

Aerosols in boreal forest: wintertime relations between formation events and bio-geo-chemical activity

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We studied wintertime aerosol formation and subsequent particle growth events that have been frequently observed in ambient air at a boreal forest site (SMEAR II station) in southern Finland. Aerosol size distributions, gas concentrations, biological activity and meteorological parameters have been measured at the site continuously since 1996. An important observation, based on flux measurements, was that all particle formation events were connected with either increased water evapo-transpiration or carbon dioxide uptake by the forest. However, increased H₂O or CO₂ fluxes did also occur on days without aerosol formation events, but these occasions were connected to cloudy or polluted days with high pre-existing aerosol concentrations. Thus, our overall conclusion is that in order for an aerosol formation event to occur, some ecological or bio-geo-chemical activity is needed. During wintertime, this activity seems to be mostly related to snow–atmosphere interactions.

Introduction

The formation and growth of new aerosol particles, and more generally, the processes affecting aerosol dynamics, the total aerosol concentration

and the particle size distribution are important issues in current atmospheric science. Atmospheric aerosols influence the global radiation balance (Charlson and Wigley 1994), ozone layer, acid rain, visibility (*see e.g.* Seinfeld and

Pandis 1998) and the inhalation dose of particulate matter (Pope *et al.* 1995).

In order to be able to understand the atmospheric, biological and geophysical processes that influence new particle formation, long-term investigations are required. Such studies have to be multidisciplinary — involving physics, chemistry, biology and meteorology. Meteorological data, including radiation, is necessary for the interpretation of the weather conditions typically encountered during the particle production events. The biological aspect includes studies of plant productivity, carbon balance and allocation as well as of photosynthesis. A comprehensive analysis of atmospheric chemistry is needed to determine the concentrations and the spatial and temporal patterns of different chemical compounds that are considered to take part in the particle formation and growth processes. From the point of view of aerosol physics, the aerosol concentrations as well as sources and sinks for aerosol particles and aerosol precursor vapors should be determined.

Aerosol formation and subsequent particle growth in ambient air have been frequently observed at SMEAR II, a boreal forest field station in southern Finland (Mäkelä *et al.* 1997, Kulmala *et al.* 1998, Aalto *et al.* 2001, Kulmala *et al.* 2001b). After their formation, the particles can grow up to accumulation mode sizes (> 100 nm) (Mäkelä *et al.* 1997). The formation bursts of the 3–5 nm-sized particles take place mostly during the spring and autumn periods, and occur only seldom during the winter.

The condensable vapour associated with particle growth has been shown to be organic (O'Dowd *et al.* 2002). Therefore, it has been hypothesized that the formation of condensable vapour is to some extent related to ecological activity, probably to photosynthesis. This brings us to the main goal of this paper: to investigate the connection between the observed particle formation and growth events and bio-geo-chemical activity (specifically photosynthesis, emissions of non-methane organic compounds, and evaporation related to snow melting) of the surrounding Scots pine forest. In late spring and summer, carbon and water fluxes are high and likely to mask the on-off behaviour between aerosol formation and bio-geo-chemical processes. Therefore we concentrated on the winter periods

(1 Nov.–31 Mar.) between 1996 and 2001, for which we analysed data of aerosol size distributions, local meteorology, micrometeorological fluxes, gaseous pollutants and plant activity.

Experiments

Hyytiälä Station

The SMEAR II station is located in a homogeneous Scots pine (*Pinus sylvestris*) stand on the top of a hill near the Hyytiälä Forestry Field Station of the University of Helsinki (61°51'N, 24°17'E, 181 m above sea level) 220 km NW of Helsinki (*see* Vesala *et al.* 1998, Kulmala *et al.* 2001b). The largest city near the SMEAR II station is Tampere, about 60 km S-SW of the measurement site.

The SMEAR II facility has been planned and implemented to determine material and energy flows in the atmosphere–vegetation–soil continuum at different temporal and spatial scales (Vesala *et al.* 1998). The SMEAR II station includes a measurement building (cottage), a 72-m high mast, a 15-m tall tower and two mini-watersheds. Gas analysers, computers and all the other sensitive equipment are located in the measurement building. The mast is used for measurements of meteorological variables and gas concentration profiles and for eddy-covariance measurements of momentum, carbon dioxide, sensible and latent heat, trace-gas and aerosol fluxes. The tower eases the installation and maintenance of gas-exchange chambers that are attached to the branches of adjacent trees. The soil measuring equipment is installed in research pits in the watersheds. A more detailed description of SMEAR II facilities can be found in Vesala *et al.* (1998) or Kulmala *et al.* (2001b).

Aerosol measurements

Sub-micron particle size distributions are determined using a Differential Mobility Particle Sizer (DMPS) (Aalto *et al.* 2001). The measurements are continuous, and the smallest detectable particle size is 3 nm. The DMPS consists of a DMA (Differential Mobility Analyser) and

a CNC (Condensation Nucleus Counter). It classifies particles into size classes depending on the electrical mobility of the particles. The different classes are separated from each other by changing the voltage difference inside the DMA. The size distribution of the sampled aerosol population is then determined in the CNC, which counts the number concentration of every size class. Two DMPS systems are located in the cottage: the first one classifies particles from 3 to 10 nm and the second from 10 nm to 500 nm. Both systems use a Hauke-type DMA (Winklmayr *et al.* 1991) and a closed-loop sheath-flow arrangement (Jokinen and Mäkelä 1997). The height of the DMA in the first system is equal to 10.9 cm and that in the second system equal to 28 cm. Before the size characterisation, the incoming aerosol is neutralised with a 2-mCi Krypton-85 beta source. The CNC:s used are TSI Model 3025 and TSI Model 3010 in the first and second systems, respectively. The DMPS measurement period is ten minutes.

