Biogenic contributions to the chemical composition of airborne particles in a coniferous forest in Germany

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Abstract

Airborne particles in and above the canopy of a middle European spruce forest were investigated in summer 2001 and in day/night rhythm in summer 2002 near Waldstein site (Fichtelgebirge, Germany).

The particles were size-segregated collected and analyzed for main components (inorganic ions, elemental and organic carbon) as well as oxalic acid and alkanes. A mass closure for the chemical composition including water was performed successfully for both years. For analysis of other organic compounds high volume (HV) samplers were used in order to obtain more particle mass. The HV filter particles were measured with GC/MS after extraction and derivatisation. The highest concentrations were found for the sugars and the dicarboxylic acids. Four terpene acids, pinonaldehyde and isoprene oxidation products were detected. Differences between day and night samples were found for pinonaldehyde (night: 13.7 ng m⁻³; day: 2.7 ng m⁻³), for pinic acid (night: 3.2 ng m⁻³; day: 9.5 ng m⁻³) and also for the 2-methyltetrols (night: 4.0 ng m⁻³; day: 8 ng m⁻³).

The detected terpene and isoprene oxidation products account only for a small part of the measured organic carbon content of particles. In all cases oxalic acid accounts for the major fraction of the speciated organic carbon. The origin of the main components like inorganic ions, OC, and EC is associated with the origin of air masses.

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1. Introduction

Biogenic volatile organic compounds (BVOCs) are estimated to exceed anthropogenic VOC emissions by one order of magnitude on the global scale (Guenther et al., 1995). Deciduous and coniferous trees emit large amounts of reactive non-methane hydrocarbons, mainly isoprene and terpenes into the atmosphere. Apparently, the ambient temperature is one of the most significant factors that influence terpene emissions (Hoffmann and Klockow, 1998). Oxidation of these compounds results in polar compounds with reduced volatility which can condense on existing particles or form new particles.

Production of biogenic secondary organic aerosols on a global basis is estimated to range between 30 and 227 Tg year⁻¹. This is a magnitude comparable to the production of biogenic and anthropogenic sulphate aerosols (Andreae and Crutzen, 1997).

Aerosols produced over forests are of special interest for several reasons. They influence the visibility of the troposphere and can affect the
climate directly by scattering and absorbing of solar radiation. Also they can act as cloud condensation nuclei and influence indirectly the climate (Penner and Novakov, 1996). They are important input variables to models to differentiate between the effects of anthropogenic aerosols and those of the naturally formed particulate matter (PM). Whereas laboratory studies have established that photochemical oxidation of monoterpenes leads to aerosol formation, there are very few field studies detecting such oxidation products in ambient aerosols (Yu et al., 1999; Kavouras et al., 1999a, b, Alves et al., 2000, Matsunaga et al., 2003).

During the last 3 years evidence from both field and laboratory studies has been obtained for the participation of isoprene in secondary organic aerosol (SOA) formation. Isoprene oxidation products with an isoprene skeleton, i.e. 2-methyltetroles, were characterized in Amazonian rain forest aerosols (Claeys et al., 2004). Laboratory studies supporting the contribution of isoprene to SOA formation include the experiments by Jang et al. (2002), who showed that acidic seed aerosol catalyzed SOA formation upon ozonolysis of isoprene, and Limbeck et al. (2003), who demonstrated that exposure of quartz filters impregnated with sulfuric acid to isoprene leads to formation of humic-like substances. It is worth mentioning that based on the laboratory studies by Pandis et al. (1991) isoprene was for a long time thought not to result in SOA formation in the atmosphere.

The described measurements were carried out within the scope of the BEWA 2000 project (Regional biogenic emissions of reactive volatile organic compounds from forests: Process studies, modelling and validation experiments). Two measurement campaigns in summer 2001 and 2002 were performed in a Norway spruce forest. First selected results of the campaign in 2001 have already been published (Plewka et al., 2003). The remaining results of the first campaign in 2001 and all results of the second campaign in 2002 are presented here.

