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Biogenic and biomass burning organic aerosol in a boreal forest at Hyytiälä, Finland, during HUMPPA-COPEC 2010

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Abstract

Submicron aerosol particles were collected during July and August 2010 in Hyytiälä, Finland, to determine the composition and sources of aerosol at that Boreal forest site. Submicron particles were collected on Teflon filters and analyzed by Fourier transform infrared (FTIR) spectroscopy for organic functional groups (OFG). Positive matrix factorization (PMF) was applied to aerosol mass spectrometry (AMS) measurements and FTIR spectra to identify summertime sources of submicron aerosol mass at the sampling site. The two largest sources of organic mass (OM) in particles identified at Hyytiälä were (1) biogenic aerosol from surrounding local forest and (2) biomass burning aerosol, transported 4–5 days from large wildfires burning near Moscow, Russia, and northern Ukraine. The robustness of this apportionment is supported by the agreement of two independent analytical methods for organic measurements with three statistical techniques. FTIR factor analysis was more sensitive to the chemical differences between biogenic and biomass burning organic components, while AMS factor analysis had a higher time resolution that more clearly linked the temporal behavior of separate OM factors to that of different source tracers even though their fragment mass spectrum were similar. The greater chemical sensitivity of the FTIR is attributed to the nondestructive preparation and the functional group specificity of spectroscopy. The FTIR spectra show strong similarities among biogenic and biomass burning factors from different regions as well as with reference OM (namely olive tree burning BBOA and α -pinene chamber secondary organic aerosol (SOA)). The biogenic factor correlated strongly with temperature and oxidation products of biogenic volatile organic compounds (BVOCs), included more than half oxygenated OFGs (carbonyl groups at 29% and carboxylic acid groups at 22%), and represented 35% of the submicron OM. Compared to previous studies at Hyytiälä, the summertime biogenic OM is 1.5 to 3 times larger than springtime biogenic OM ($0.64 \mu\text{g m}^{-3}$ and $0.4 \mu\text{g m}^{-3}$, measured in 2005 and 2007, respectively), even though it contributed only 35% of OM. The biomass burning factor contributed 25% OM on average and up to 62% OM during

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three periods of transported biomass burning emissions: 26–28 July, 29–30 July, and 8–9 August, with OFG consisting mostly of carbonyl (41 %) and alcohol (25 %) groups. The high summertime terrestrial biogenic OM ($1.7 \mu\text{g m}^{-3}$) and the high biomass burning contributions ($1.2 \mu\text{g m}^{-3}$) were likely due to the abnormally high temperatures that resulted in both stressed boreal forest conditions with high regional BVOC emissions and numerous wildfires in upwind regions.

1 Introduction

Boreal forests produce a large amount of global SOA from the emissions of high molecular weight, reactive biogenic volatile organic compounds (BVOC) such as monoterpenes and sesquiterpenes (Seinfeld and Pandis, 2006). BVOC emissions are higher and generally more reactive than anthropogenic VOC, making them potent sources of organic aerosol (Atkinson, 2000; Eerdekens et al., 2009; Laaksonen et al., 2008; Yassaa et al., 2012). Globally the oxidation of BVOCs is estimated to produce $12\text{--}70 \text{ TgCyr}^{-1}$ of SOA (Hallquist et al., 2009), and anthropogenic emissions may significantly enhance biogenic SOA formation (Carlton et al., 2010; Hoyle et al., 2011).

Biogenic emissions are one way that forests play an important role in the emission of primary and secondary organic aerosol (POA, SOA). It is believed that biomass burning is the largest source (90 %) of global primary organic carbon (POC), estimated at $31\text{--}45 \text{ TgCyr}^{-1}$ (Bond et al., 2004). Biomass burning also emits large amounts of organic trace gases that can react in the atmosphere to form SOA; however, the contribution of biomass burning emissions to SOA formation is unknown (Hallquist et al., 2009). Field studies report a range of SOA concentrations from aging fire plumes, with enhancement of organic mass (OM) ranging from 30–400 % relative to fresh plume conditions (Decarlo et al., 2010; Heringa et al., 2011; Yokelson et al., 2009). These enhancements are consistent with smog chamber studies of SOA formation from biomass burning emissions (Cubison et al., 2011; Hennigan et al., 2011).