Chamber measurements

The leaf-level, gas exchange measurement system consists of shoot chambers, each of which encloses one pine shoot. They are equipped with a pneumatic system for controlling the opening and closing of the chambers, magnetic valves, gas analyzers (CO_2 , H_2O , O_3 and NO_x), pipelines, air pumps and mass flow controllers. The measurements are performed using two different chamber types. The bigger ones are cylindrical, made of acrylic, and their volume is 3.6 litres. The volume of the smaller box-shaped ones is 1 litre and they are made of a combination of quartz glass and acrylic. Photosynthetically active radiation (PAR) is measured on top of the chambers with LiCor 190 SB PAR sensors, and the temperature inside the chambers is measured with copper-constantane thermoelements (Hari *et al.* 1999).

The chambers are kept open most of the time, which provides an environment close to the ambient for the shoots. During a measurement, the pneumatic system closes the lids of the chambers for 60–70 seconds, depending on the chamber. When a chamber is closed, the air flow-

ing out to the gas analyser is compensated by an inflow of ambient air or of air from a pipeline regulated by a mass flow controller. This keeps the total pressure constant.

The gas concentrations in a chamber are recorded every five seconds during a measurement, starting from when the chamber closes and continuing until the lid opens again. The CO_2 and water vapour concentrations are measured with infrared absorption analysers (Hartmann & Braun URAS 4). The NO_x concentration is measured with a chemiluminescence analyser (TEI 42S, Thermo Environmental Instruments) and O_3 concentration by an ultraviolet absorption analyser (API 400, Advanced Pollution Instrumentation) (Vesala *et al.* 1998, Jansson *et al.* 2001).

In wintertime we are working near the limit to detect fluxes. Therefore, we can estimate that the relative error is around 50% for water vapour and some 20% for other gases.

Flux measurements

The ecosystem-level CO_2 and H_2O fluxes were measured using the eddy covariance (EC) technique described for instance in Aubinet *et al.* (2000). The measurement system includes a Solent ultrasonic anemometer (Solent Research 1012R2, Gill Instruments Ltd, Lymington, Hampshire, England) to measure the three wind speed components and the sonic temperature, and a closed-path infrared gas analyser (LI-6262, Li-Cor Inc., Lincoln, Nebraska, USA), which measures the CO_2 and H_2O concentrations. The signals are digitised and recorded at 21 Hz. These trace gas flux instruments are typically used in EC flux systems of CO_2 and H_2O and their operational principles have been described extensively in the literature (e.g. Moncrieff *et al.* 1997). The measurements are conducted at the heights of 23.3 and 46.0 m. More details of the specific setup of the EC measurement system can be found in Rannik *et al.* (1998). The micrometeorological fluxes of momentum, heat, CO_2 and H_2O have been calculated as 30-min averages according to commonly accepted procedures (Aubinet *et al.* 2000). Except for momentum, upward fluxes from the ecosystem to the atmosphere are defined to be positive.

During winters we are working near the detection limit of the system. The overall relative error is around 20%.

Volatile organic compound (VOC) measurements

The VOC samples were collected on adsorbent tubes filled with Tenax-TA and Carbopack-B using pumped sampling and constant-flow type pumps (SKC). The pumps were calibrated each day before the measurements were conducted. The flow rate and sampling time used were about 100 ml min⁻¹ and 30 min, respectively. MnO₂-coated copper meshes placed on a Teflon holder were employed in front of the sampling tubes to destroy ozone.

The adsorbent tubes were analysed using a thermodesorption instrument (Perkin-Elmer ATD-400) connected to a gas chromatograph (HP 5890) with a HP-1 column (60 m, inner diameter 0.25 mm) and a mass-selective detector (HP 5972). The samples were concentrated in the thermodesorption instrument in a cold trap (-30 °C) filled with Tenax-TA. The samples were analysed using selected ion mode (SIM). The analytical system did not allow the separation of myrcene and β -pinene; their total amount was therefore quantified as β -pinene. A calibration was performed using liquid standards in methanol solutions. Standard solutions were injected onto adsorbent tubes that were flushed with helium flow (100 ml min⁻¹) for five minutes in order to remove the methanol. The detection limits for monoterpenes were about 10 pptv. A detailed description of the whole measurement equipment is given in Hakola *et al.* (2001).

Data analysis

We analysed whether or not the days of the investigated winter periods (1996–2001) exhibited aerosol formation and/or any kind of bio-geo-chemical activity (events of increased carbon dioxide or water vapour flux). The different aerosol or flux events were classified according to their clarity. Because any emissions from

nearby towns or from the field station itself can affect the measured gas and particle concentrations, those days with wind direction from the station (determined as the sector between 215° and 265°) were specially marked in the data.