2. Experimental methods

2.1. Sampling

The BEWA2000 field campaigns were carried out in July/August 2001 and 2002 at the forest ecosystem research site Waldstein of the Bayreuth Institute for Terrestrial Ecosystem Research in the Fichtelgebirge mountain range in north eastern Bavaria, Germany. The highest peaks in this mountainous area reach altitudes of up to 1053 m. The measurement equipment was placed on a scaffolding tower with a total height of 30 m. It is situated 776 m asl at 50°09’N and 11°52’E.


The meteorology and air chemistry data (NOx, NH3, and O3) are discussed by Klemm et al. (2006), therefore, in this work only a short description is given. No particle collection was performed on rainy days. The air masses originated in 2001 from sector W to N. In 2002 two different groups were observed: from 20 July 2002 to 23 July 2002 the air masses came in to central Europe from North Sea over the Netherlands and Belgium, between 28 July 2002 and 31 July 2002 the air masses travelled from eastern Europe over the Bohemian basin to the Waldstein site.

2.1.1. Size segregated impactor sampling for ions, alkanes, EC and OC

Two stage low pressure Berner cascade impactors with a flow rate of 75 l min⁻¹ and the aerodynamic cut off diameters of 0.05/0.14/0.42/1.2/3.5/10 μm were used for sampling of particles.

During the 2001 campaign the size segregated particles were collected in 12 and 24 m height in order to detect differences in and below the canopy of the forest. No significant difference could be found for the two sampling heights for the main components. Therefore, during the 2002 campaign size segregated particles were collected only in 12 m height in a day/night rhythm.

The relative humidity (RH) in the impactors during sampling was held constant at about 60% to produce a data set obtained under constant RH. Constant RH from 60% prevents sampling errors due to particle bounce off (Vasiliou et al., 1999), and secondly, allows the sampling of particles of the same air mass on the same stage independent of variation in the ambient RH. Humidity was controlled by a humidity sensor directly before sample air was entering the impactor and regulated by heating or cooling of the inlets. They consisted of a bundle of seven 3/4” stainless steel tubes of 1.5 m length for each impactor (Neusüß et al., 2000).

Tedlar (polyvinyl fluoride) and aluminium foils were used as sample substrates in the impactors for
the analysis of ionic compounds as well as particulate carbon. Tedlar foils were cleaned with diluted H₂O₂ (5%) and deionised water before use. The aluminium foils were heated to 350°C for at least 2 h. For analysis of alkanes two Curie point foils (see Section 3.4) were placed on impactor stage 1–4.

2.1.2. Filter sampling for analysis of organic compounds

The samples for analysis of organic compounds were collected on quartz fibre filters (MK 360, Munktell) with a high volume sampler (DHA-80, Digitel Elektronik Hegnau, Switzerland), equipped with an inlet for particles <2.5 μm. The flow rate was 500 l/min. During the 2001 campaign only day samples with high solar radiation in 12 and 24 m height were collected, see Plewka et al. (2003).

Additionally to the sampling in two different sampling heights in 2001 a day/night rhythm is introduced during the 2002 campaign. Day samples were collected between 10 a.m. and 6 p.m. and the night samples were collected between 10 p.m. and 6 a.m., respectively. Three days, respectively nights were collected on one filter in order to obtain enough particle mass for analysis. Some filters were combined for analysis depending on the collected particle mass.

3. Analysis

3.1. Mass

The particle mass on the impactor foils was determined by weighing the aluminium foils before and after exposure. Before weighing these foils were conditioned at 20 ± 2°C and a constant humidity of 50 ± 5% for at least 48 h. A UMT 2 electronic microbalance (Mettler-Toledo) equipped with a filter set for filters up to 110 mm diameter and with a reading precision of 0.1 μg and a reproducibility of 2 μg was used. The quartz fibre filters were weighed under the same controlled conditions before and after exposure by a Mettler-Toledo AT 261 with a reading precision of 10 μg.

