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Semi-empirical parameterization of size-dependent atmospheric nanoparticle growth in continental environments

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Abstract

The capability to accurately yet efficiently represent atmospheric nanoparticle growth by biogenic and anthropogenic secondary organics is a challenge for current atmospheric large-scale models. It is, however, crucial to predict nanoparticle growth accurately in order to reliably estimate the atmospheric cloud condensation nuclei (CCN) concentrations. In this work we introduce a simple semi-empirical parameterization for sub-20 nm particle growth that distributes secondary organics to the nanoparticles according to their size and is therefore able to reproduce particle growth observed in the atmosphere. The parameterization includes particle growth by sulfuric acid, secondary organics from monoterpene oxidation ($SORG_{MT}$) and an additional condensable non-monoterpene organics ("background"). The performance of the proposed parameterization was investigated using ambient data on particle growth rates in three size ranges (1.5–3 nm, 3–7 nm and 7–20 nm). The growth rate data was acquired from particle/air ion number size distribution measurements at six continental sites over Europe. The longest time series of 7 yr (2003 to 2009) was obtained from a boreal forest site in Hyytiälä, Finland, while about one year of data (2008–2009) was used for the other stations. The extensive ambient measurements made it possible to test how well the parameterization captures the seasonal cycle observed in sub-20 nm particle growth and to determine the weighing factors for distributing the $SORG_{MT}$ for different sized particles as well as the background mass flux (/concentration). Besides the monoterpene oxidation products, background organics with a concentration comparable to $SORG_{MT}$, around 6×10^7 cm^{-3} (consistent with an additional global SOA yield of 100 Tg yr^{-1}) was needed to reproduce the observed nanoparticle growth. Simulations with global models suggest that the "background" could be linked to secondary biogenic organics that are formed in the presence of anthropogenic pollution.

1   Introduction

Atmospheric aerosol particles affect our life multiple ways – they can cause adverse health effects (Nel et al., 2005), reduce visibility (Cabada et al., 2004), and affect the Earth's climate. Aerosols influence climate directly by scattering and absorbing solar radiation (Bohren and Huffman, 1983) and indirectly via cloud formation (Ramanathan et al., 2001). Sufficiently large aerosol particles with dry diameters of around 70 nm (Dusek et al., 2006) can act as cloud condensation nuclei (CCN) and form cloud droplets. Cloud properties are affected by the composition and concentration of CCN (Rosenfeld et al., 2008) whereas the concentration of CCN depends strongly on the atmospheric aerosol size distribution (Pierce and Adams, 2007).

The formation of new aerosol particles from vapors has been observed frequently in the atmosphere (Kulmala et al., 2004; Kulmala and Kerminen, 2008), and the subsequent growth of the newly formed particles to CCN sizes is common in many types of continental boundary layers (Kerminen et al., 2012). Atmospheric modeling suggests that new particle formation is an important source of global CCN (Spracklen et al., 2008; Merikanto et al., 2009). However, gaps in our understanding of particle formation and growth processes bring uncertainty to the quantitative estimation of CCN production from new particle formation (Spracklen et al., 2008; Pierce and Adams, 2009). The growth of freshly-formed nanoparticles by vapor condensation is a major factor determining whether these particles reach sizes where they can act as CCN and influence climate (Kulmala et al., 1998; Kerminen and Kulmala, 2002; Kuang et al., 2009). This growth needs to be represented accurately enough in atmospheric models to yield correct predictions of the contribution of atmospheric new particle formation to CCN concentrations (Riipinen et al., 2011).

Ambient and laboratory studies have shown that sulfuric acid participates in the first steps of new particle formation (Weber et al., 1996; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Sipilä et al., 2010; Vehkamäki and Riipinen, 2012; Kulmala et al., 2013), but sulfuric acid condensation is not enough to reproduce particle growth

rates observed in the ambient conditions (Kuang et al., 2010; Sipilä et al., 2010; Pierce et al., 2011, 2012a; Riipinen et al., 2011, 2012; Kulmala et al., 2013). Therefore other compounds, e.g. organics or ammonia/amines, are expected to be important already in the early growth of freshly nucleated particles (O'Dowd et al., 2002; Smith et al., 2005,

5   2008; Pierce et al., 2011; Riipinen et al., 2012; Vehkamäki and Riipinen, 2012; Kulmala et al., 2013). Several recent studies point to the importance of organic compounds in growing atmospheric nanoparticles to climatically relevant sizes (e.g. Kulmala et al., 1998; Kuang et al., 2010; Yli-Juuti et al., 2011; Riipinen et al., 2012 and references therein), and capturing this organic contribution has been shown to be important for

10 CCN predictions on regional scale (Riipinen et al., 2011).

Oxidation of volatile organic compounds (VOCs) and their subsequent condensation to the particulate phase is known to be an important source of atmospheric aerosol mass. The aerosol constituents formed through these oxidation reactions and their subsequent condensation to the particulate phase are called secondary organic aerosol

15 (SOA). Traditionally biogenic VOCs (BVOC), such as monoterpenes (MT) and isoprene, are thought to be the dominant source of atmospheric SOA (e.g. Kanakidou et al., 2005; Hallquist et al., 2009), but recent studies suggest also a notable anthropogenic contribution to SOA formation (Volkamer et al., 2006; Zhang et al., 2007; Heald et al., 2011; Hoyle et a., 2011; Spracklen et al., 2011).

20 The capability of an SOA component to grow a nanoparticle to CCN-sizes depends on the volatility, i.e. the evaporation tendency, of the compound, as well as the size and composition of the particle (see, e.g. Pierce et al., 2011; R. Zhang et al., 2012; Vehkamäki and Riipinen, 2012 and references therein). The contribution of SOA to nanoparticle growth would thus be straightforward to calculate if the identities and

25 volatilities of the organic compounds constituting SOA would be known. This is unfortunately not the case. There are thousands of different organic compounds in the atmosphere and their properties are difficult to constrain (Goldstein and Galbally, 2007; Hallquist et al., 2009) – this applies particularly to the compounds with the lowest volatility which are most likely to grow the smallest particles (e.g. Pierce et al., 2011). The

volatility assumed for the SOA in atmospheric models affects significantly the way this condensing material modifies the atmospheric aerosol size distribution (see, e.g. Riipinen et al., 2011; Donahue et al., 2011; X. Zhang et al., 2012). Current atmospheric large-scale models differ considerably in the ways they treat the condensation of SOA:

5　some assign the SOA a range of volatilities but assume it to be in thermodynamic equilibrium (Yu and Luo, 2009) while others assume the SOA to be completely non-volatile (Spracklen et al., 2005a,b; Pierce and Adams, 2009; Makkonen et al., 2012). The former approach tends to underestimate the growth of freshly-formed nanoparticles (and thus their contribution to CCN), while the latter is expected to somewhat overpredict it

10　if the total SOA is correctly predicted by the model (Riipinen et al., 2011). Approaches that capture the contribution of SOA to atmospheric nanoparticle growth in a simple yet physically and chemically reasonable manner are needed to improve atmospheric models.

Several recent observations from different field sites suggest that the condensational

15　growth rates of ambient nanoparticles increase with particle size (Hirsikko et al., 2005; Manninen et al., 2010; Yli-Juuti et al., 2011; Kuang et al., 2012). Yli-Juuti et al. (2011) also observed a correlation between monoterpene concentrations and 7–20 nm particle growth in the boreal forest site of Hyytiälä, Finland – indicating the importance of monoterpene oxidation products in the growth process. Also a clear seasonal variation

20　in the growth of 3–20 nm particles was observed in Hyytiälä, with highest values during the summer (Dal Maso et al., 2005; Hirsikko et al., 2005; Riipinen et al., 2011; Yli-Juuti et al., 2011). The growth of the smallest sub-3 nm particles in Hyytiälä, on the other hand, has not been observed to show such seasonality (Hirsikko et al., 2005; Yli-Juuti et al., 2011).

25　In this paper we introduce a simple semi-empirical parameterization for distributing monoterpene-SOA onto aerosol particle populations in a way that it reproduces sub-20 nm particle growth. The parameterization is aimed to be simple enough to be used in large-scale atmospheric models. The size-dependent parameterization includes condensational growth of particles by sulfuric acid, secondary organics from monoterpene

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oxidation (SORG$_{MT}$) and an additional condensing (presumably organic) species. The parameterization is based on data on atmospheric nanoparticle growth rates from six field sites: the boreal forest site of Hyytiälä (seven years of particle growth data) and a year worth of data from five other European field stations. The sensitivity of the parameterization to the input concentrations of sulfuric acid and monoterpenes (and their oxidation products) is tested, and its implications and potential for use in atmospheric models is discussed.