We determined the relative humidity (in percentage values) and cloudiness of the days with aerosol or bio-geo-chemical events and divided the values of cloudiness into three classes: cloudy (1), half-cloudy (½) and sunny (0). We gave a major emphasis to the weather conditions in the morning, especially if the weather changed significantly during the day, because aerosol formation events usually occur before noon. When analysing the results, we divided the days with bio-geo-chemical activity into aerosol formation event days and non-aerosol formation days.

Aerosol formation events

As the size distribution of the aerosol particle population was measured continuously, we could observe from the DMPS plots if particle bursts occurred during the day. Furthermore, we subjectively classified these events into three different quality classes. To avoid systematic errors in the classification process, two different working groups evaluated the data and compared their results with an earlier classification. Class 1 included clearly visible events of formation and subsequent growth of 3-nm particles. In class 2, the formation of 3-nm particles was clear but subsequent growth was not as intense as in class 1. In class 3, the aerosol formation was associated with growth that was either insignificant or not very pronounced in time. Days on which no aerosol formation event was observed were classified as non-event days. Due to the uncertainty in the class 3 events, the following analysis is based on class 1 and class 2 events only. Fig. 1 shows examples of all event classes described above.

The growth rate of nucleation mode particles and the formation rate of 3-nm particles can be determined directly from the aerosol size distribution measurements. The vapour concentration and vapour source rate can be estimated by means of the concepts of condensation and coagulation sinks (Kulmala *et al.* 2001a).

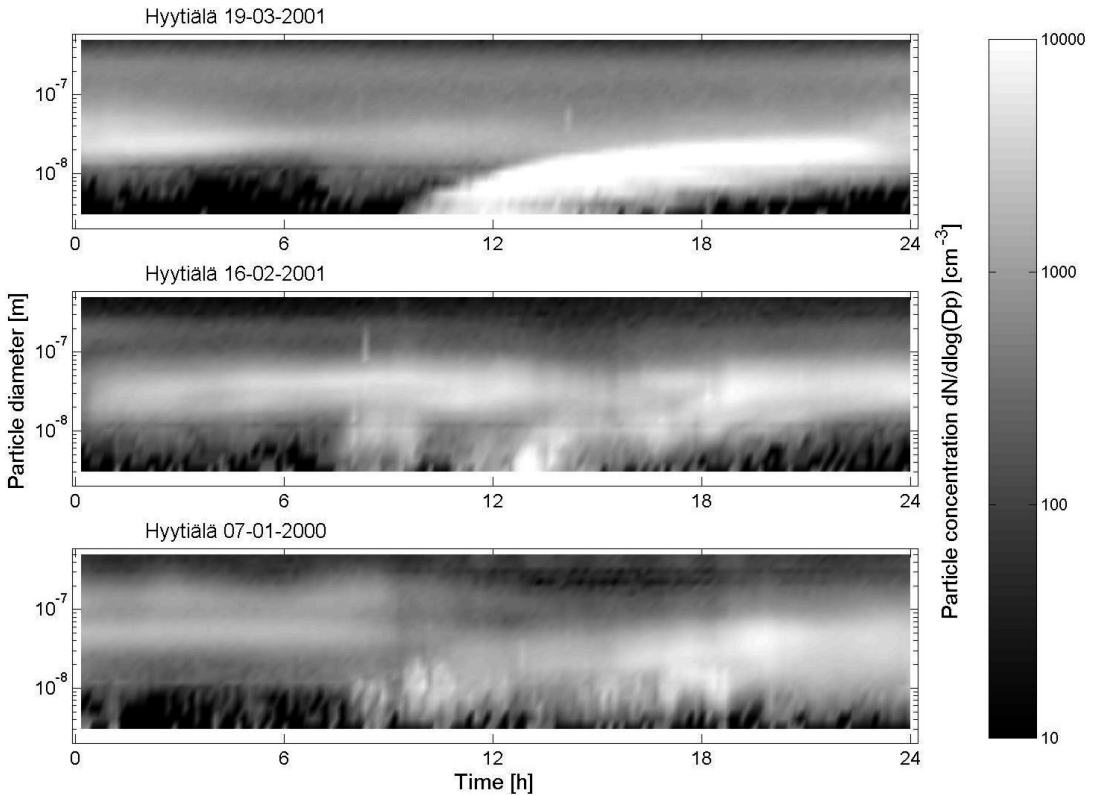


Fig. 1. Examples of DMPS plots for class 1, 2 and 3 particle event days.

Bio-geo-chemical events

Chambers

We quantified biological activity by means of shoot chambers that measure the CO_2 exchange between the trees and the atmosphere. The number of chambers used in the measurements differed from winter to winter. We classified the activity events according to the strength of photosynthesis. Class 0 (*see* Table 1) indicates that no event (no photosynthesis) took place. Classes 1, 2 and 3 correspond to the clearest, the rather clear and the most unclear events, respectively. There were differences between the chambers: an event could be clearer in one chamber than in another. We evaluated the amount of CO_2 that was consumed in photosynthesis by calculating the area between the plotted diurnal CO_2 exchange curve and the estimated mean level of respiration. The latter was determined from night-time measurements — without light, no photosynthesis can occur and the changes in nocturnal CO_2 exchange are due

only to respiration. We evaluated the amount of consumed CO_2 separately for the morning (08:00–12:00) and for the afternoon (12:00–16:00).