3.2. Ionic compounds and oxalic acid

The ionic compounds were measured from the exposed Tedlar foils. They were cut into small pieces and leached in 1 ml of deionised water by 10 min shaking and 10 min sonicating. The filtrated samples were analyzed by capillary zone electrophoresis (Spectra Phoresis 1000, Thermoquest). The instrument is equipped with a fused silica capillary with an inner diameter of 75 μm and a length of 70 cm. The applied electrical field was 420 V cm⁻¹. A more detailed description of this method is given by Neusüß et al. (2000).

3.3. Organic and elemental carbon (OC/EC)

Carbon was determined with a two-step thermographic method using a carbon analyser C-mat 5500 (Ströhlein). In a first step the aluminium foil with the sample was heated rapidly to 590°C under N₂. Those carbon compounds that evaporate under these conditions are referred to as OC. Elemental carbon (EC) was determined in a second step by heating the sample under O₂ to 650°C whereby all remaining carbon was oxidised to CO₂. Under these conditions all carbon in the first or second step is oxidised and the resulting CO₂ is detected by an NDIR detector. Blank values were subtracted. Under these conditions carbonates were not affected (Petzold and Nießner, 1996). Further details of the carbon analysis are described by Plewka et al. (2004).

3.4. Analysis of alkanes

The alkanes were measured on the Curie point foils using a high temperature thermodesorption method. A Curie point pyrolyzer (JHP-3s, Japan Analytical Industry C., Ltd.) is mounted on a Perkin Elmer gas chromatograph coupled with mass spectrometer. A Fe/Ni alloy (50% Fe, 50% Ni) with a Curie point of 510°C is used as ferromagnetic material. The high volume filter aliquotes with the aerosol mass inside are wrapped in the foils and put in the pyrolyzer. The ferromagnetic foil with the particles is heated very rapidly to the Curie point temperature in the presence of a high frequency magnetic field. The organic compounds were evaporated, not pyrolyzed and introduced by a helium carrier into the GC/MS system (gas chromatography/mass spectrometry). A comparison between the solvent extraction and the thermodesorption with following measurement by GC/MS showed a good agreement and is demonstrated by Neusüß et al. (2000). Perdeuterated tetracosane was added as internal standard on the Curie point foil.

3.5. Single organic compounds from filter samples

The quartz fibre filters were Soxhlet extracted with CH₂Cl₂/MeOH (4:1) for 22 h. The Soxhlet
tubes were extracted with CH₂Cl₂ for 24 h before use to obtain low blank values.

The sample extract was then concentrated to a volume of about 600 µl, measured with a syringe, and then separated into three fractions of about 200 µl each. The first fraction was used for the determination of the nonpolar compounds alkanes, pinonaldehyde and ketones. The polar compounds, like dicarboxylic acids and terpenoic acids were methylated with BF₃-MeOH and measured in the second fraction. The third fraction for the determination of methyltetrols, sugars and alcohols was silylated with BSTFA (N,O-bis(trimethylsilyl)-trifluoracetamide) before the analysis by GC/MS. The silylation reagent contained 1% of the catalyst trimethylchlorosilane. The individual fractions were spiked with 1-chlorohexadecane as internal standard for quantification. Response factors of this internal standard and the organic compounds were determined before and included in the calculation of concentrations. A more detailed description of this method is published by Plewka et al. (2003).

Chemical standard compounds were bought from Sigma Aldrich and Fluka. Cis-norpinic acid was not commercially available. This compound was synthesized by oxidative cleavage of verbenone (Cella, 1983). The reference compounds for the isoprene oxidation products 2-methylthreitol and 2-methylyrithitol were synthesized according to Claeys et al. (2004) from 2-methyl-2-vinyloxirane. For the quantification of the methyltetrols the response factor of erythritol was used, as described in the cited paper. Pinonaldehyde was also not commercially available and synthesized by oxidative bond cleavage of pinanediol with periodic acid (Glasius et al., 1997).