2 Materials and methods

2.1 Theoretical approach

2.1.1 Growth parameterization

To parameterize the seasonality and size-dependence of nanoparticle growth rates, we express the total condensational mass flux (in $kg\,s^{-1}$) onto a particle with diameter d_p as a sum of the mass fluxes of sulfuric acid and organics:

$$I_{tot}(d_p) = I_{SA}(d_p) + k_{MT}(d_p) \cdot I_{SORG,MT}(d_p) + k_{bg}(d_p) \cdot I_{SORG,bg}(d_p), \tag{1}$$

where I_{SA} is the mass flux caused by sulfuric acid, $I_{SORG,MT}$ is the maximum mass flux by monoterpene first-order oxidation products (denoted as SORG$_{MT}$), and $I_{SORG,bg}$ is the mass flux from other condensable compounds, presumably organics that have not originated from monoterpene oxidation and do not have a seasonal dependence (denoted as SORG$_{bg}$). $k_{MT}(d_p)$ and $k_{bg}(d_p)$ are weighing factors describing the fractions of $I_{SORG,MT}$ and $I_{SORG,bg}$ that condense onto nanoparticles having diameter d_p, and have values between 0 and 1. Figure 1 illustrates the processes that are accounted for in our analysis – formation of condensable vapors and their condensation onto nanoparticles.

One of the aims of this work is to present a semi-empirical approach that is usable in large-scale models, and thus Eq. (1) is a highly simplified representation of the reality

and contains several assumptions. First, I_{SA}, $I_{SORG,MT}$ and $I_{SORG,bg}$ are calculated assuming totally non-volatile vapors, which is certainly an approximation but in line with the way that many global models treat the condensation of sulfuric acid and organics onto nanoparticles (e.g. Spracklen et al., 2005a,b; Pierce and Adams, 2009). For

5 sulfuric acid this assumption is probably reasonable, as its saturation vapor pressure is known to be extremely low in atmospheric conditions (see, e.g. Kulmala and Laaksonen, 1990). For organic species with varying volatilities this assumption may cause problems (Pierce et al., 2011), as small particles reach equilibrium more quickly than large particles (due to Kelvin effect and the larger surface-area/volume ratio in small

10 particles); thus, the condensable fraction of $SORG_{MT}$ as well as $SORG_{bg}$ can depend strongly on particle size. This effect is indirectly taken into account with the k values in Eq. (1). Furthermore, $I_{SORG,MT}$ is calculated based on the first-order oxidation products of monoterpenes and thus represents the maximum possible mass flux of $SORG_{MT}$ from the first-stage oxidation. This assumption as well is in line with what many of the

15 global models assume. Another key assumption is the presence of the "background organics" mass flux $I_{SORG,bg}$, which is constant throughout the year and represents all the condensable material that is not sulfuric acid or $SORG_{MT}$ (or at least not correlated with them). There are several hints pointing to the importance of the additional mass flux in Eq. (1). It is clear that not all condensable organics originate from or corre-

20 late with monoterpenes (Spracklen et al., 2011). While BVOCs are probably the most important source of SOA in continental environments, there are also anthropogenic impacts on SOA formation (see, e.g. Hoyle et al., 2011 and references therein). For instance, Spracklen et al. (2011) found that the SOA mass estimated using traditional SOA sources (i.e. monoterpenes, isoprene, biomass burning and the aging of primary

25 organic aerosol) was low compared to ambient observations, and a large additional SOA source – correlated with anthropogenic CO sources – was needed to explain the observations. $I_{SORG,bg}$ could represent this "extra SOA". We will show that this type of additional contribution is needed to reproduce the observed growth rates of atmospheric nanoparticles.

Mass fluxes I_{tot}, I_{SA} and $I_{SORG,MT}$ in Eq. (1) were determined using ambient observations complemented with data from chemical transport model GLOMAP (Global Model of Aerosol Processes, Spracklen et al., 2008). The mass fluxes (/vapor concentrations) of the background species, $I_{SORG,bg}$, and the k values (k_{MT} and k_{bg}) were obtained through least-square method by fitting Eq. (1) to the ambient data on sub-20 nm particle growth. Above 20 nm the SORG$_{MT}$ was assumed to condense kinetically, i.e. assuming no evaporation from the particles, and thus a weighing factor (k_{MT}) of unity. Also for the "background", the k_{bg} for 7–20 nm size range and above was assumed unity. The details of the fitting procedure are outlined in the following sections.

2.1.2 Mass fluxes

The condensation onto atmospheric nanoparticles is observed as an increase in their size, and often quantified with the diameter growth rate (GR, in ms^{-1} or nmh^{-1}). The relation between GR and I_{tot} for particles with diameter d_p and density ρ_p (see Table 1) is

$$I_{tot}(d_p) = \frac{1}{2}\pi\rho_p d_p^2 GR(d_p). \tag{2}$$

In this study I_{tot} was obtained using size-dependent particle growth rates (for size ranges 1.5–3 nm, 3–7 nm, 7–20 nm) determined from ambient particle/ion number size distributions (see Sect. 2.2.1). The particle diameters used to represent the three size classes were 2 nm, 5 nm and 14 nm, respectively.

The mass fluxes of sulfuric acid and SORG$_{MT}$ onto nanoparticles were calculated using the approach presented by Lehtinen and Kulmala (2003) (also Nieminen et al., 2010), where the mass flux of a condensable vapor v (kgs^{-1}) is written as

$$I_v(d_p) = 2\pi(d_v + d_p)(D_v + D_p(d_p))\beta_m(\alpha_m, Kn)m_v C_v, \tag{3}$$

where d_v, D_v and m_v are the diameter, diffusion coefficient and mass of the vapor molecule, respectively. D_p is the diffusion coefficient of a particle with diameter d_p and

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C_v is the molecular concentration of the vapor. β_m is the correction factor for transition regime mass transfer (Fuchs and Sutugin, 1971)

$$\beta_m(\alpha_m, Kn) = \frac{1 + Kn}{1 + \left(0.377 + \frac{4}{3\alpha_m}\right)Kn + \frac{4}{3\alpha_m}Kn^2}, \tag{4}$$

where α_m is the mass accommodation coefficient and Kn is the Knudsen number. Kn is defined as (Lehtinen and Kulmala, 2003)

$$Kn = \frac{2\lambda}{d_v + d_p}, \tag{5}$$

where λ is the mean free path

$$\lambda = \frac{3(D_v + D_p)}{\sqrt{\overline{c_v}^2 + \overline{c_p}^2}}, \tag{6}$$

in which $\overline{c_v}$ and $\overline{c_p}$ are the mean thermal speeds of the vapor molecule and the particle, respectively. The equations that were used for determining the mean thermal speeds and diffusion coefficients of molecules and particles are shown in Appendix A. Values for the parameters used in Eqs. (3)–(6) for determining $I_{SA}(d_p)$ and $I_{SORG,MT}(d_p)$ are given in Table 1. The background vapor was assumed to have the same properties as the SORG$_{MT}$. Parameter values were converted to SI-units before substitution to the presented equations.

2.2   Data sets

2.2.1   Particle growth rates

Sub-20 nm particle growth was investigated in Hyytiälä, Finland during 2003–2009 (Yli-Juuti et al., 2011 and Table 2) and at five other sites around Europe during 2008–2009

as a part of EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality interactions, see Kulmala et al., 2011) project (Manninen et al., 2010 and Table 2). In addition to Hyytiälä, the other European sites were in Melpitz (Germany), Hohenpeissenberg (Germany), Vavihill (Sweden), Finokalia (Greece) and K-puszta (Hungary). All the stations were background sites with slightly different characteristics. The environments varied from relatively clean boreal forest site (Hyytiälä, Vesala et al., 1998; Kulmala et al., 2001a; Hari and Kulmala, 2005) to more polluted rural areas (Melpitz, Vavihill and K-Puszta) and from a site with marine influence (Finokalia) to a high-altitude station (Hohenpeissenberg). More detailed information on the EUCAARI measurement stations can be found in Manninen et al. (2010).

Particle growth rates were determined for three size ranges, 1.5–3 nm, 3–7 nm and 7–20 nm, from ambient particle/air ion number size distributions measured with an AIS (Air Ion Spectrometer, Mirme et al., 2007) and a NAIS (Neutral cluster and Air Ion Spectrometer). In Hyytiälä also DMPS (Differential Mobility Particle sizer, Aalto et al., 2001) and BSMA (Balanced Scanning Mobility Analyzer, Tammet, 2006) data were included in the analysis. DMPS can detect small particles down to 3 nm sizes and therefore particle growth in the size ranges of 3–7 nm and 7–20 nm could be determined. Using BSMA data particle growth in 1.5–3 nm and 3–7 nm was determined. Growth rates were obtained using an approach described in detail by Hirsikko et al. (2005) – maximum particle/ion concentration of every size bin was followed through particle growth. More information on the growth rate analysis can be found in Yli-Juuti et al. (2011) for Hyytiälä and in Manninen et al. (2010) for the other EUCAARI sites. Monthly medians of the GR values were used for all further analysis since they are expected to describe well the average growth process of newly formed particle. Monthly GRs could not be determined for each month for each station due to the small amount of data (around one year of observations) for the sites except for Hyytiälä. However, all the stations had at least six months of GR data (Hyytiälä 12 months corresponding to in total 421 GR data points, Melpitz 6 months and 30 data points, Hohenpeissenberg 9 months and

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17 data points, Vavihill 7 months and 22 data points, Finokalia 9 months and 17 data points, and K-puszta 11 months and 68 data points).