Eddy flux

The amount of daytime CO_2 net exchange between the whole forest ecosystem and the atmosphere was determined for each bio-geo-chemical activity day from the eddy covariance measurement data the same way as for the chamber data: by integrating over a plotted diurnal cycle. We studied each morning and afternoon (before and after 12:00) separately and again determined the respiration level from night-time measurements. To reduce the uncertainty arising from random variation in the measured fluxes, we evaluated the integrals by summing over smooth curves that were fitted to the observations. The respiration level was subtracted from these curves in order to determine the CO_2 exchange related to photosynthetic activity only.

Table 1 (across the opening). Different measured and calculated parameters for all aerosol formation event days (classes 1 and 2) of the five winters 1996 to 2001. H₂O flux = 1 signifies measured flux, Chamber data = 0 means no flux, 1 means clearest event etc., Wind = 1 for direction between 215 to 265 degree, Clouds: 0 = cloudless, ½ = half cloudy, 1 = completely cloudy, general: x = bad data, empty space = no data available, AM = morning (08:00–12:00) and PM = afternoon (12:00–16:00).

Date	Part. event class	Cond. sink (mol cm ⁻³ s ⁻¹)		CO ₂ fluxes (233) EC technique (mmol m ⁻²)		CO ₂ fluxes (460) EC technique (mmol m ⁻²)		H ₂ O fluxes EC tech.	CO ₂ uptake event class Chamber no.										Wind 215–265 degree						
		AM	PM						0	1	2	4	7	8	9	103									
28.01.1997	2	0.0002	0.0003					1																	
17.02.1997	1	0.0014	0.0014					1																	
19.02.1997	2	0.0023	0.0017					1																	
05.03.1997	2	0.0005	0.0007	x	x																				
07.03.1997	2	0.0013	0.0014	x	x			x																	
09.03.1997	2	0.0007	0.0016	x	x																				
14.03.1997	2	0.0003	0.0003	-0.121	-7.474			1																	
16.03.1997	2	0.0012	0.0006					1																	
31.01.1998	2	0.0016	0.0029	-0.933	-2.592			1						0											
17.02.1998	2	0.0007	0.0004					1						x											
22.03.1998	2	0.0041	0.0029	0.000	-6.515	0.000	-3.724	1						2										1	
23.03.1998	2	0.0050	0.0038					1						2										1	
13.03.1999	1	0.0038	0.0043					1						x					x	x	x				
14.03.1999	2	0.0078	0.0067	1.788	-8.061			1						x					x	x	x				
30.03.1999	1	0.0028	0.0034	-32.089	-51.304	-12.761	-30.577	1						x					2	x	x				
17.01.2000	2	0.0003	0.0002			-6.558	-14.455	1						1					1						
05.02.2000	1	0.0003	0.0007					1						0					3						1
08.03.2000	2	0.0007	0.0008					1																	
11.03.2000	1	0.0011	0.0013					0.000	-6.057	1				x				x							
12.03.2000	1	0.0008	0.0006					1						x				x							1
28.03.2000	2	0.0014	0.0015					1						3				1							1
29.03.2000	1	0.0030	0.0026					1						3				1							1
16.02.2001	2	0.0011	0.0007	-0.674	-12.977			1						3				3					1		
20.02.2001	2	0.0005	0.0006	-7.240	-13.141			1						3				3					2		1
22.02.2001	2	0.0018	0.0019					1						0				0					0		
24.02.2001	2	0.0023	0.0026					1						0				0					0		
07.03.2001	1	0.0020	0.0006					1						0				0					0		
08.03.2001	2	0.0015	0.0016					1						0				0					0		
17.03.2001	1	0.0012	0.0013					1						0				0					x		
18.03.2001	2	0.0024	0.0023					1						0				0					x		
19.03.2001	1	0.0017	0.0018					1						0				0					x		
20.03.2001	2	0.0031	0.0018					1						0				0					x		
25.03.2001	1	0.0018	0.0004					1						0				0					x		
26.03.2001	1	0.0011	0.0011					1						0				0					x		

The results were then compared with the corresponding CO₂ exchange results acquired from chamber measurement data. A clear diurnal cycle in the H₂O flux was denoted as 1.

Results and discussion

Table 1 shows the characteristics of all class 1 and 2 aerosol formation event days observed during the winters (1 Nov.–31 Mar.) of 1996–2001. The table also includes (i) the integrated amounts of net CO₂ exchange and whether or not a H₂O flux event occurred, both measured

with the EC technique, and (ii) the event class of the CO₂ uptake measured with the different chambers. Furthermore, the table shows condensation sinks, cloudiness, wind direction (if from locally polluted direction), temperature, pressure, relative humidity, UV-A radiation as well as SO₂, NO_x, ozone and water vapour concentrations.

