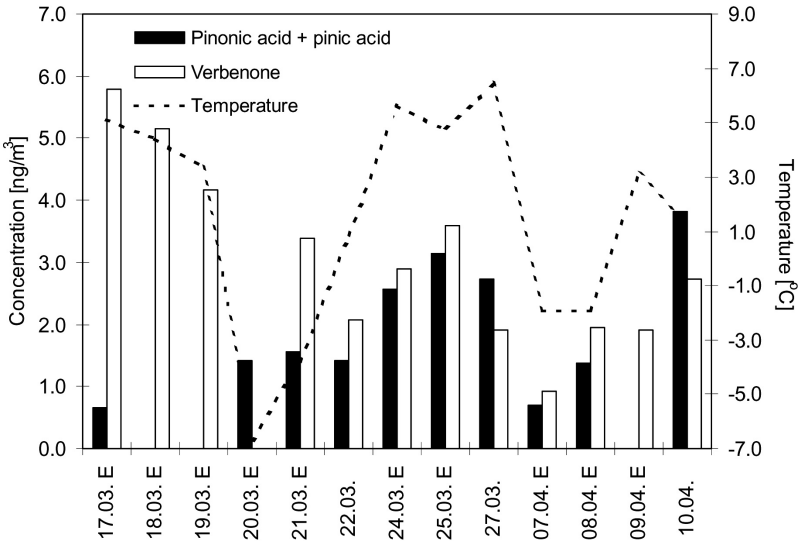

Fig. 5. Correlation of pinonic acid and pinic acid concentrations (summed) and verbenone concentration with mean air temperature during the sampling for aerosol samples collected at Hyytiälä, Finland, in March–April 2003. Sampling time 08:00–16:00 EET, sampling periods two hours (17 Mar.–22 Mar.) and four hours (24 Mar.–10 Apr.). "E" after the date indicates a day when an atmospheric new particle formation event was observed. Pinonic acid and pinic acid were not determined in the samples collected on 18 Mar., 19 Mar. and 9 Apr.

differ on cold and warm days, however, indicating that factors other than temperature have a more significant influence on the day-to-day variations. In contrast to this, the concentrations of pinonic and pinic acids showed a clear day-to-day correlation with temperature (Fig. 5), consistent with the temperature dependence of the precursor monoterpene emissions (Hakola *et al.* 2003). Verbenone showed a similar trend.

Atmospheric new particle formation

The concentrations of the quantified monoterpene oxidation products did not show a correlation with atmospheric new particle formation events (Fig. 5). However, the distribution of *n*-alkanes and *n*-alkanoic acids differed on particle formation event and non-event days. Both the maximum and average concentrations of long-chain *n*-alkanes ($> C_{22}$) were higher on event days than on non-event days. In a similar way, $< C_{18}$ *n*-alkanoic acid homoloques dominated on event days, whereas their longer chain homologues ($> C_{18}$) were more abundant on non-event days (Fig. 6). However, there were only a few non-event days during the campaign, and thus, a consistent statistical interpretation of the data was not feasible. The final reason for the observed predominance of long-chain *n*-alkanes and *n*-alkanoic acids $< C_{18}$ on particle formation event days requires further study.

Conclusions

Efficient analytical techniques are crucial for obtaining information about the formation and chemical composition of atmospheric aerosol particles. Reliability is enhanced if the instrumental techniques support and complete each other, as in this work. Moreover, the application of several techniques allows the disadvantages of a particular method to be minimised and the advantages to be maximised. Multidimensional systems, and systems integrating sample pretreatment with the final analysis, appear to be valuable tools in the aerosol analysis and deserving of further development.

We identified almost 160 organic compounds in the aerosol samples, with concentrations ranging from picogrammes to nanogrammes per cubic meter of air. The day-to-day variations in the concentrations of certain compounds could