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Several different apportionment techniques have been used to identify the biogenic contribution to total OM, most recently including factor analysis, organic tracers, ^{14}C , and OC/EC analysis (Table 1). The biogenic SOA fraction has been found to contribute from 10 to 65 % of the measured OM in or near forested regions. The majority of studies used factor analysis of AMS measurements, in conjunction with tracer correlations and air mass backtrajectories to identify biogenically influenced OM. The AMS-derived biogenic factors were identified as oxygenated organic aerosol (OOA), typically having O/C ratios ranging from 0.22–0.54 (Finessi et al., 2012; Raatikainen et al., 2010; Setyan et al., 2012; Slowik et al., 2010). The OOA factors correlated strongly ($r > 0.7$) with BVOC oxidation products and the spectra were enhanced with a few mass fragments (m/z 29, 43, and 58) that have been identified in SOA from α -pinene photooxidation (Shilling et al., 2009) and from plant emission photooxidation (Kiendler-Scharr et al., 2009). However, these mass fragments are not specific to biogenically influenced OOA factors and have been observed in hydrocarbon-like organic aerosol (HOA), biomass burning organic aerosol (BBOA), and semi-volatile oxygenated organic aerosol (SV-OOA or OOA-2) (Slowik et al., 2010; Sun et al., 2011; Zhang et al., 2005). In addition to AMS factor analysis, FTIR spectroscopy provides quantitative OM and functional group concentrations that have been used to identify OM sources by using characteristic OFG mixtures to specify the source factors (Ahlm et al., 2012; Frossard et al., 2011; Hawkins and Russell, 2010; Hawkins et al., 2010; Liu et al., 2012; Russell et al., 2011; Schwartz et al., 2010; Shaw et al., 2010; Takahama et al., 2011). Comparison of factor analysis from simultaneous AMS and FTIR measurements can reduce the uncertainties of PMF, providing a more robust OM apportionment to sources (Frossard et al., 2011; Hawkins and Russell, 2010; Liu et al., 2012).

The Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry (HUMPPA-COPEC 2010) study was conducted at the SMEAR II (Hari and Kulmala, 2005) boreal forest research station in Hyytiälä, Finland, in July and August 2010 with an impressive suite of simultaneous particle and gas-phase measurements. The primary goals of the campaign

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include investigating summertime aerosol chemistry and photochemistry of biogenic volatile organic compounds (BVOCs) (Williams et al., 2011). In this analysis, we focus on the characterization of the organic aerosol during HUMPPA-COPEC 2010 using two independent analytical methods of organic measurement (FTIR and AMS techniques) and three separate statistical methods (clustering, factorization, potential source contributions) to apportion OM to biogenic and biomass burning sources. We also compare the differences in the chemical composition of biogenic and biomass burning particles to previous field campaigns and reference materials. This approach allows us to provide the most robust apportionment of OM for summertime Hyytiälä completed to date and to identify the relative advantages of different OM measurement techniques.

2 Methods

2.1 Sample collection

Submicron particles and gases were sampled from 12 July to 12 August 2010 in southern Finland (Latitude $61^{\circ} 51' N$; Longitude $24^{\circ} 17' E$) at 181 m above sea level (m a.s.l.). Atmospheric particles were measured by Fourier transform infrared (FTIR) spectroscopy, compact time-of-flight mass spectrometry (C-ToF-AMS), atmospheric pressure chemical ionization mass spectrometry (APCI-MS), X-ray fluorescence (XRF), and Scanning Transmission X-Ray Microscopy with Near-Edge Absorption Fine Structure (STXM-NEXAFS). A suite of gas phase species, including SO_2 , CO, NO_x , O_3 , OH, and biogenic VOCs, were also measured during the campaign. A complete description of the field site and instruments deployed is provided by Williams et al. (2011).

2.2 FTIR and XRF analysis

Submicron particles were collected 4 m above ground level, approximately mid-canopy level, in temperature controlled housing on 37 mm Teflon filters (Pall Inc., 37 mm diameter, 1.0 μm pore size) located downstream of a 1 μm sharp-cut cyclone (SCC 2.229

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PM1, BGI Inc.). The aerosol particles were dried (Silica orange gel 13767, Sigma-Aldrich, USA) to below 25 % relative humidity prior to the cyclone. Back filters were also collected to quantify VOC adsorption and artifacts; however, absorbance on all back filters was below limit of detection (LOD). Filter duration varied from 6 to 12 h, in addition to duplicate 24 h filters. To reduce evaporative losses, samples were stored and transported at 0 °C prior to analysis in La Jolla, California, by a Tensor 27 spectrometer equipped with a DTGS detector (Bruker, Billerica, MA). Organic functional groups were quantified from FTIR absorbance spectra based on the linear response of peak area to the number of moles of organic bonds (Gilardoni et al., 2007; Maria et al., 2002, 2003). An automated peak-fitting algorithm described by Russell et al. (2009b) and Takahama et al. (2013) was used to quantify organic functional groups, which included saturated aliphatic C-CH (alkane), unsaturated aliphatic C=CH (alkene), aromatic C=CH, non-acid organic hydroxyl C-OH (alcohol), primary amine C-NH₂, non-acid carbonyl C=O (aldehyde, ketone or ester carbonyl), and carboxylic acid COOH groups. Alkene and aromatic groups were below the limit of quantification (LOQ) for all samples collected during the field campaign. Both organonitrate and organosulfate groups were detected at 860 cm⁻¹ and 876 cm⁻¹, respectively. A modified peak-fitting algorithm described by Day et al. (2010) was used to quantify organonitrate groups. Due to overlapping absorbance of carbonate and bisulfate at 876 cm⁻¹, a hexane rinsing method described in Gilardoni et al. (2007) and in Russell et al. (2009b) is used to quantify organosulfate. 24 of 65 samples contained absorbance at 876 cm⁻¹, but no samples were above the LOQ.