Connection between aerosol formation and bio-geo-chemical events

During the observed winters, the formation and growth of atmospheric aerosols occurred most fre-

Clouds	Temperature (°C)		SO ₂ (ppb)		NO _x (ppb)		O ₃ (ppb)		H ₂ O (ppth)		Rel. humidity (%)		Pressure (hPa)		UV-A (kJ m ⁻²)	
	AM	PM	AM	PM	AM	PM	AM	PM	AM	PM	AM	PM	AM	PM	AM	PM
0	-7.6	-7.4	0.03	0.02	0.65	0.65	40.45	39.15	3.00	2.79	85.24	78.37	983	988		
½	-12.8	-7.8	0.91	0.86	1.75	1.75	37.19	37.98	2.21	2.87	96.94	85.13	1007	1009		
½	-9.7	-6.6	1.43	0.94	1.98	1.98	39.75	41.54	2.77	2.96	94.15	79.13	997	996		
0	-0.1	3.7	0.18	0.07	0.93	0.93	42.46	44.49	4.13	3.82	68.33	48.20	998	999		
0	1.5	5.8	0.25	0.26	10.53	10.53	38.34	42.24	5.26	5.23	78.38	57.09	1008	1006		
0	3.0	7.4	0.23	0.35	1.54	1.54	39.54	43.71	5.22	4.57	69.94	44.63	1006	1004	145.4	228.8
0	-2.6	-1.0	0.08	0.09	0.61	0.61	37.14	41.18	2.62	1.74	51.16	30.12	982	985	219.4	269.7
0	-6.9	-3.5	0.24	0.10	0.59	0.59	34.39	37.12	2.06	2.07	56.69	43.38	988	990	235.0	249.1
0	-18.7	-16.1	0.29	0.58	0.74	0.74	36.88	36.10	1.35	1.49	95.13	84.00	988	989	47.4	80.6
0	-20.9	-18.2	1.02	0.72	1.60	1.60	34.28	35.52	1.32	1.43		97.69	997	1001	103.6	147.7
0			0.31	0.37	2.23	2.23	35.09	45.24	4.17	2.95	83.40	41.66	1016	1019	275.5	326.1
0			1.11	0.43	2.51	2.51	42.78	46.37	3.17	2.87	56.32	39.03	1023	1021	287.8	338.4
0	-5.3	-0.7	0.96	1.91	2.64	2.64	45.89	49.53	2.27	2.91	55.82	50.85	1013	1014	212.9	261.7
0	-4.1	1.5	2.73	1.80	4.37	4.37	41.72	50.24	3.21	3.77	71.90	56.19	1015	1015	220.0	269.1
½	7.7	10.2	0.61	0.55	4.43	4.43	46.66	50.96	4.86	4.72	46.67	38.00	999	999	319.9	368.1
1	-0.9	-0.7	0.09	0.09	0.66	0.66	40.04	38.79	4.53	4.41	76.24	73.32	963	963	25.3	38.1
0	-3.4	-2.5	0.25	0.28	1.03	1.03	41.49	42.13	3.74	3.68	77.21	71.62	983	987	61.6	89.4
x		-3.8	0.20	0.97	0.97	0.97	41.89			3.98		83.81		973		
0	-8.0	-4.0	0.35	0.58	1.12	1.12	43.91	44.57	2.73	2.92	80.21	63.10	985	986	219.4	278.6
0	-5.4	-1.1	0.19	0.23	0.76	0.76	42.73	44.64	2.86	2.82	69.36	49.75	993	994	229.0	287.2
0	-1.4	2.1	0.38	0.45	1.38	1.38	46.78	50.46	2.48	2.11	46.15	30.05	1009	1008	313.3	361.8
0	-0.8	3.4	1.31	0.60	2.90	2.90	47.06	51.42	2.82	3.14	49.17	40.48	1005	1003	322.9	382.7
0	-1.8	2.0	0.24	0.12	1.35	1.35	36.30	39.45	4.38	3.97	82.09	56.48	1002	1003		
0	-0.1	1.5	0.06	0.07	1.10	1.10	36.74	38.89	5.29	5.10	86.10	73.62	984	983		
0	-16.9	-14.5	1.23	1.96	1.76	1.76	36.84	38.25	1.42	1.65	84.86	80.96	977	979		
0	-21.4	-14.5	1.28	1.76	1.18	1.18	33.91	35.46	1.14	1.58	99.70	77.92	982	982		
0	-6.5	-1.6	0.32	0.13	1.03	1.03	37.77	41.26	3.05	3.33	80.49	60.79	994	996	195.8	253.8
½	-7.0	-0.5	0.38	0.40	3.97	3.97	33.84	38.38	2.95	3.01	82.50	51.21	1001	1000	187.3	244.9
0	-6.4	-3.4	0.43	0.24	0.87	0.87	38.04	40.91	2.60	2.04	68.61	42.87	993	992	244.6	296.8
½	-9.1	-5.7	1.67	1.17	1.28	1.28	38.40	42.33	2.09	2.23	67.91	55.09	987	986	212.9	245.5
0	-7.2	-2.6	1.02	0.88	1.31	1.31	43.24	47.69	2.44	1.88	68.07	36.90	987	987	255.5	312.9
0	-8.8	-1.3	0.54	0.38	1.29	1.29	37.37	43.25	2.42	2.65	76.30	47.30	989	989		327.3
0	-6.8	-0.6	0.18	0.07	0.66	0.66	39.71	42.59	2.15	1.83	59.95	31.18	995	994	301.4	354.2
0	-4.3	-0.6	0.18	0.16	0.95	0.95	40.26	44.25	2.24	2.07	50.79	35.32	995	995	309.3	317.1

quently in March, most likely because of intense photochemical activity due to higher UV-radiation in this month. In December no aerosol formation events were observed, probably due to the lack of solar radiation. The number of aerosol formation events increased from January to March. In November, only class 3 events were observed.