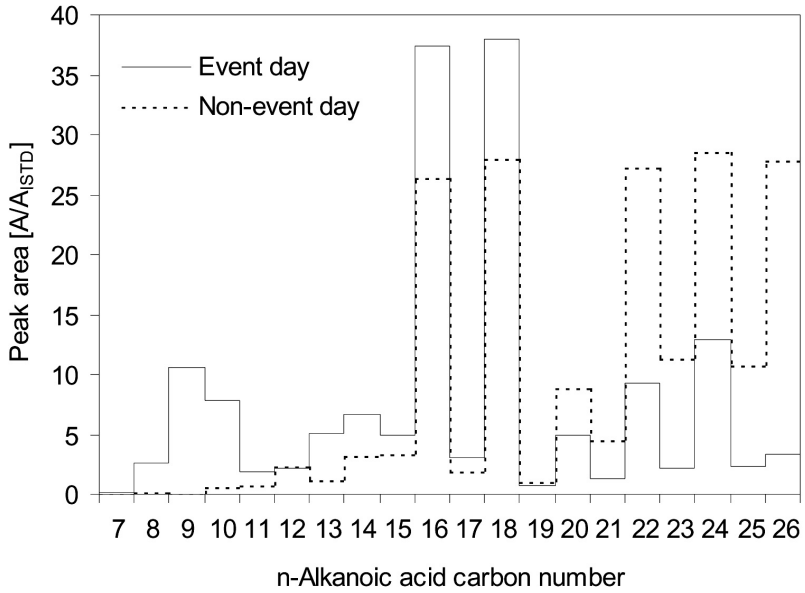

Fig. 6. Homologous distribution of *n*-alkanoic acids (carbon chain-length C_7–C_{26}) in aerosol samples collected at Hyytiälä, Finland, in March–April 2003, on a day when atmospheric new particle formation occurred (event day) and on a day when the formation did not occur (non-event day).

mostly be explained by the ambient temperature. Comparison of days when new particle formation took place with days when formation did not occur, however, revealed higher concentrations of long-chain *n*-alkanes (> C_{22}) and < C_{18} *n*-alkanoic acids on particle formation event days. The reason for this is not yet entirely clear.

The duration of the sample collection affected the concentrations of the compounds, presumably due to reactions on the filter or evaporation from it during the sampling. The propensity for reactions and/or evaporation means that the sampling period should be as short as possible. Short sampling periods are also required to obtain information on concentration variations in short enough time intervals during particle formation events. Additionally, size-separating sampling techniques should be used to obtain a clearer picture of the compounds participating in the particle formation process. In view of the low concentrations of the compounds in rural atmospheres, and the errors occurring during sampling, the development of portable instruments suitable for *in situ* measurements should be considered essential.

References

Abas M.R.B. & Simoneit B.R.T. 1996. Composition of extractable organic matter of air particles from Malaysia: initial study. *Atmos. Environ.* 15: 2779–2793.

Alves C., Pio C. & Duarte A. 2001. Composition of extractable organic matter of air particles from rural and urban Portuguese areas. *Atmos. Environ.* 35: 5485–5496.

Anttila P., Hyötyläinen T., Heikkilä A., Jussila M., Finell J., Kulmala M. & Riekkola M.-L. 2005. Determination of organic acids in aerosol particles from a coniferous forest by liquid chromatography–mass spectrometry. *J. Sep. Sci.* 28: 337–346.

Azevedo D.A., Santos C.Y.M. & Aquino Neto F.R. 2002. Identification and seasonal variation of atmospheric organic pollutants in Campos dos Goytacazes, Brazil. *Atmos. Environ.* 36: 2383–2395.

Boy M., Petäjä T., Dal Maso M., Rannik Ü., Rinne J., Aalto P., Laaksonen A., Vaattovaara P., Joutsensaari J., Hoffmann T., Warnke J., Apostolaki M., Stephanou E.G., Tsapakis M., Kouvarakis A., Pio C., Carvalho A., Römmp A., Moortgat G., Spring C., Guerther A., Greenberg J., Ciccioli P. & Kulmala M. 2004. Overview of the field measurement campaign in Hyytiälä, August 2001 in the framework of the EU project OSOA. *Atmos. Chem. Phys.* 4: 657–678.

Bunce N.J., Liu L., Zhu J. & Lane D.A. 1997. Reaction of naphthalene and its derivatives with hydroxyl radicals in the gas phase. *Environ. Sci. Technol.* 31: 2252–2259.

Cass G.R. 1998. Organic molecular tracers for particulate air pollution sources. *Trend. Anal. Chem.* 17: 356–366.

Castillo M. & Barcelo D. 2001. Characterization of organic pollutants in textile wastewaters and landfill leachate by using toxicity-based fractionation methods followed by liquid and gas chromatography coupled to mass spectrometric detection. *Anal. Chim. Acta* 426: 253–264.

Fine P.M, Cass G.R. & Simoneit B.R.T. 2002. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern

United States. *Environ. Sci. Technol.* 36: 1442–1451.

Fraser M.P., Yue Z.W., Tropp R.J., Kohl S.D. & Chow J.C. 2002. Molecular composition of organic fine particulate matter in Houston, TX. *Atmos. Environ.* 36: 5751–5758.

Glasius M., Duane M. & Larsen B.R. 1999. Determination of polar terpene oxidation products in aerosols by liquid chromatography–ion trap mass spectrometry. *J. Chromatogr. A* 833: 121–135.

Hakola H., Tarvainen V., Laurila T., Hiltunen V., Hellén H. & Keronen P. 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.* 37: 1623–1634.