After FTIR analysis, a subset of filters was sent to Chester Labnet (Tigard, Oregon) for X-ray fluorescence (XRF) analysis to provide concentrations of Na and heavier elements (Maria et al., 2003; Russell et al., 2009b). Elements that were above LOQ on more than 30 % of the filters include: Al, Si, P, S, K, Ca, V, Cr, Fe, Co, Cu, Zn, Se, Br, and Pb.

2.3 Single-particle spectromicroscopy

Single particles were impacted on silicon nitride windows (Si_4N_3 , Silson Ltd.) on 26 and 29 July and frozen at 0°C prior to analysis. Single particles were analyzed at the Advanced Light Source (Lawrence Berkeley National Laboratory, Berkeley, CA) on
5 Beamline 5.3.2 by Scanning Transmission X-ray Microscopy with Near-Edge X-ray Absorption Fine Structure (STXM-NEXAFS) spectroscopy. Single particles were analyzed at the carbon K-edge for single-particle organic functional groups by scanning through energy levels 278–320 eV (Kilcoyne et al., 2003). Spectra were processed using an automated algorithm to provide information on single-particle organic functional group
10 abundance, size, and morphology (Takahama et al., 2007, 2010).

2.4 Aerosol mass spectrometry

The Aerodyne Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc., Billerica, MA, Canagaratna et al., 2007) measures submicron particle chemical composition using time-of-flight mass spectrometry, approximately 5 min time resolution. The variant of
15 the device used in this study was a C-ToF AMS that features a shorter than usual particle time-of-flight chamber, which results in increased transmission of both particles and gas, and therefore also a larger air signal than in most AMS designs (Drewnick et al., 2005).

The AMS aerosol mass is then assigned into subgroups of different chemical composition: sulfate, organic, nitrate, ammonium, and chloride mass fragments (Alfarra et al., 2004; Allan et al., 2003). The AMS does not efficiently vaporize compounds that are
20 “non-refractory” at 600°C , such as sea salt, black carbon or crustal material. Particulate water is not included in the AMS measurements. The collection efficiency (CE) of 0.43 was determined from a comparison with DMPS derived mass concentrations in size range 3–600 nm. The neutral-aerosol/base CE was estimated for time periods when the aerosol acidity was neutral, as determined by the ratio of ammonium to sulfate + nitrate. For periods with non-neutralized sulfate, when the molar ammonium
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was substantially less than twice the molar sulfate, indicating elevated aerosol acidity, a higher value was used, based on a linear correction function similar to that of Quinn et al. (2006), ($EB = -(1 - CE)([NH_4]/[SO_4]) + 1$, where $CE = 0.43$). During the measurement period the mass fraction of nitrates was consistently low, below 10 %, causing no distinguishable CE effects.

Oxygen to carbon ratios (O/C) were calculated from two independent techniques: AMS and FTIR. C-ToF-AMS O/C ratios were estimated from the f_{44} , ratio of m/z 44 (COO^+ ion) relative to the total ion mass, proxy described by Aiken et al. (2008). For FTIR measurements, O/C was determined by the sum of oxygen atoms in the oxygen-containing functional groups (alcohol, carboxylic acid, and carbonyl), which was normalized by the total carbon atoms of all organic functional groups measured (Russell et al., 2009b).

2.5 Organic acids

On-line measurements of organic acids in gas- and particle-phase during HUMPPA-COPEC 2010 were carried out with an Atmospheric Pressure Chemical Ionization Mass Spectrometer (APCI-MS; Finnigan LCQ; Kuckelmann et al., 2000). The measurements were conducted in the main SMEAR II cottage, next to the C-ToF-AMS, both sampling from a stainless steel inlet at mid-canopy height (8 m).