Some bio-geo-chemical activity, either according to the eddy flux measurements of CO₂ or H₂O or to the chamber measurements of CO₂, was observed during all aerosol formation event days (Table 1 and Figs. 2 and 3). However, we found no correlation between the occurrence of particle bursts and the daily amounts of CO₂

uptake. The fluxes were higher in the afternoon. There was no observable difference in the CO₂ uptake amounts between the days with aerosol formation events and the days without aerosol events. Photosynthetic activity was observed on nine aerosol event days out of 34 in both the eddy and the chamber data — the chamber CO₂ event days partly overlapped the eddy CO₂ event days (Table 1). Several photosynthetically active days showed no aerosol formation (Fig. 3). These days were all either cloudy or polluted.

The differences in CO₂ exchange between the eddy covariance and the chamber measurements were smaller when their results were compared

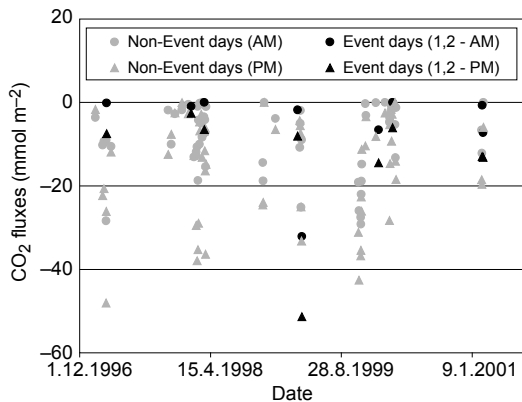


Fig. 2. Integrated values of CO₂ fluxes measured with EC technique for all days with physiological activity during the winter of 1996 to 2001.

within each single year separately than when all the years were combined and the results of each month were compared over all the years. This is probably because the locations of the chambers varied from year to year. The eddy covariance system was also moved from one height to another on two occasions. During wintertime, CO₂ respiration from the soil can be stored in the snow for short periods, and its release can cause CO₂ pulses to the atmosphere. This can lead to differences in the timing of CO₂ fluxes between the eddy covariance and the chamber measuring systems. As stated before, both techniques detected photosynthetic activity on nine aerosol event days, five out of which were the same. So the probability that one system would detect a CO₂ event and the other system would not was around 50% on aerosol event days. The discrepancies between the results of the two systems and the fact that photosynthesis and the net CO₂ uptake are very low in winter support the inclusion of H₂O flux events as indicators of plant-physiological activity. However, increased H₂O fluxes can also arise from evaporation from the surface of snow. Therefore in this paper we speak about bio-geo-chemical events, which include biological activity (mainly photosynthesis) and snow evaporation.

Other relations

The integrated values of O₃ concentration were also calculated both for mornings (08:00–12:00)

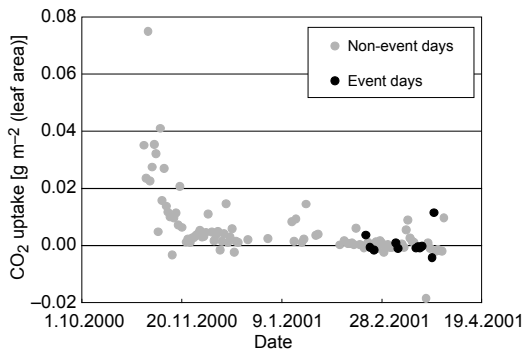


Fig. 3. Integrated values of CO₂ fluxes (uptake) measured with chamber technique for all days with physiological activity in the mornings of winter 2000–2001 (08:00–12:00).

and afternoons (12:00–16:00). These values were divided into two groups: days with and without aerosol formation. However, no correlation between O₃ and aerosol formation events could be recognized.

Further, we analysed different meteorological parameters in order to find out what kind of conditions favour the formation of new particles. We found that on aerosol event days, relative humidity was lower than on non-event days. The aerosol event days were also generally sunnier than the other days. These results agree completely with those of Boy and Kulmala (2002) and indicate that also in the winter months the formation of new aerosol particles only occurs on cloud-free days with low concentrations of water molecules.

Formation and growth rates of aerosol particles

The condensation sink indicates how rapidly vapour molecules condense onto pre-existing particles, whereas the coagulation sink describes how rapidly nanometre-sized aerosol particles are removed through coagulation (Kulmala *et al.* 2001a). By using the DMPS data, it was possible to calculate the condensation sink for vapour molecules and the coagulation sinks for particles with diameters of 1, 2 and 3 nm as a function of time for all days. All sink terms evolve in a similar way in time as has been described in a previous study analysing the data gathered

from Hyytiälä during springtime (Kulmala *et al.* 2001a).