4. Results and discussion

4.1. Particle mass

In Fig. 1(left) the size-segregated mass concentration is shown in (12 m) and above (24 m) the canopy spruce forest for the Golden Days in the 2001 campaign. The mean total PM concentration (PM₁₀) amounted to about 14 (12 m) and 16 µg m⁻³ (24 m). No significant difference between the total mass concentration and the single size ranges could be found between the two sampling heights. Differences on the impactor stages 4 and 5 (1.2/3.5/10 µm) of the time periods 25–27 July 2001 and 28–30 July 2001 could be attributed to local contamination. Also the contribution of the main particle components nitrate, sulphate, ammonium and the sum parameters OC and EC was similar for the two sampling heights.

In Fig. 1(right) the particle mass concentration for the Golden Days measured in 2002 is shown. The average total mass concentration of particles (PM₁₀) resulted about 17 (day) and 16 µg m⁻³ (night). The mean distribution of mass concentration of particle single size ranges (0.05/0.14/0.42/1.2/3.5/10 µm) was found to be about 1.03/0.97, 4.44/4.59, 6.11/6.53, 2.94/2.24, 3.17/2.01 µg m⁻³ for day/night, respectively. The higher mass concentration of the larger particles at day was due to the important high mass content at 21 July 2002 (day) which probably was caused by a local source.

Fig. 1. Size-segregated particle mass concentration on Golden Days in canopy (12 m) and above canopy (24 m) in 2001 (left) and canopy in day (D)/night (N) rhythm in 2002 (right).
A comparison between the gravimetric determined mass with the impactor measurements and number derived mass concentrations, measured with a Differential Mobility Particle Sizer (DMPS) in the size range between 3 and 800 nm is shown by Held (2004). The DMPS measurements and the gravimetric determined mass agree very well, i.e. physical mass closure is achieved.

4.2. Chemical composition and mass closure

The main components nitrate, sulphate, ammonium, OC, EC and the minor ions chloride, sodium, magnesium, potassium and calcium have been measured in size segregated particles in order to elucidate the chemical composition of the particles in the forest. In the Electronic supplemental material (ESM) the measured size-segregated concentrations for particulate mass, Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, Ox\textsuperscript{2−}, Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, OC, EC for the selected Golden Days are listed in Table 1 for 2001 and Table 2 for 2002.

A mass closure was performed with the concentration of all measured ionic and carbonaceous components and the water content of the particles. The sum of these compounds was compared with the weighed particle mass. For the calculation the sum parameter OC was converted to organic material (OM) by a factor of 2.1 (Turpin and Lim, 2001). The water content was roughly estimated by the following approach (Neusüß et al., 2002):

$$m_{\text{H}_2\text{O}} = m_{\text{dry}} \left( \frac{\rho_{\text{wet}}}{\rho_{\text{dry}}} f - 1 \right)$$

with $m_{\text{H}_2\text{O}}$, resulting water content, $m_{\text{dry}}$, chemical estimated mass (ions and carbonaceous material, $\rho_{\text{wet}}$ and $\rho_{\text{dry}}$ density of wet/dry particles.

The volume growth factor for spheric particles is defined by

$$f = \left( \frac{D_{\text{wet}}}{D_{\text{dry}}} \right)^3$$

with $D_{\text{wet}}$ and $D_{\text{dry}}$ diameter of wet and dry particles.

In a first approximation from other measurements for the density ratio $\rho_{\text{wet}}/\rho_{\text{dry}}$ a value of 0.93 and for the volume growth factor $(1.1)^3 = 1.33$ was used (Neusüß et al., 2002). This procedure is not very sensitive for small particles (0.05–0.14 μm) if the carbon content amounts to 50%. The water

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The results are shown in Fig. 2a for the 2001 campaign and in Fig. 2b for 2002. The chemical mass closure can be appreciated as good with an identification of determined particle mass of about 80% for the small particles (0.05–0.42 μm), 100% for the size range 0.42–1.2 μm and 60–80% for the larger particles (1.2–10 μm). The unidentified part for the coarse particles can be attributed to insoluble and not determined crustal material.