2.2.2 Concentration of sulfuric acid

To investigate the sensitivity of our approach to the gas phase concentrations of sulfuric acid (C_{SA}), we tested two different approaches for estimating C_{SA} in Hyytiälä: a calculation with GLOMAP (Spracklen et al., 2005a,b) and a sulfuric acid proxy presented by Petäjä et al. (2009) (see Table 2) expressed as

$$C_{SA} = k_{SA} \frac{C_{SO_2} \cdot UVB}{CS}, \qquad (7)$$

where $k_{SA} = 8.4 \times 10^{-7} \cdot UVB^{-0.68} \, m^2 \, W^{-1} \, s^{-1}$, C_{SO_2} is the concentration of SO$_2$, UVB is the intensity of ultra-violet radiation, and CS is the condensation sink for sulfuric acid molecules calculated from the particle number size distribution (DMPS) data (see, e.g. Kulmala et al., 2001b). For the other European stations sulfuric acid concentrations were obtained directly from GLOMAP.

2.2.3 Concentration of SORG$_{MT}$

To test the robustness of our approach with respect to variations in the concentrations of the monoterpenes and their oxidation products, three different sources of data were used for monoterpene concentrations in Hyytiälä: GLOMAP simulations for the year 2008 using GEIA database based on MEGAN (Model of Emissions of Gases and Aerosols from Nature, Guenther et al., 1995) for monoterpene emissions, observations with the PTR-MS (Proton Mass Transfer Mass Spectrometer, Lindinger et al., 1998) that was operating during 2007–2009, and a semi-empirical parameterization for monoterpene concentrations based on ambient temperatures (Lappalainen et al., 2009; see Table 2). Concentrations of SORG$_{MT}$, were then determined using the monoterpene concentrations. This results in altogether five different data sets for the concentrations

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of SORG$_{MT}$ in Hyytiälä: one directly from GLOMAP with the complete gas phase chemistry, emissions and losses included, one assuming that condensable SORG$_{MT}$ corresponds to 1 % of the monoterpene concentrations from GLOMAP (estimated comparing the concentrations of MT and SORG$_{MT}$ from GLOMAP), and three from calculations based on ambient concentrations of O$_3$ and OH combined with monoterpenes from GLOMAP, PTR-MS or the temperature-dependent parameterization by Lappalainen et al. (2009). For the other European sites concentrations of SORG$_{MT}$ were obtained directly from GLOMAP.

Concentrations of SORG$_{MT}$ can be calculated based on the oxidation rates of monoterpenes with O$_3$ and OH-radical, yielding the steady-state concentrations of the first-order oxidation products

$$C_{\text{SORG,MT+OH}} = \frac{k_{\text{OH}} \cdot C_{\text{OH}} \cdot C_{\text{MT}}}{\text{CS}} \text{ and}$$
$$C_{\text{SORG,MT+O}_3} = \frac{k_{\text{O}_3} \cdot C_{\text{O}_3} \cdot C_{\text{MT}}}{\text{CS}}, \tag{8}$$

where $k_{\text{OH}} = 7.5 \times 10^{-11}\,\text{cm}^3\,\text{molec}^{-1}\,\text{s}^{-1}$ and $k_{\text{O}_3} = 1.4 \times 10^{-17}\,\text{cm}^3\,\text{molec}^{-1}\,\text{s}^{-1}$ are rate constants determined specifically for monoterpene oxidation in Hyytiälä (Hakola et al., 2003; Yli-Juuti et al., 2011), C_{MT} is the monoterpene concentration and C_{O_3} and C_{OH} are the concentrations of O$_3$ and OH-radical, respectively. C_{O_3} was obtained from mast measurements in Hyytiälä. C_{OH} was calculated with the parameterization by Petäjä et al. (2009)

$$C_{\text{OH}} = \left(\frac{c}{a}\text{UVB}^{0.3}\right)^{0.52^{-1}}, \tag{9}$$

where $a = 8.6 \times 10^{-10}$ and $c = 1.4 \times 10^{-7}$. The total concentration of SORG$_{MT}$ ($C_{\text{SORG,MT}}$) was calculated by adding up $C_{\text{SORG,MT+OH}}$ and $C_{\text{SORG,MT+O}_3}$. We thus define SORG$_{MT}$ as the steady-state concentration of the monoterpene first-order oxidation products, and assume that the growing nanoparticles do not contribute significantly

to the condensation sink CS. This is a reasonable assumption for most atmospheric background sites.

Only daytime values (09:00–15:00 LT) of sulfuric acid and $SORG_{MT}$ concentrations were included in the analysis to represent the conditions during particle formation events that usually occur during day (Kulmala et al., 2004; Yli-Juuti et al., 2011). For the parameterization analysis, monthly median vapor daytime concentrations were used. Due to good data coverage for sulfuric acid, daytime concentrations during new particle formation days were used whereas for $SORG_{MT}$, daytime concentrations of all the available data (including days with observed particle formation as well as days when no new particles were formed) were used.

2.3 Fitting to ambient data

Size-dependent weighing factors for distributing the $SORG_{MT}$ to sub-20 nm particles (k_{MT} values in Eq. 1) and the mass fluxes of additional condensable vapors were estimated by fitting Eq. (1) to the ambient data. Ambient growth rates were used to determine the total mass fluxes in the three size classes (1.5–3 nm, 3–7 nm and 7–20 nm) and the concentrations of sulfuric acid and $SORG_{MT}$ were used to determine I_{SA} and $I_{SORG,MT}$. Fitting was done separately for the three size ranges using a least-squares method (function *lsqcurvefit* in Matlab) with a relative tolerance of 10^{-15}. The k_{MT} values for distributing the $SORG_{MT}$ were limited between 0 and 1, and the $I_{SORG,bg}$ was allowed to get any positive values. Based on the $I_{SORG,bg}$ and corresponding vapor concentrations (obtained using Eq. 3), weighing factors (k_{bg}) for distributing the $SORG_{bg}$ were estimated assuming that $I_{SORG,bg,7-20}$ is at the kinetic limit. Initial guesses for the k_{MT} values and/or for the $I_{SORG,bg}$ did not affect the fitting results, i.e. all the fits converged to a unique solution.

The fitting was done both using the Hyytiälä data alone (altogether 7 yr of GR data) and data from the six European sites including Hyytiälä. The mass flux fits were done to 12 data points. For Hyytiälä, the differently defined concentrations of sulfuric acid

and SORG$_{MT}$ were used to test the performance of the parameterization and to test its sensitivity to the input data. The EUCAARI data was used to obtain parameterization with weighing factors, k_{MT} and k_{bg}, and background concentration, $C_{SORG,bg}$ (corresponding $I_{SORG,bg,7-20}$), representative of the sub-20 nm particle growth on a broader
5 continental scale.

3   Results

3.1   Growth parameterization using seven years of data from Hyytiälä

3.1.1   Seasonal variation of SORG$_{MT}$ and sulfuric acid concentrations

Figure 2 illustrates the monthly medians of the concentrations of SORG$_{MT}$ and sulfuric
10 acid. The highest sulfuric acid concentrations were observed during spring time, and in general the concentrations of sulfuric acid were lower than those of SORG$_{MT}$. The two approaches for obtaining the sulfuric acid concentrations (GLOMAP calculations and the proxy using Eq. 7) gave very similar results, especially taking into account that the GLOMAP data represents a 2.8° × 2.8° grid box around Hyytiälä, while the
15 proxy calculation is based on in-situ data. In the fittings for Hyytiälä, the two data sets were combined and average concentration was used (the gray curve in Fig. 2). Due to larger amount of sulfuric acid data from proxy calculations the average sulfuric acid concentration was closer to that calculated with the proxy.

The seasonal pattern in the differently defined concentrations of SORG$_{MT}$ was simi-
20 lar, the concentrations peaking in the summer. The seasonal variation in SORG$_{MT}$ was less pronounced using the measured monoterpene concentrations or the temperature-dependent measurement-based parameterization, as compared with the values obtained from GLOMAP. The difference between the approaches was greatest during winter. It should be also noted that only biogenic emissions are taken into account in
25 GLOMAP as well as in the temperature-dependent parameterization. In Hyytiälä there

are also some monoterpene emissions of anthropogenic origin, for instance because of a sawmill nearby (Liao et al., 2011).