Jacobson M.C., Hansson H.-C., Noone K.J. & Charlson R.J. 2000. Organic atmospheric aerosols: Review and state of the science. *Rev. Geophys.* 38: 267–294.

Kallio M., Hyötyläinen T., Jussila M., Hartonen K., Palonen S., Shimmo M. & Riekkola M.-L. 2003. Semi-rotating cryogenic modulator for comprehensive two-dimensional gas chromatography. *Anal. Bioanal. Chem.* 375: 725–731.

Kourtchev I., Ruuskanen T., Maenhaut W. & Claeys M. 2005. Observation of 2-methylsterols and related photooxidation products of isoprene in boreal forest aerosols from Hyytiälä, Finland. *Atmos. Chem. Phys. Discuss.* 5: 2947–2971.

Kubátová A., Vermeylen R., Clayes M., Cafmeyer J. & Maenhaut W. 2002. Organic compounds in urban aerosols from Gent, Belgium: Characterization, sources and seasonal differences. *J. Geophys. Res.* 107: ICC5/1–ICC5/12

Kulmala M., Vehkamäki H., Petäjä T., Dal Maso M., Boy M., Lauri A., Kerminen V.-M., Birmili W. & McMurry P.H. 2004. Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol. Sci.* 35: 143–176.

Kulmala M., Hämeri K., Aalto P.P, Mäkelä J.M., Pirjola L., Nilson E.D., Buzorius G, Rannik Ü., Dal Maso M., Seidl W., Hoffman T., Janson R., Hansson H.-C., Viisanen Y., Laaksonen A. & O'Dowd C.D. 2001. Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* 53B: 324–343.

Limbeck A. & Puxbaum H. 1999. Organic acids in continental background aerosols. *Atmos. Environ.* 33: 1847–1852.

O'Dowd C.D., Aalto P, Hämeri K., Kulmala M. & Hoffmann T. 2002. Atmospheric particles from organic vapours. *Nature* 416: 497–498.

Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R. & Simoneit B.R.T. 1993a. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 27: 636–651.

Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R. & Simoneit B.R.T. 1993b. Sources of fine organic aerosol. 3. Road dust, tire debris and organometallic brake lining dust: roads as sources and sinks. *Environ. Sci. Technol.* 27: 1892–1904.

Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R. & Simoneit B.R.T. 1993c. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.* 27: 2700–2711.

Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R. & Simoneit B.R.T. 1998. Sources of fine organic aerosol. 9. Pine, oak and synthetic log combustion in residential fireplaces. *Environ. Sci. Technol.* 32: 13–22.

Shimmo M., Adler H., Hyötyläinen T., Hartonen K., Kulmala M. & Riekkola M.-L. 2002. Analysis of particulate polycyclic aromatic hydrocarbons by on-line coupled supercritical fluid extraction–liquid chromatography–gas chromatography–mass spectrometry. *Atmos. Environ.* 36: 2985–2995.

Shimmo M., Anttila P., Hartonen K., Hyötyläinen T., Paatero J., Kulmala M. & Riekkola M.-L. 2004a. Identification of organic compounds in atmospheric aerosol particles by on-line supercritical fluid extraction–liquid chromatography–gas chromatography–mass spectrometry. *J. Chromatogr. A* 1022: 151–159.

Shimmo M., Jäntti J., Aalto P., Hartonen K., Hyötyläinen T., Kulmala M. & Riekkola M.-L. 2004b. Characterization of organic compounds in aerosol particles in Finnish forest by on-line coupled supercritical fluid extraction–liquid chromatography–gas chromatography–mass spectrometry. *Anal. Bioanal. Chem.* 378: 1982–1990.

Simoneit B.R.T. 1986. Characterization of organic constituents in aerosols in relation to their origin and transport: a review. *Int. J. Environ. Anal. Chem.* 23: 207–237.

Simoneit B.R.T. & Mazurek M.A. 1982. Organic matter of the troposphere II. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmos. Environ.* 16: 2139–2159.

Stephanou E.G. & Stratigakis N. 1993. Oxocarboxylic and α,ω-dicarboxylic acids: photo-oxidation products of biogenic unsaturated fatty acids present in urban aerosols. *Environ. Sci. Technol.* 27: 1403–1407.

Turpin B.J., Saxena P. & Andrews E. 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmos. Environ.* 34: 2983–3013.

Winterhalter R., Van Dingenen R., Larsen, B.R., Jensen, N.R. & Hjorth J. 2003. LC–MS analysis of aerosol particles from the oxidation of α-pinene by ozone and OH-radicals. *Atmos. Chem. Phys. Discuss.* 3: 1–39.

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