Sulphate and ammonium have clearly higher concentrations on the small particles up to 1.2 μm than on the larger particles during both years. In 2001 nitrate and the remaining ionic components are concentrated on the larger particles from 1.2 to 10 μm. The EC fraction is in the small particles (up to 0.42 μm) twice higher than in the larger particles. The reason for the difference between 12 and 24 m height in the size range PM$_{0.05-0.14}$ cannot be explained easily. All components show this effect but only in two out of four measurement periods.

In 2002 (see Fig. 2b) the mean contribution of OM to the particle mass has its highest value of about 50% in the size range of 0.05–0.14 μm. These particles have the largest surface per mass and secondary organic aerosol formed through photo-oxidation of volatile biogenic organic compounds can condense on this large surface. In the other size ranges the OM fraction is in the range between 25% (0.42–1.2 μm) and 35% (1.2–10 μm). The higher mass fraction for the larger particles for OM can be caused by plant detritus and pollen, as well as fungal spores. The average value for the EC content is about 7% with low differences between the size ranges. Sulphate has the highest mass fraction of about 50% in the particle size range 0.42–1.2 μm during day time but in the smallest particles (0.05–0.42 μm) the sulphate fraction is higher at night. The ammonium mass fraction in the smaller particles (0.05–0.42) decreases by a factor of two in the night. This can be explained by lower gaseous concentrations of ammonia during the night, typically 35–65% of the day mixing ratios with one exception on July 29. Nitrate shows the highest mass fraction in the larger particles (1.2–10 μm). The metallic cations and the unidentified material (20–40%) caused by abrasion and dispersion of crustal material have also the largest fraction in the larger particles (1.2–10 μm).

4.3. Organic single species

4.3.1. Size-resolved measurements of alkanes and oxalic acid

Size-resolved measurements for the alkanes were performed with Curie point pyrolysis GC/MS as
thermodesorption method only for the 2001 campaign. During the campaign in 2002 the collected particle mass was too low for the analysis of alkanes because of the shorter sampling time. For the smallest particles in 2001 no alkane were detected due to the very low collected particle mass. In Fig. 3 the alkane concentrations for the particle size range 0.14–1.2 µm are presented. The alkane concentrations vary strongly with the particle size and between the sampling days. The carbon preference index (CPI_{odd}) factors were increasing with particle size, except for the first sampling period, when the alkane concentrations were also higher. This could be a hint at an anthropogenic influence such as combustion of fossil fuels. Combustion of fossil fuels mainly emits the same concentrations of odd and even numbered \( n \)-alkanes, whereas plants release mainly odd numbered \( n \)-alkanes with a concentration maximum from \( C_{29} \) and \( C_{33} \) (Rogge et al., 1993a). These alkanes are contained in waxes on the leaves or needles of the plants. The impact of mechanical forces such as the wind and abrasion by other leaves is thought to be the principal mechanism for the input of plant wax into the atmosphere. This phenomenon may explain the increasing CPI_{odd} factor with increasing particles size, because mechanical abrasion processes emit large particles.
Oxalic acid is the most abundant single organic compound in the analyzed samples. Therefore, size resolved measurements were possible. The concentration in Table 1 was calculated as sum of impactor stages 1, 2 and 3, i.e. for particles in the size range \(0.05–1.2\,\mu m\). The mean size-segregated oxalate concentrations of particles are shown in Fig. 4 in and above the canopy (2001) as well as during day and night (2002). The distribution of oxalate concentration follows the distribution of particle mass and sulphate in the direction \(\text{PM}_{0.42–1.2} > \text{PM}_{0.14–0.42} > \text{PM}_{1.2–3.5}\). A significant difference in and above the canopy was not found. The mean oxalate concentration over the whole particle size range was between 86 and 100 ng m\(^{-3}\) with no significant day/night difference. The interesting observation is made that in the size range 0.14–0.42\,\mu m a tenfold higher concentration of oxalate was found at night. This is consistent with a secondary formation process of this compound but no conclusions can be drawn about its anthropogenic or biogenic origin.