The concentrations of $SORG_{MT}$ determined using the monoterpene data from GLOMAP were in close agreement with each other (see Fig. 2). The small differences can be explained by the differences in the O_3, OH concentrations and the condensation sink (CS) used in the calculations. The variations are reasonable, since the model is not expected to capture the local changes in oxidant or aerosol concentrations that are observed with on-line measurements. There was a high peak in the $SORG_{MT}$ concentrations obtained directly from the GLOMAP in November (see Fig. 2). This peak was removed from the data analysis.

3.1.2 Parameterization with differently calculated concentrations of $SORG_{MT}$

The weighing factors (k_{MT}) for distributing the $SORG_{MT}$ obtained from the mass flux fits using the five different data sets for the $SORG_{MT}$ for Hyytiälä (see Fig. 2 and Sect. 2.2.3) are presented in Table 3. While the mass flux fit showed some sensitivity to the input organic mass flux ($I_{SORG,MT}$), relatively similar results and behavior were obtained using the different $SORG_{MT}$ data sets: the smallest particles were not growing by $SORG_{MT}$ but by sulfuric acid and the "background" condensing species, due to the lack of seasonal variation in the observed GRs ($k_{MT,1.5-3}$ was 0 for all the data sets) (see Fig. 3 for the observed seasonal behavior of GRs). The k_{MT} values for 3–7 and 7–20 nm particles ranged from 0.2 to 0.4 and from 0.6 to 1, respectively. The largest particles were thus affected most by the $SORG_{MT}$ condensation. The vapor concentration, $C_{SORG,bg}$, calculated based on the background mass flux $I_{SORG,bg,7-20}$ was of the same order of magnitude (10^7 cm^{-3}) using different data sets (see Table 3). Weighing factors (k_{bg}) for distributing the $SORG_{bg}$ are also presented in Table 3.

The monthly growth rates obtained from the mass flux fit for the three size ranges (1.5–3 nm, 3–7 nm and 7–20 nm) using the concentrations of $SORG_{MT}$ calculated using monoterpene concentrations from GLOMAP are presented in Fig. 3 (upper panel, see

Table 3 for the fitting parameters). The ambient growth rates observed during 2003–2009 in Hyytiälä are shown for comparison. The fit produced the seasonal pattern of particle growth rates well – the highest growth rates were observed during summer months in particle sizes 3–7 nm and 7–20 nm whereas the growth of the smallest particles (1.5–3 nm) was independent on the season.

A line was fitted to the (GR_{fit}, GR_{obs})-data to determine how close the data points were to a 1 : 1 line (described by the slope of the fitted line) and whether there was a systematic bias in the fitted growth rates (the intercept of the fitted line). The values of the slope and the intercept for each of the fitted cases are given in Table 3, along with the Pearson correlation coefficients and their p values for the fitted vs. observed growth rates of all the size ranges combined. We chose the simple Pearson correlations for the statistical analysis since no autocorrelation between the observed GRs was found. The correspondence between the GR_{obs} and GR_{fit} was generally very good: the slopes of the fitted lines varied between 1.0 and 1.4, and the systematic biases were less than 1 nm h^{-1} (for 4 cases out of 5 less than 0.3 nm h^{-1}). These variations are similar to or less than the typical uncertainty in the observed GR values due to the experimental uncertainties and data analysis method (see Yli-Juuti et al., 2011; Leppä et al., 2013).

The correspondence between the GR_{obs} and GR_{fit} using $SORG_{MT}$ (calculated with GLOMAP) is shown in Fig. 3 (lower panel) for all the available data (monthly median GR_{obs} separately from years 2003–2009). The reason for the accumulation of the data points is that GR_{fit} is getting only one value per month (k_{MT}, k_{bg} and $C_{SORG,bg}$ determined using monthly medians of $SORG_{MT}$ over a single year) while the monthly median GR_{obs} changes through years. There was a clear positive correlation between the fitted and observed GRs accounting all the GR data from different size ranges ($R = 0.80$, $p < 10^{-5}$). In general the correlation between the fitted and observed GRs in a certain size range was the better the more variability GRs showed, i.e. the best correlation was observed in the 7–20 nm size range ($R = 0.81$, $p < 10^{-5}$). For the smallest size class correlation was the poorest ($R = -0.15$, $p = 3 \times 10^{-1}$) even though the fitted GRs clearly corresponded to those observed (see Fig. 3). The correspondence between the GR_{obs}

and GR$_{fit}$ was very good – data points were aligned on the 1 : 1 line. These results show that the fit is able to capture the observed growth rates and their seasonal pattern in Hyytiälä. The good agreement shows that the seasonal variability is clearly more important in determining the growth rates as compared with the interannual variability
5 (represented by the y-directed scatter in the data in Fig. 3).

To test the robustness of Eq. (1) as a parameterization function, the fits were also performed setting the $I_{SORG,MT}$ and the $I_{SORG,bg}$ to zero one at a time. Neither the SORG$_{MT}$ nor the SORG$_{bg}$ could produce the observed GRs alone. Figure 4 illustrates the case where the background mass flux is assumed zero, i.e. only SORG$_{MT}$ and sulfuric acid
10 are growing the particles. Even though the seasonal variation in the particle growth can be estimated fairly well without the background, the GRs are systematically underestimated especially during colder seasons when the concentrations of SORG$_{MT}$ are low. If only the constant background mass flux is accounted for, the seasonal variation of the GRs in the size ranges of 3–7 nm and 7–20 nm cannot be reproduced (Fig. 5).

15 ## 3.2 Growth parameterization using EUCAARI data

The proposed parameterization (Eq. 1) performed relatively well in Hyytiälä. To obtain results relevant also on broader scale, data sets from other measurement stations around Europe were included in the analysis. Monthly median growth rates averaged over all the stations were used in the mass flux fitting. For the concentrations of the
20 SORG$_{MT}$ and sulfuric acid, we used data from GLOMAP (average over all the stations), thus ensuring consistent treatment of all the stations. The results obtained from the analysis for Hyytiälä (Sect. 3.1.2) give confidence on using the concentrations of SORG$_{MT}$ directly from GLOMAP in the fitting, as the correspondence between fitted and ambient growth rates was reasonable.

25 Figure 6 shows how well the fit produced the observed growth rates using data from all the six stations. The correspondence between the fitted and observed growth rates was relatively good taking into account that we fitted Eq. (1) to averaged data from six sites with very different characteristics. The correlation coefficient obtained was

$R = 0.45$ ($p < 10^{-5}$) with a slope and intercept of 0.8 and $0.9\,\mathrm{nm\,h^{-1}}$ for the linear fit to GR-data points. The weighing factors for the $\mathrm{SORG_{MT}}$ and the $\mathrm{SORG_{bg}}$ obtained from the mass flux fit are presented in Table 4. Results using all the available data (six stations, Hyytiälä included) and data excluding Hyytiälä (five stations) are shown. The weighing factors (k_{MT}) were the same in both cases with 0 for 1.5–3 nm, 0.7 for 3–7 nm and 1 for 7–20 nm. Background concentrations ($C_{\mathrm{SORG,bg}}$) were also similar, around $6 \times 10^7\,\mathrm{cm^{-3}}$ like the k_{bg} values for both cases.

The growth of the nanoparticles (3–$10\,\mathrm{nm\,h^{-1}}$) could be predicted within on average 15 % using Eq. (1). The performance of the parameterization got poorer with lower growth rate values: observed GR of $2\,\mathrm{nm\,h^{-1}}$ was overestimated by as much as 50 % on average. Of the thermodynamic parameters used in the mass flux equations (see Table 1), the densities of the aerosol particles ρ_p and the organics ρ_{ORG} had the greatest influence on the fit parameters – $k_{MT,3-7}$, and $C_{\mathrm{SORG,bg}}$ both being around 20 % lower/higher with lower/higher densities ($1.3/1.7\,\mathrm{g\,cm^{-3}}$) compared to the base case (other k_{MT} values and k_{bg} values were not affected). Lowering the accommodation coefficients $\alpha_{m,SA}$ and $\alpha_{m,ORG}$ to 0.9 increased both the $k_{MT,3-7}$ and $C_{\mathrm{SORG,bg}}$ values around 15 % (other k_{MT} values and k_{bg} values were not affected). A positive bias of $2\,\mathrm{nm\,h^{-1}}$ in the observed GRs increased the $C_{\mathrm{SORG,bg}}$ with 50 % increasing also $k_{bg,1.5-3}$ by 25 % (other k_{bg} were not affected), whereas a negative bias of $2\,\mathrm{nm\,h^{-1}}$ gave approximately 50 % lower $C_{\mathrm{SORG,bg}}$ with 60 % and 15 % lower $k_{bg,1.5-3}$ and $k_{bg,3-7}$ values, respectively. The k_{MT} values for distributing the $\mathrm{SORG_{MT}}$ were not affected. The highest uncertainties are associated with the determination of the growth of sub-3 nm particles from observations (e.g. Yli-Juuti et al., 2011; Leppä et al., 2013) partly explaining the poorer correspondence between fitted and observed growth in 1.5–3 nm size range (see Fig. 6).