We determined the mean condensation sink for each day with bio-geo-chemical activity. The mean condensation sinks are listed in Table 1 for the period before noon (08:00–12:00), denoted by CS1, and for the afternoon (12:00–16:00), denoted by CS2. A comparison of the condensation sinks in the winter months show a definite increase from January to March. The condensation sink is generally lower on event days. A high condensation sink implies that a large part of the vapour is consumed in condensation and, therefore, a smaller amount is available for the formation of new particles. Thus the probability for an event to occur on a day with a large condensation sink is small.

The formation rate of 3-nm-particles as well as their subsequent growth rate can be estimated from the measured aerosol size distribution data. We restricted our analysis to events classified as 1 or 2, most of which occurred in March. The results, summarised in Table 2, are in agreement with those from an earlier analysis performed for springtime data (Kulmala *et al.* 2001a). In our data, the average monthly growth rates varied only slightly from January to March, but the average formation rates of small particles were clearly higher in the spring. Moreover, only insignificant differences between the properties of class 1 and class 2 events could be seen.

The main mechanism behind the observed growth of small particles is generally suggested to be the condensation of non-volatile organic

compounds on the surface of the particles. However, as no direct empirical information concerning these species has been found, we had to use indirect methods when estimating their properties (Kulmala *et al.* 2001a). Assuming that condensation of a single compound X is responsible for particle growth, the approximate atmospheric concentration level of X and its production rate can be evaluated during the aerosol formation events (*see* Kulmala *et al.* 2001a). The results, summarised in Table 3, agree with our previous calculations (Kulmala *et al.* 2001a). The source rates of species X were typically highest during March, which is the month with the most intense formation bursts. In contrast, there were only small monthly differences in the average concentration of compound X during the aerosol formation events.

From the DMPS-plots, we determined the starting times of the formation events as the time of the day when the bursts of the 3-nm particles were first observed. Most of the events began between 09:00 and 13:00. The formation events started typically later in January than in March (Fig. 4).

Analysis of monoterpenes concentration data

Trees and other plants produce a variety of hydrocarbons, e.g. monoterpenes (α -pinene, camphene, sabinene, 3-carene, β -pinene, limonene and 1,8-cineol). In the atmosphere, monoterpe-

Table 2. Statistic values of aerosol formation and growth rates for all class 1 and 2 events during the five winters 1996 to 2001.

		Event class 1	Event class 2	January	February	March
Formation rate ($\text{cm}^{-3} \text{s}^{-1}$)	Arithmetic mean	0.55	0.57	0.21	0.45	0.65
	Geometric mean	0.47	0.31	0.20	0.27	0.43
	S.D.	0.34	0.83	0.08	0.59	0.76
	Max.	1.35	3.43	0.31	1.86	3.43
	Min.	0.18	0.09	0.16	0.09	0.12
Growth rate (nm h^{-1})	Arithmetic mean	2.37	2.61	2.21	2.68	2.51
	Geometric mean	2.27	2.44	2.16	2.54	2.35
	S.D.	0.78	1.03	0.60	0.90	1.01
	Max.	4.22	5.03	2.90	4.04	5.03
	Min.	1.41	1.26	1.82	1.50	1.26

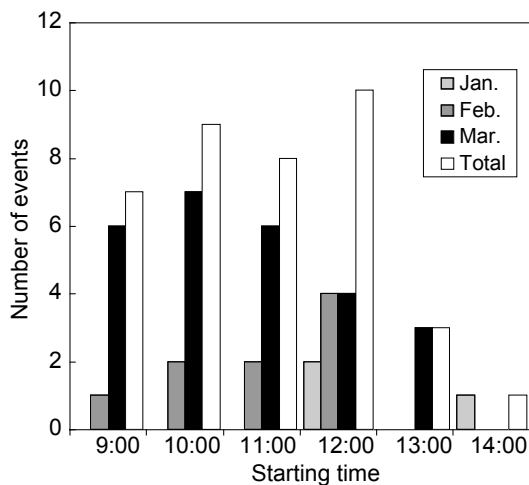


Fig. 4. Starting times of particle bursts for all aerosol formation events in classes 1 and 2.

nes can react with OH, O₃ and NO₃ to produce acids, aldehydes and ketones which all may participate in the formation of new particles (e.g. Seinfeld and Pandis 1998). Hydrocarbon concentrations, measured in Hyytiälä every third or fourth day during the winter 2000–2001, were investigated in order to find a connection between them and the particle formation event days. VOC (volatile organic compounds) measurements were carried out only on four class 1 or 2 event days. The monoterpene measurements were too scarce to shed light on how aerosol pro-

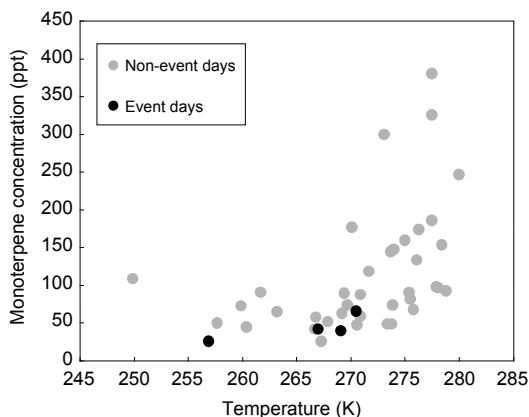


Fig. 5. Temperature against the concentration of monoterpenes for the winter 2000–2001.

duction is connected to monoterpene emissions. Also, the VOC concentrations were usually close to the detection limit of the analysing system.