4.3.2. Bulk concentrations of single organic compounds for particles smaller than 2.5\,\mu m

The main focus of the measurements was the identification and quantification of terpene and isoprene oxidation products on particles. Many single organic compounds were detected in the high volume filter samples. The concentrations for all compounds and also the OC concentration, determined from the high volume filter, are listed in Table 1. During the period of 8th to 13th July no night measurement values exist because of problems with the high volume sampler.

4.3.2.1. Pinonaldehyde. Pinonaldehyde was quantified in the gas and particle phase. Table 1 shows the variation of the concentrations of pinonaldehyde on particles during day and night. The concentration of pinonaldehyde on particles was higher during the night. One reason for this observation could be the lower ambient temperatures during the night. Pinonaldehyde is a volatile compound and the gas phase concentration is usually much higher than the particle phase concentration. This fact is clearly demonstrated by gas phase measurements of pinonaldehyde during this measurement campaign (Müller et al., 2006). The gas phase concentrations of pinonaldehyde are up to hundred times higher than the particle phase concentrations. The calculated phase ratios between gas phase and particle phase concentrations of pinonaldehyde and other terpenoidic compounds from this campaign and available literature data are listed in Table 2. Yu et al. (1999), found a gas phase concentration of 280 ng m\(^{-3}\) and a particle concentration of 1 ng m\(^{-3}\) in the San Bernadino National Forest, California.
The night concentrations of pinonaldehyde in the gas phase are also slightly higher than the day concentrations. The averaged gas phase day concentration of pinonaldehyde over the whole filter sampling period was 300 ng m$^{-3}$, whereas the averaged night gas phase concentration was 350 ng m$^{-3}$. One reason for this observation might be the photochemical degradation of pinonaldehyde during daytime. In the presence of sunlight producing OH radicals pinonaldehyde can undergo both photolysis and OH reactions. Its lifetime against the OH radical amounts to a few hours, while its lifetime against the nitrate radical present at night is in the range of a few days (Jaoui and Kamens, 2003). A second possible explanation for the higher night concentration of pinonaldehyde in the gas and particle phase is a formation by nitrate radical chemistry in the night. Berndt and Böge (1997) examined the reaction of nitrate radicals with $\alpha$-pinene and found pinonaldehyde as main product.

4.3.2.2. Terpenoic acids. The cis-isomers of pinic, pinonic and norpinic and norpinonic acid were detected and quantified. The results are shown in Fig. 5 and Table 1. Very small peaks of the other isomers of pinonic and norpinic acid were also detected but not quantified. One isomer of norpinonic acid could be also found. Pinic acid shows the highest concentration of the terpenoic acids. The night concentrations are slightly higher than the day concentrations. One reason for the higher night concentrations of pinic acid could be the lower ambient temperatures during the night. Yu et al. (1999) found approximately 10 times higher gas phase concentrations than particle concentration in San Bernardino National Forest in California. These authors measured pinic acid concentrations of 11.5 ng m$^{-3}$ in the gas phase and 0.5 ng m$^{-3}$ in the particle phase. In contrast, Kavouras et al. (1999a) found concentrations of 0.0–7.10 ng m$^{-3}$ in the gas phase and concentrations of 0.4–4.4 ng m$^{-3}$ in the particle phase. A second reason for the higher night concentrations for pinic acid could be a possible formation by the nitrate radical during the night.

 Except during the first sampling period the concentration of pinic acid was higher above the canopy of the forest than in the forest probably due to the higher actinic radiation.