The fitting parameters were based on monthly GR data. To test the performance of the parameterization on a daily basis, daily GRs were calculated for the six sites (using the parameters from Table 4) and compared with the observed GRs (see Fig. 7). The

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agreement on a daily basis is naturally poorer (the slope of the fitted line being 0.7 and the systematic bias $1.3\,\mathrm{nm\,h^{-1}}$, correlation coefficient of 0.38) as compared with the monthly data, but still deemed to be reasonable.

4 Discussion: on the implications and applicability of the parameterization

The parameterization based on Eq. (1) and the semi-empirical fitting parameters is a simplistic representation of the sub-20 nm particle growth and distribution of $SORG_{MT}$ and $SORG_{bg}$ onto the aerosol size distribution, but it captures the observed behavior of nanoparticle growth relatively well. Oxidation of atmospheric isoprene – another important source of SOA in Europe – has not been accounted for in the parameterization in order to keep the parameterization simple and as easy as possible to apply to global models. Due to relatively good correspondence between the observed GRs and the GRs produced by the parameterization, inclusion of other seasonal-dependent organics, other than those from MT oxidation, was not necessary. Particle growth rates obtained from the parameterization increase with particle size, as observed in various environments around the world (e.g. Hirsikko et al., 2005; Iida et al., 2008; Manninen et al., 2010; Yli-Juuti et al., 2011; Kuang et al., 2012; Kulmala et al., 2013), and the magnitude and seasonal pattern of the growth rates is similar to observations (Kulmala et al., 2004; Dal Maso et al., 2005; Hirsikko et al., 2005; Manninen et al., 2010). The parameterization is also fairly insensitive to the method of calculating the sulfuric acid and monoterpene concentrations, as long as their temporal patterns and order of magnitude are reasonable.

Two alternative sets of fitting parameters were presented: one that was based on 7 yr of size distribution data from Hyytiälä, Finland, and one based on about one year of data from 6 European sites with different characteristics. The strength of the former is the longer temporal span (and thus better statistics on the GR values) and better selection of input data for the fitting, while the latter covers spatially more diverse environments with different gas phase compositions and meteorological conditions.

The results from the two fittings gave qualitatively similar results, with the k_{MT} factors for distributing the $SORM_{MT}$ being 0 for the 1.5–3 nm particles and approaching 1 as the particles grew towards 20 nm. For the 3–20 nm particles, the fits to Hyytiälä data gave slightly lower k_{MT} factors ($k_{MT,3-7} = 0.2$–0.4 and $k_{MT,7-20} = 0.6$–1.0, depending on the $SORG_{MT}$ data) than the corresponding values based on the EUCAARI data ($k_{MT,3-7} = 0.7$ and $k_{MT,7-20} = 1.0$). The concentration of the "background" condensable species were of the order of 10^7 cm^{-3} for both data sets, the fits to the EUCAARI data giving slightly higher values than the fits to the Hyytiälä data. It should be borne in mind that these concentrations describe the $SORG_{bg}$ during specific conditions of well characterized daytime new particle formation.

The CCN production is very sensitive to the competition between growth and coagulation losses (Kerminen and Kulmala, 2002; Pierce and Adams, 2007; Kuang et al., 2009; Riipinen et al., 2011; Vehkamäki and Riipinen, 2012). The size-dependence of particle growth thus needs to be accounted to accurately predict the contribution of new particle formation to CCN concentrations in atmospheric models (Kuang et al., 2012). The $k_{MT}(d_p)$ values presented in this paper offer a relatively straightforward way of doing this in any model that calculates the condensation of $SORG_{MT}$ similarly to that of sulfuric acid (i.e. as non-volatile and distributed to the aerosol surface area) – as they can be used to simply multiply the contribution of nanoparticles with size d_p to the condensation sink when distributing the $SORG_{MT}$ to the aerosol size distribution. This method is also applicable when distributing the "background" organics.

The choice of a set of appropriate k_{MT} values for distributing the $SORG_{MT}$ (Tables 3 and 4) for a specific model depends on the application (e.g. the way the monoterpene emissions are treated). The average values based on the Hyytiälä data were 0, 0.3 and 0.8 for $k_{MT,1.5-3}$, $k_{MT,3-7}$, and $k_{MT,7-20}$, with $C_{SORG,bg} = 3 \times 10^7$ cm^{-3}. The corresponding values for the EUCAARI data were 0, 0.7 and 1, with $C_{SORG,bg} = 6 \times 10^7$ cm^{-3}. For studies focusing on boreal forest conditions the former should be used, whereas for cases studying more variable larger regions the latter is probably better. It should be noted that the data used in this analysis is limited – only temperate continental bound-

ary layer sites were studied – and therefore we cannot conclude how the nanoparticle growth should be parameterized in global models for other kinds of environments, e.g. over the arctic areas or deserts.

In addition to the size-dependent growth of nanoparticles by $SORG_{MT}$, condensation of an additional "background" vapor with no seasonal dependence was needed to reproduce the observed growth. This was largely due to the fact that the growth of the smallest 1.5–3 nm particles did not show seasonal dependence (i.e. grew when there were practically no biogenic monoterpenes around) and on the other hand grew faster than just sulfuric acid condensation could explain. There are multiple possible explanations for this. Here we discuss a few of them and apply model simulations using a global model to support our discussion.

One possible candidate for the "background" vapor is a combination of anthropogenic and biogenic organics, for instance SOA formed from biogenic organics in the presence of anthropogenic pollution (Hoyle et al., 2011; Spracklen et al., 2011). Another possible explanation for the relatively fast season-independent growth of the smallest nanoparticles could be the contribution of, e.g. amines or ammonia, which could both contribute to the growth of sub-3 nm particles, as well as influence the calculated contribution of sulfuric acid (Kirkby et al., 2011; Kulmala et al., 2013). It should, however, be noted that an accurate determination of the GR values below 3-nm is very challenging and thus subject to relatively large errors, particularly for the smallest particle growth rates (see, e.g. Yli-Juuti et al., 2011; Leppä et al., 2013). This naturally adds uncertainty to the parameterization as well. The concentration of the "background" vapor thus probably cannot be constrained further than within an order of magnitude based on our data. It is notable, however, that the concentration values obtained from the fits are relatively large, comparable to those of sulfuric acid and $SORG_{MT}$ (Tables 3 and 4). The contribution of this material also varies with particle size, as indicated by the weighing factors (k_{bg}) (Tables 3 and 4).

While the size-dependent weighing factors for the distribution of $SORG_{MT}$ onto nanoparticles are relatively straightforward to implement to models, we realize that the

inclusion of the background condensable species might be problematic as it requires an emission of an unidentified precursor. This precursor could be similar to the extra SOA treated by Spracklen et al. (2011), or e.g. a fraction of some other condensable material treated in the model as discussed above. We used the GEOS-Chem-TOMAS model (as described in Pierce et al., 2012b) to study the seasonal behavior of this extra SOA and to determine if it can be used to describe our "background". As suggested by Spracklen et al. (2011), $100\,\mathrm{Tg\,SOA\,yr^{-1}}$ correlated with anthropogenic CO emissions was added to the model beyond the standard biogenic SOA-precursor emissions. These extra SOA emissions contributed to annual-mean condensable organic vapor concentrations of about $1 \times 10^8\,\mathrm{cm^{-3}}$ in the model grid cell containing Hyytiälä. These concentrations are a factor of 3 higher than was calculated for the "background" condensable organics for larger particles at Hyytiälä and about 50 % higher than the "background" condensable organics at the other 5 sites. The high bias against Hyytiälä may be expected since the large, $4° \times 5°$ grid boxes in GEOS-Chem-TOMAS may include many anthropogenic sources in the Hyytiälä grid box that would not affect the measurements at this remote location. Furthermore, the seasonal cycle of these extra condensable organics (± a factor of 2) is significantly weaker than the seasonal cycle in monoterpenes (± a factor of 5–10) and is driven primarily by the seasonal variation in BL height (which causes an maximum concentration in the winter). The weak seasonal cycle is consistent with our analysis here where a constant "background" organic concentration was sufficient. Thus, we conclude that the extra, non-traditional-biogenic sources of SOA (e.g. the $100\,\mathrm{Tg\,SOA\,yr^{-1}}$ correlated with anthropogenic CO emissions, Spracklen et al., 2011) may be responsible for the "background" organic concentrations in our study.