We also checked whether or not monoterpene concentrations correlated with temperature or photosynthetic activity. A weak correlation with temperature was found (Fig. 5). This dependence is well known for monoterpene emissions (Fuentes *et al.* 2000) and these measurements show that emissions may be dependent on the temperature also during wintertime. There seemed to be a trend that high concentrations of VOCs and relatively high temperatures were correlated with increased CO₂ fluxes (Fig. 6).

Table 3. Statistic values of source rates and the concentration of the condensing organic vapours for all class 1 and 2 events during the five winters 1996 to 2001.

		January	February	March
Source rate of condensing organic vapour (cm ⁻³ s ⁻¹) (CS restricted to morning)	Average	1.2E+04	6.3E+04	9.8E+04
	S.D.	6.0E+03	3.7E+04	1.3E+05
	Max.	1.9E+04	1.2E+05	6.4E+05
	Min.	6.0E+03	1.0E+04	1.3E+04
Source rate of condensing organic vapour (cm ⁻³ s ⁻¹) (CS restricted to afternoon)	Average	1.5E+04	6.3E+04	4.7E+04
	S.D.	9.0E+03	3.4E+04	6.2E+04
	Max.	2.5E+04	1.3E+05	2.9E+05
	Min.	9.0E+03	2.2E+04	5.0E+03
Concentration of condensing organic vapour (cm ⁻³)	Average	3.6E+07	4.4E+07	4.1E+07
	S.D.	1.0E+07	1.5E+07	1.6E+07
	Max.	4.7E+07	6.6E+07	8.2E+07
	Min.	3.0E+07	2.4E+07	2.1E+07

For comparison: Kulmala *et al.* 2001a

Estimated source term: from 7.5E+04 to 1.1E+05 molecules cm⁻³ s⁻¹

Estimated concentration: from 2.5E+07 to 4.0E+07 molecules cm⁻³

However, more continuous measurements of volatile organic compounds are necessary for a comprehensive analysis. However, the influence of monoterpenes on aerosol formation depends not only on their concentrations but also on their oxidation rates, since a significant fraction of oxidation products are condensable (see e.g. Seinfeld and Pandis 1998).

Conclusions

In this work, aerosol formation and bio-geo-chemical activity data obtained from the SMEAR II station (Hyttiälä Forestry Field Station, Finland) during five winters from 1996 to 2001 were analysed. Our aim was to get a better understanding on the interplay between physical, meteorological, biological, geophysical and chemical factors during particle formation events.

Furthermore, we calculated the condensation and coagulation sinks for all the days of the five winters and the formation and growth rates for the obvious aerosol event days. The condensation sink had a minimum in January and the values were smaller on aerosol event days than on non-event days. The formation rates of new particles showed up to a three-fold increase from January to March.

Some bio-geo-chemical activity was observed during all aerosol formation event days. The activity was related either to photosynthesis via CO₂ fluxes or to snow evaporation or plant transpiration via water fluxes. The main question was which one would seem to be more important.

The role of photosynthesis was investigated by several methods. First, we analysed the correlation between the occurrence of aerosol formation events and the daily amount of CO₂ uptake measured with either the eddy covariance system or the chamber technique. However, no correlation was found. Second, we analysed monoterpene concentrations as these compounds are believed to influence particle formation (e.g. Jansson *et al.* 2001). We were able to verify the dependence of the rate of monoterpene emissions on temperature also for wintertime. The suspected correlation between monoterpene concentrations and photosynthetic activity could not be verified, however, because of the lack of a

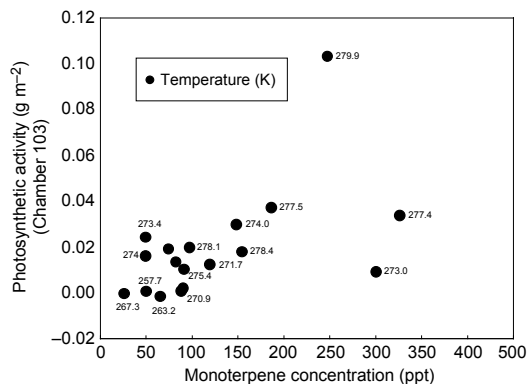


Fig. 6. Photosynthetic activity in the afternoon (measured by chambers) against the concentration of monoterpenes for the winter 2000–2001.

sufficient amount of data. This indicates a need for more measurements during wintertime.

The role of snow in atmospheric chemistry (Domine and Shepson 2002) and also in the formation of atmospheric aerosols (Bigg 1997) has recently been investigated and found to be significant. Our aerosol formation events were typically related to water fluxes. In winter and early spring, increased water fluxes are more likely to be the result of evaporation from the surface of snow than of plant transpiration. Therefore, our present results support the idea that snow evaporation and, more generally, the snow-atmosphere interactions might be important during wintertime aerosol formation events. However, more detailed studies on snow physics and chemistry are needed.

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