 No clear trend could be observed for pinonic acid. According to Yu et al. (1999), this compound has also a high gas phase concentration. These authors found a gas phase concentration of pinonic acid of 202 ng m$^{-3}$ and a particle concentration of 0.8 ng m$^{-3}$. Kavouras et al. (1999b) found concentrations for pinonic acid of 0.0–4.65 ng m$^{-3}$ in the gas phase and concentrations of 1–25.7 ng m$^{-3}$ in the particle phase. Bilde and Pandis (2001) measured vapour pressures of pinic, cis-pinonic and trans-norpinic acid. These authors found that the measured vapour pressures fall between those of glutaric and adipic acid. These acids are assumed to predominantly exist in the particle phase rather than in the gas phase. Norpininic and norpinonic acid were also present in all collected aerosol samples. The mass spectrum for norpinonic acid obtained in the present work for a day sample (Fig. 6) was similar to that reported by Koch et al. (2000) and that recorded for a reference compound. The concentrations for norpinic and norpinonic acid are similar and are in the sub ng range. No clear trend could be observed between day and night and the two sampling heights for these acids.

![Fig. 5. Concentrations of terpene acids.](attachment:image)
4.3.2.3. 2-Methyltetrols. The 2-methyltetrols are oxidation products of isoprene, which were discovered by Claeys et al. (2004) in natural aerosols from the Amazonian rain forest and have more recently also been reported for European forest sites (Ion et al., 2005; Kourtchev et al., 2005).

During this field campaign the 2-methyltetrols could be also detected in a norway spruce forest in middle Europe. Table 1 shows the variation of the concentrations of the 2-methyltetrols during day and night and between the two sampling heights. As expected, the concentrations were lower than in the Amazonian rain forest and were found to be in the range between 0.5 and 15.7 ng m$^{-3}$. No clear trend could be observed between the two sampling heights, but the averaged day concentrations (8.4 ng m$^{-3}$) are higher than the night concentrations (4.0 ng m$^{-3}$). The observed day/night difference (factor 2) is similar to that observed in a recent study by Ion et al. (2005) which is in agreement with the suggested formation of these compounds through photooxidation of locally emitted isoprene.

4.3.2.4. Dicarboxylic acids and sugars. The dicarboxylic acids succinic, glutaric, adipic, pimelic, octanedioic and azelaic acid have been quantified from the high volume filter samples. The concentrations of dicarboxylic acids were decreasing with the number of carbon atoms, except for azelaic acid, and are shown in Table 1. No dependency on sampling height and time could be observed, what is in contrast to the generally assumed predominantly photochemical formation of these compounds. The presence of dicarboxylic acids in atmospheric aerosols may result from primary emissions and secondary photochemical reactions. They were detected in automobile exhaust and from meat cooking (Kawamura and Kaplan, 1987; Rogge et al., 1991). Rogge et al. (1993a) also analyzed particulate abrasion products from leaf surfaces of plants and could not found dicarboxylic acids. The most important source for dicarboxylic acids seems to be the photochemical oxidation of organic compounds. This is demonstrated by measurements of Kawamura and Ikushima (1993) and Rogge et al. (1993b). Measurements of dicarboxylic acids in the arctic showed clearly increased concentrations after the arctic sunrise in comparison to the dark period before (Kawamura et al., 1996). This is also a strong indication for a photochemical formation of dicarboxylic acids. Graham et al. (2003) also found generally higher concentrations of short dicarboxylic acids in day time samples than in night time samples of Amazonian aerosol. Azelaic acid originates from the oxidation of the unsaturated fatty acids oleic acid (18:1) and linoleic acid (18:2) (Stephanou and Stratigakis, 1993; Kawamura and Gagosian, 1987). These authors proposed that oleic acid undergoes photochemically induced oxidation yielding $\omega$-oxocarboxylic acids, aldehydes, carboxylic acids, and dicarboxylic acids with predominantly C$_9$ species. These unsaturated fatty acids are emitted to the atmosphere from microbial sources and from the processing, degradation and combustion of plant and animal constituents. Pollen, leaf cells and bacteria also contain unsaturated fatty acids so that the precursors for azelaic acid abound in a forest (Madonna et al., 2001). These facts should be the reason for the high concentrations of azelaic acid found in this study which shows the second highest concentration for the dicarboxylic acids after succinic acid.
High concentrations were also found for the sugar alcohol arabitol and the anhydrosugar levoglucosan. Arabitol is assumed to be associated with primary biological aerosol particles like pollen and fungal spores (Graham et al., 2003). Levoglucosan is known to be derived solely from the breakdown of polysaccharide materials during biomass burning and therefore serves as excellent indicator for the contribution of biomass burning to the overall aerosol mass (Simoneit et al., 1999). In the silylated fraction much more large peaks with the typical mass spectrum for silylated sugars \((m/z: 217; 204)\) were detected but they were not quantified. Other authors also reported high concentrations of saccharidic compounds such as glucose and fructose in summer aerosols (Pashynska et al., 2002) or Amazonian wet season aerosols (Graham et al., 2003) which were attributed to plant pollen.