If other aerosol modelers wish to use this "extra SOA" approach to create the "background" SOA, we recommend using the following k_{bg} values for the size dependence of condensation for the "background" organics for larger continental regions: $k_{bg,1.5-3} = 0.3$, $k_{bg,3-7} = 0.8$ and $k_{bg,7-20} = 1.0$ (for the boreal forest $k_{bg,1.5-3} = 0.4$, $k_{bg,3-7} = 0.8$ and $k_{bg,7-20} = 1.0$). On the other hand, if no "background" vapor is rep-

resented in the model (i.e. $C_{\text{SORG,bg}} = 0$), we recommend using the k_{MT} factors determined without $I_{\text{SORG,bg}}$ in Eq. (1), i.e. $k_{\text{MT,1.5−3}} = 0.2$, $k_{\text{MT,3−7}} = 0.5$ and $k_{\text{MT,7−20}} = 1.0$ for the boreal forest and $k_{\text{MT,1.5−3}} = 1.0$, $k_{\text{MT,3−7}} = 1.0$ and $k_{\text{MT,7−20}} = 1.0$ for larger continental regions. It should be noted, however, that neglecting the "background" contri-
5 bution is likely to result in underprediction of the magnitude of the growth rates although their seasonal dependence is captured (see Fig. 4).

Our parameterization is expected to give satisfactory results for nanoparticle growth on the scale at which many global models operate (Figs. 3, 6, 7). There are still several improvements that can be expected as the mechanistic understanding of the SOA
10 formation and nanoparticle growth processes increases. One of the caveats related to the commonly-used methods of determining ambient size-dependent growth rates is the coupling of particle size with time (see, e.g. Kuang et al., 2012). We do not expect this to be an issue over the time scales at which we are operating (as we do not consider diurnal variation in the vapor concentrations), and acknowledge that the temporal
15 variation is probably a factor contributing the semi-empirical parameters k_{MT} and k_{bg}. We showed that the parameterization can also reasonably capture particle growth with a higher time resolution (daily growth) while it is also clear that the parameterization cannot capture well every single growth episode (see Fig. 7). Another potential point of improvement is related to the mechanistic understanding of the role of amines and
20 ammonia, which are important in the early steps (below 3 nm) of nanoparticle formation and growth (see, e.g. Berndt et al., 2010; Kirkby et al., 2011; Riipinen et al., 2012; Yu et al., 2012; Kulmala et al., 2013), affecting also the predicted contribution of sulfuric acid on the GR values. As new knowledge on the early steps of the growth is obtained the parameterization should be updated accordingly. It should be also noted that coag-
25 ulational growth of nanoparticles was not accounted for in the parameterization. This is certainly a good assumption in remote environments with relatively low aerosol concentrations, but will add uncertainty to the fit parameters in more polluted environments (see, e.g. Kerminen and Kulmala, 2002; Stolzenburg et al., 2005; Leppä et al., 2011).

5 Summary and conclusions

We have introduced a semi-empirical parameterization of atmospheric nanoparticle growth as a function of ambient concentrations of sulfuric acid and first-order oxidation products of monoterpenes ($SORG_{MT}$), the latter multiplied by a fitted weighing factor with values between 0 and 1. Through its dependence on the monoterpene oxidation products, the formula couples nanoparticle growth to the distribution of $SORG_{MT}$ to the atmospheric aerosol size distribution. The weighing factors for the distributing $SORG_{MT}$ onto 1.5–3 nm, 3–7 nm and 7–20 nm particles were determined using seven years (2003–2009) of particle growth rate data from Hyytiälä, and a year (2008–2009) of corresponding data from five other sites around Europe (see Eq. (1), and Tables 3 and 4 for the weighing factors). The results indicate that as the particles get larger, a greater fraction of the $SORG_{MT}$ can condense onto the particles and grow them. This result is reasonable in the light of the thermodynamics of evaporation (the Kelvin and composition effects on the equilibrium vapor pressures of organic species), and in line with atmospheric observations.

Besides the condensation of sulfuric acid and $SORG_{MT}$, a third condensing vapor, referred to as "background" was needed to explain the observed nanoparticle growth rates. The concentration of this vapor was assumed to be constant throughout the year and its value was determined to be of the order of 10^7 cm^{-3} through fits to ambient data (see Tables 3 and 4 for the detailed values). The background concentration was comparable to that of sulfuric acid and the monoterpene oxidation products, and thus contributes significantly to the growth of the atmospheric nanoparticles, especially at the smallest particle sizes. The exact identity of this "background" vapor (or vapor mixture) is not clear, although it can be speculated to account for non-monoterpene organics or, e.g. the impacts of amines on the growth of the smallest particles. As the amount of available data on atmospheric nanoparticle growth and gas phase composition increases, explaining this "background" contribution or its dependence on environmental parameters is an interesting topic for a future study.

To study the performance of the parameterization function and its sensitivity to input data, different ways of estimating the $SORG_{MT}$ concentrations were used. The fit showed some sensitivity to the input data (see Table 3 and Sect. 3.1.2 for details), but the overall patterns and magnitude of the fitting parameters were consistent in the different investigated cases. Similarly, although some differences between the results from Hyytiälä alone and all the six European sites existed (see Tables 3 and 4) the results were consistent. The weighing factors for $SORG_{MT}$ condensation consistently increased with size, being 0 for 1.5–3 nm particles and approaching unity (i.e. kinetic limit) for 20 nm particles. The concentration of the "background" vapor was of the order of 10^7 cm^{-3} for both cases while the condensation of the background was size-dependent. The parameterization function produced the observed monthly growth rates well, usually within factor of 2 and often within 30 %.

Since the CCN production from nucleation is very sensitive to the competition between coagulational scavenging and condensational growth, we expect the presented parameterization to improve the performance of atmospheric models in predicting the contribution of new particle formation to CCN concentrations. To verify its usefulness and performance in the future, however, the parameterization should be tested within a large-scale atmospheric model, and evaluated against a growth rate data set independent of the data utilized to obtain it.

Appendix A

Diffusion coefficient for vapor molecules (D_v) in a background gas (air) can be determined by using a semi-empirical formula presented by Poling et al. (2001)

$$D_v = \frac{0.001 T^{1.75}}{p \left(\Sigma_{air}^{1/3} + \Sigma_v^{1/3} \right)} \sqrt{\frac{1}{M_{air}} + \frac{1}{M_v}}, \tag{A1}$$

where D_v is given in $\mathrm{cm^2\,s^{-1}}$, T is temperature (in Kelvin units), p is pressure (in atm units), M_{air} is molar mass of air (in $\mathrm{g\,mol^{-1}}$) and M_v is molar mass of the vapor (in $\mathrm{g\,mol^{-1}}$), $\Sigma_{\mathrm{air}}^{1/3}$ is diffusion volume of air and $\Sigma_v^{1/3}$ is diffusion volume of condensable vapor (can be obtained from tabulated diffusion volumes of atoms, see e.g. Poling et al., 2001).

Diffusion coefficient for particles of a certain size (d_p) in a medium (air) can be determined from

$$D_p = \frac{k_B T C_c}{3\pi\mu d_p}, \tag{A2}$$

where k_B is Boltzmann constant, T is temperature, μ is dynamic viscosity of the air and C_c is Cunningham slip correction factor that is determined from the relation between the dimension of the particle and air molecules. C_c can be determined using the following expression

$$C_c = 1 + \frac{2\lambda}{d_p}\left(1.257 + 0.4\exp\left(-\frac{1.1 d_p}{2\lambda}\right)\right), \tag{A3}$$

where λ is the mean free path of an air molecule and the numerical coefficients were obtained from Allen and Raabe (1982).

Mean thermal speed of a vapor molecule (molar mass M_v) is

$$\overline{c_v} = \sqrt{\frac{8RT}{\pi M_v}}, \tag{A4}$$

where R is gas constant. Mean thermal speed of a particle (mass m_p) is

$$\overline{c_p} = \sqrt{\frac{8 k_B T}{\pi m_p}}. \tag{A5}$$

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Table 1. Values for parameters used in this study for surrounding air, for condensable vapors (sulfuric acid and organics ($SORG_{MT}$ and $SORG_{bg}$)) and for particles.

Surrounding air	
Pressure, p	1 atm (10^5 Pa)
Temperature, T	285 K
Molar mass, M_{air}	29 g mol^{-1}
Dynamic viscosity, μ_{air}	1.8×10^{-5} kg m^{-1} s^{-1}
Mean free path of air molecules, λ_{air}	64 nm
Sulfuric acid	
Density, ρ_{SA}	1.8 g cm^{-3}
Molar mass, M_{SA}	98 g mol^{-1}
Mass of a SA molecule, m_{SA}	98 amu
Diameter of a SA molecule, d_{SA}	0.56 nm[a]
Diffusion coefficient, D_{SA}	0.1 cm^2 s^{-1}[b]
Mass accommodation coefficient, $\alpha_{m,SA}$	1
Organics	
Density, ρ_{ORG}	1.5 g cm^{-3}
Molar mass, M_{ORG}	186 g mol^{-1}
Mass of a organic molecule, m_{ORG}	186 amu
Diameter of a organic molecule, d_{ORG}	0.73 nm[a]
Diffusion coefficient, D_{ORG}	0.1 cm^2 s^{-1}[b]
Mass accommodation coefficient, $\alpha_{m,ORG}$	1
Particle properties	
Density, ρ_p	1.5 g cm^{-3}

[a] Calculated using liquid density and vapor molecular mass.
[b] Calculated according to semi-empirical formula by Poling et al. (2001). See also Appendix A.