4.3.2.5. Jasmonic acid and trimethylpentadecanone. Jasmonic acid and its methyl esters are ubiquitous in plants and were detected in all samples. They have hormone properties and help regulating plant growth and they seem to participate in leaf senescence and in the defence mechanism against fungi. To the authors knowledge, jasmonic acid has not been described as an aerosol component until the recent study of Plewka et al. (2003). Trimethylpentadecanone is described in the literature as a photooxidation product of phytol of chlorophyll which has been identified in aerosol particles by Alves et al. (2000).

5. Conclusions

The size-segregated chemical composition of particles in and above the canopy of a coniferous forest in Germany have been measured in a day/night rhythm. The main components like the sum parameters OC and EC and the inorganic ions could be attributed to the origin of air masses by trajectories. The main particle composition appears to be determined by long distance transport in a forest in middle Europe. The organic compounds and the terpene and isoprene oxidation products were of special interest for the presented study. These compounds were extracted from high volume filter samples and after extraction, methylation or silylation measured with GC/MS. Four different terpene acids could be quantified. Pinic acid showed the highest concentrations. Night concentrations were higher than the day concentrations, possibly due to lower ambient temperatures during the night. Except during the first sampling period the concentration of pinic acid was higher above the canopy of the forest than in the forest, caused by the photochemical formation of this compound. No clear trend could be observed for the other terpene acids. As expected, the gas phase concentration of pinonaldehyde was much higher than the particle concentrations. Night concentrations of pinonaldehyde were slightly higher in the gas as well as in the particle phase. In contrast, the averaged day concentrations of the 2-methyltetrols as oxidation products from isoprene were higher than the night concentrations. The concentrations for the dicarboxylic acids were decreasing with the number of carbon atoms, except for azelaic acid. The silylated fraction contained many saccharidic compounds, which were attributed to plant pollen and fungal spores. For future work attention should be focused on simultaneous gas phase measurements of the terpenoic acids. The existing literature data are very controversial and therefore not helpful for interpretations. A further point is that the measured photooxidation products of \(\alpha\)-pinene and isoprene only contribute to a small fraction of the OC in a forest aerosol. Biogenic volatile organic compounds emitted by trees can also form oligomeric humic-like substances after photooxidation. These oligomeric substances cannot be measured with GC/MS. Furthermore, bioaerosols such as plant pollen and fungal spores play an important role for the OC mass. The saccharidic compounds that are characteristic for fungal spores and the sugars that are characteristic for plant pollen represent only a small fraction of the OC in these bioaerosols. The rest is biopolymeric material and cannot be analyzed with techniques such as GC/MS, too.

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Appendix A. Electronic supplemental material

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References