Table 2. The data sets (monthly medians) used for fitting Eq. (1). Nanoparticle diameter growth rates (GR), concentrations of sulfuric acid (C_{SA}) and monoterpenes (C_{MT}). The GR data sets are the same as those used by Yli-Juuti et al. (2011) and Manninen et al. (2010). See text for details.

Data set	Hyytiälä	Other European sites
GR (NAIS/AIS)	2003–2007	2008–2009
GR (BSMA)	2003–2009	–
GR (DMPS)	2003–2009	–
C_{SA} (Petäjä et al., 2009)	2003–2007	–
C_{SA} (GLOMAP)	2008	2008
C_{MT} (Lappalainen et al., 2009)	2003–2009	–
C_{MT} (PTR-MS)	2007–2009	–
C_{MT} (GLOMAP)	2008	2008

Table 3. Average concentrations of $SORG_{MT}$ ($C_{SORG,MT}$, cm^{-3}) and sulfuric acid (C_{SA}, cm^{-3}) as well as the background concentration ($C_{SORG,bg}$, cm^{-3}) and weighing factors (k_{MT} and k_{bg}) from the mass flux fit in Hyytiälä. Differently defined concentrations of $SORG_{MT}$ ($I_{SORG,MT}$) were used to test the functioning of the fit and its sensitivity to input data. Pearson's correlation coefficients (R) with p values (in parenthesis) and parameters, a and b ($nm\,h^{-1}$), obtained from a linear fit between the observed growth rates (GR_{obs} in $nm\,h^{-1}$) (2003–2009, monthly medians for each year) and the growth rates obtained from the mass flux fit (GR_{fit} in $nm\,h^{-1}$) are presented.

	1 % MT (GLOMAP)	$SORG_{MT}$ (directly from GLOMAP)	$SORG_{MT}$ (calculated, GLOMAP)	$SORG_{MT}$ (calculated, PTR-MS)	$SORG_{MT}$ (calculated, MT-parameterization
C_{SA}	0.1×10^7	0.1×10^7	0.1×10^7	0.1×10^7	0.1×10^7
$C_{SORG,MT}$	2.3×10^7	1.9×10^7	2.5×10^7	3.7×10^7	5.6×10^7
$k_{MT,1.5-3}$	0	0	0	0	0
$k_{MT,3-7}$	0.2	0.3	0.2	0.4	0.2
$k_{MT,7-20}$	0.8	1.0	0.8	1.0	0.6
$C_{SORG,bg}$	3.8×10^7	3.8×10^7	3.6×10^7	2.1×10^7	2.5×10^7
$k_{bg,1.5-3}$	0.4	0.3	0.4	0.7	0.6
$k_{bg,3-7}$	0.7	0.7	0.8	0.9	0.8
$k_{bg,7-20}$	1.0	1.0	1.0	1.0	1.0
Correlation $R(p)$ GR_{obs} vs. GR_{fit}	0.78 ($< 10^{-5}$)	0.80 ($< 10^{-5}$)	0.80 ($< 10^{-5}$)	0.65 ($< 10^{-5}$)	0.67 ($< 10^{-5}$)
Linear fit $GR_{obs} = a \cdot GR_{fit} + b$	$a = 1.1$ $b = -0.1$	$a = 1.4$ $b = -0.7$	$a = 1.1$ $b = -0.1$	$a = 1.0$ $b = 0.2$	$a = 1.0$ $b = 0.1$

Table 4. Average concentrations of SORG_{MT} ($C_{\text{SORG,MT}}$, cm^{-3}) and sulfuric acid (C_{SA}, cm^{-3}) as well as the background concentration ($C_{\text{SORG,bg}}$, cm^{-3}) and weighing factors (k_{MT} and k_{bg}) from the mass flux fit using EUCAARI data (including and excluding Hyytiälä). Monthly median growth rates were averaged over all the six European stations (Hyytiälä included, 2003–2009). Pearson's correlation coefficients (R) with p values (in parenthesis) and parameters, a and b (nm h^{-1}), obtained from a linear fit between the observed growth rates (GR_{obs} in nm h^{-1}) (monthly medians for each station) and the growth rates obtained from the mass flux fit (GR_{fit} in nm h^{-1}) are presented.

	Six sites	Five sites
C_{SA}	0.5×10^7	0.7×10^7
$C_{\text{SORG,MT}}$	0.9×10^7	0.8×10^7
$k_{\text{MT,1.5-3}}$	0	0
$k_{\text{MT,3-7}}$	0.7	0.7
$k_{\text{MT,7-20}}$	1.0	1.0
$C_{\text{SORG,bg}}$	5.8×10^7	6.4×10^7
$k_{\text{bg,1.5-3}}$	0.3	0.3
$k_{\text{bg,3-7}}$	0.7	0.8
$k_{\text{bg,7-20}}$	1.0	1.0
Correlation $R(p)$ GR_{obs} vs. GR_{fit}	0.45 ($< 10^{-5}$)	0.45 ($< 10^{-5}$)
Linear fit $\text{GR}_{\text{obs}} = a \cdot \text{GR}_{\text{fit}} + b$	$a = 0.8$ $b = 0.9$	$a = 0.7$ $b = 0.8$

Fig. 1. Schematic about the processes leading to nanoparticle growth from the perspective of the parameterization – formation of SORG$_{MT}$, SORG$_{bg}$ and sulfuric acid from biogenic volatile organic compounds (BVOCs) and anthropogenic pollution via atmospheric oxidation and condensation of these vapors onto nanoparticles. Model simulations with GEOS-Chem-TOMAS (Pierce et al., 2012b) show that SORG$_{bg}$ can be linked to the products of oxidation of biogenic organics in the presence of anthropogenic pollutants (Hoyle et al., 2011; Spracklen et al., 2011).
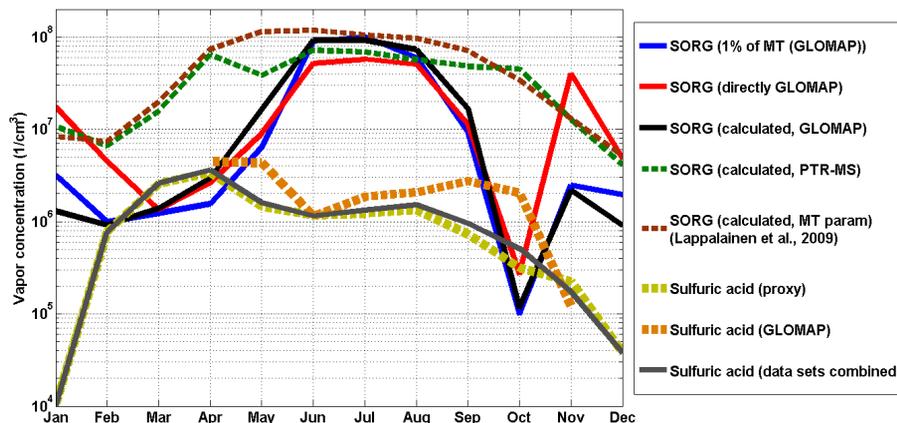
Fig. 2. Time series of monthly median daytime concentrations of SORG$_{MT}$ in Hyytiälä, Finland, determined five different ways – three of which rely mostly on GLOMAP data and the two others on measurement data from the PTR-MS and from the MT parameterization by Lappalainen et al. (2009). Also the monthly median sulfuric acid concentrations are presented.
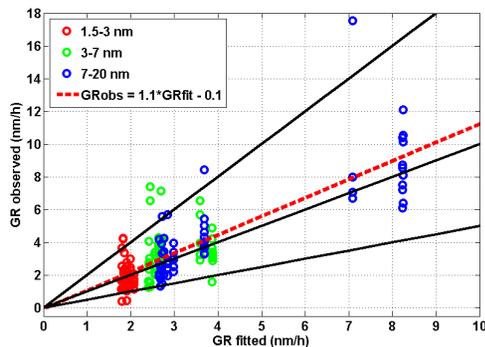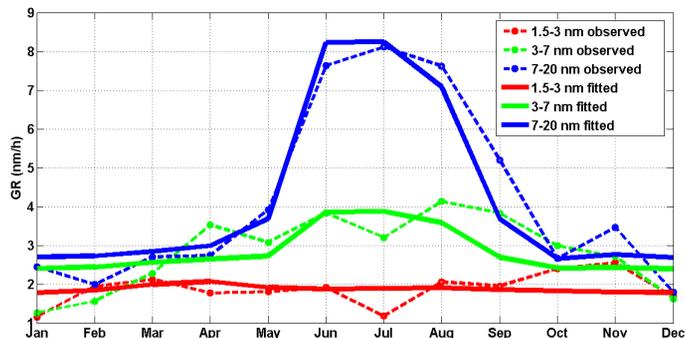
Fig. 3. Observed monthly median growth rates for three size ranges during 2003–2009 in Hyytiälä (symbols and dashed lines) and the growth rates from the mass flux fit (solid lines) using concentrations of $SORG_{MT}$ calculated using MT concentrations from GLOMAP (upper figure). See Table 3 for the fitting parameters. The correspondence between growth rates from the mass flux fit and from the ambient observations (monthly median growth rates for each year) is presented in the lower figure with a linear curve fitted to all the data points. Also 1 : 1, 2 : 1 and 1 : 2 lines (black lines) are shown.
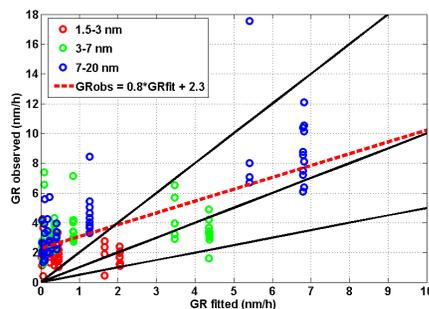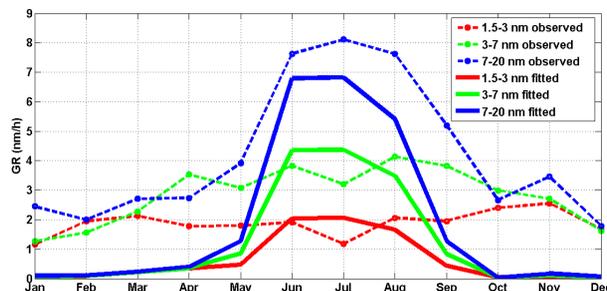
Fig. 4. Observed monthly median growth rates for three size classes during 2003–2009 in Hyytiälä (symbols and dashed lines) as well as the growth rates obtained from the mass flux fit (solid lines) when background mass flux is assumed to be zero (upper figure). The weighing factors for distributing the $SORG_{MT}$ (calculated using MT concentrations from GLOMAP) corresponding to the best fit were $k_{MT,1.5-3} = 0.2$, $k_{MT,3-7} = 0.5$ and $k_{MT,7-20} = 1.0$. The correspondence between the growth rates from the mass flux fit and from the ambient observations is presented in the lower figure with a linear curve fitted to all the data points. Also $1 : 1$, $2 : 1$ and $1 : 2$ lines (black lines) are shown. The fit can produce similar seasonal behavior as observed in the ambient conditions. However, the GRs are clearly underestimated during cold months when the emissions of MT are low.

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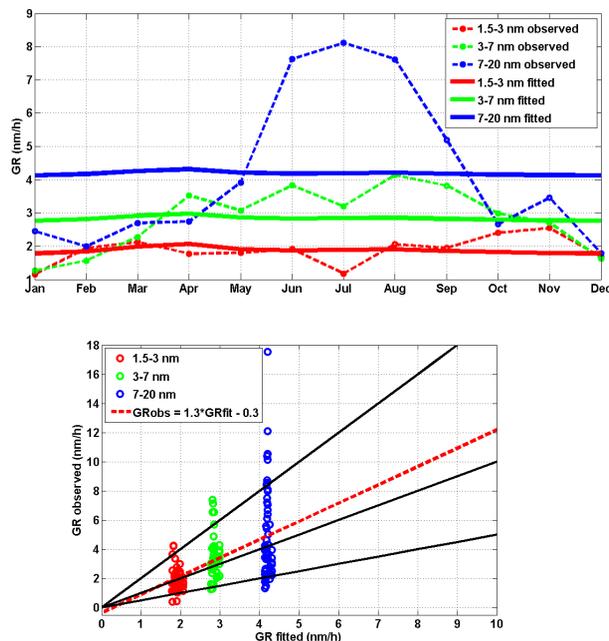
Fig. 5. Observed monthly median growth rates for three size classes during 2003–2009 in Hyytiälä (symbols and dashed lines) as well as the growth rates obtained from the mass flux fit (solid lines) when organic mass flux ($I_{SORG,MT}$) is assumed to be zero (upper figure). The background concentration obtained from the fit was $C_{SORG,bg} = 5.7 \times 10^7$ cm^{-3} with weighing factors for SORG$_{bg}$ 0.2 for 1.5–3 nm, 0.6 for 3–7 nm and 1 for 7–20 nm. The correspondence between the growth rates from the mass flux fit and from the ambient observations is presented in the lower figure with a linear curve fitted to all the data points. Also 1 : 1, 2 : 1 and 1 : 2 lines (black lines) are shown. The seasonal behavior in 3–20 nm particles cannot be captured this way.
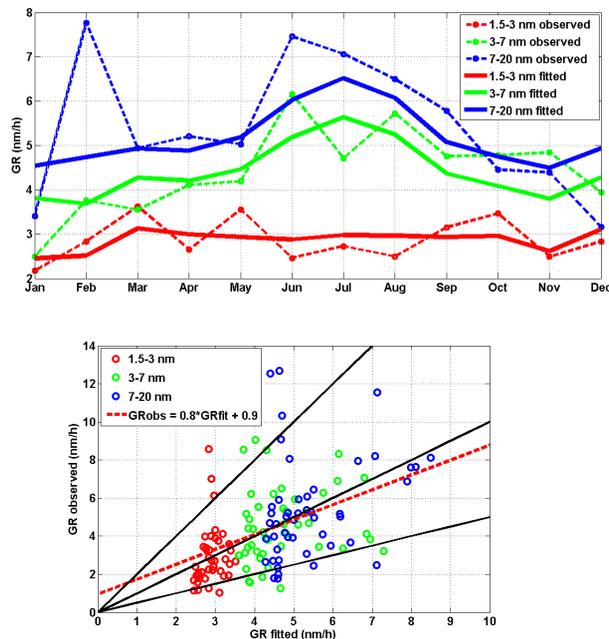
Fig. 6. Ambient monthly median growth rates averaged over all the studied European sites (symbols and dashed lines) for three size ranges and the growth rates from the mass flux fit (solid lines) using SORG$_{MT}$ obtained directly from GLOMAP (upper figure). See Table 4 for the fitting parameters. The GR data from February was not included in the fitting since it was strongly affected by one high-GR event day (GR$_{7-20}$ > 20 nm h^{-1}) in Finokalia and therefore, this data point was not reliable. The correspondence between the growth rates from the mass flux fit and from the ambient observations (monthly median growth rates for each station) is presented in the lower figure with a linear curve fitted to all the data points. Also 1 : 1, 2 : 1 and 1 : 2 lines (black lines) are shown.

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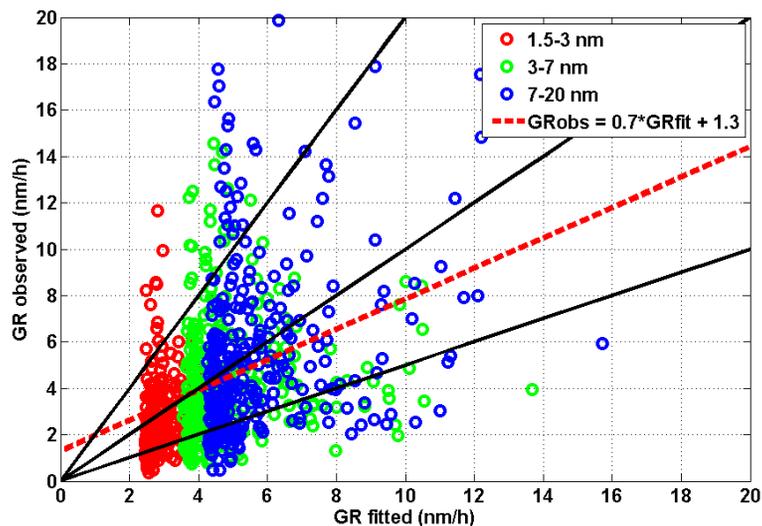
Fig. 7. The correspondence between the growth rates from the mass flux fit and from the ambient observations (daily growth rates for each station) with a linear curve fitted to all the data points. Also 1 : 1, 2 : 1 and 1 : 2 lines (black lines) are shown. The correlation coefficient between the GR_{fit} and the GR_{obs} was 0.38 with a p value of $< 10^{-5}$.

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