Ambient aerosol was enriched in front of the APCI-MS by using a miniature Versatile Aerosol Concentration Enrichment System (mVACES, Geller et al., 2005) to improve the sensitivity by a factor of approximately 7.5, while retaining the measurement frequency of one spectrum per minute. Afterwards, the enriched aerosol stream was led through a heated ceramic tube (350 °C) in order to vaporize the aerosol particles for ionization. The ionization was achieved by using corona discharge at 3 kV, which produces O_2^- -ions as primary ions. Consequently, all gaseous molecules, having higher gas-phase acidities than O_2^- , were ionized. In intervals of 3 h, gas-phase compounds were measured for half an hour, by switching a HEPA filter in front of the ion source. Linear interpolation between the gas-phase measurements and subtraction from the total

signal resulted in the particle-phase signal. A more detailed description is provided by Vogel et al. (2012). Particulate organic acids correlated well with FTIR carboxylic acid functional groups and FTIR OM (see Supplement for more details).

2.6 Additional measurements

Other supporting particle-phase and gas-phase measurements include O₃, SO₂, CO, NO_x, and meteorological data that are recorded throughout the year at the Hyytiälä SMEAR-II site, details of which are described by Hari and Kulmala (2005) and Junninen et al. (2009). Proton Transfer Reaction Mass Spectrometer (PTR-MS, Lindinger et al., 1998; Taipale et al., 2008) provided mixing ratios of several VOCs (Williams et al., 2011). Pentane and butane were measured by a modified fast GC-MS described in detail by Johnson (2011). Monoterpenes and chiral monoterpenes were measured by Gas Chromatography Mass Spectrometry (GC-MS) (Yassaa and Williams, 2005; Yassaa et al., 2012). Black carbon mass concentrations were measured by an aethalometer (Margee Scientific). A comprehensive list of the instrumentation, including time resolutions, detection limits, and inlet locations is provided by Williams et al. (2011).

2.7 PMF and PSCF

Positive Matrix Factorization (PMF) was applied to FTIR and AMS spectra to identify the components that contribute to the time series of the measured particle-phase chemical mixtures (Paatero and Tapper, 1994). Recently PMF has been successfully applied to both FTIR and AMS spectra to separate organic components associated with different sources (Frossard et al., 2011; Hawkins and Russell, 2010; Russell et al., 2009b; Schwartz et al., 2010; Ulbrich et al., 2009; Zhang et al., 2011). PMF was applied to both baselined FTIR and AMS spectra. Results for 2, 3, 4, 5, and 6 factor solutions for each measurement type were examined for FPEAK (rotation) values from -1.2 to 1.2 and seed values of 1, 10, and 100. Solutions were considered to be potential candidates if explained variation and OM reconstruction was maximized, *Q* value was minimized,

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colinearity amongst the factors was reduced, factor spectra were non-degenerate, and tracer correlations were meaningful. Additional details describing PMF parameters are listed in the Supplement.

Potential source contribution functions (PSCF) were used to identify geographical source regions that were associated with the observed aerosol composition and air-mass backtrajectories, based on co-occurrence of high concentration samples (Pekney et al., 2006). PSCF used 4 day air mass backtrajectories calculated by the HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2013). Hourly backtrajectories were calculated 200 m a.g.l. at Hyytiälä for the duration of the campaign. PSCF were calculated for submicron OM, concentrations and mass fractions of organic functional groups, and PMF factors from FTIR and AMS.

3 Results from HUMPPA-COPEC campaign measurements

3.1 Aerosol particle composition (organic, inorganic, and elemental)

Hyytiälä is influenced by biogenic aerosols, transported pollution from continental Europe and western Russia, and occasionally impacted by biomass burning emissions in the summer months (Williams et al., 2011). During the summer measurements of 2010, a high pressure region, stationed east of Finland for an extended period of time, resulted in abnormally high temperatures ($T_{\max} = 32.4\text{ }^{\circ}\text{C}$, $T_{\text{avg}} = 20.0\text{ }^{\circ}\text{C}$). The high temperatures resulted in enhanced biogenic OM as well as increased wildfires in western Russia. The chemical composition of biogenically influenced submicron particles measured at Hyytiälä is described in detail below.

3.1.1 Organic mass and functional group composition: campaign averages and high-OM events

Particle-phase mass at Hyytiälä was dominated by organic components (with an average mass concentration of $4.4\text{ }\mu\text{g m}^{-3}$) and varied significantly throughout the

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campaign ($\pm 3.1 \mu\text{g m}^{-3}$) due to local sources (i.e. sawmill activity, Eerdekens et al., 2009; Liao et al., 2011) and long-range transport of Russian biomass burning emissions (Fig. 1) (Williams et al., 2011). Submicron particle mass (PM_{1}) measured as the sum of non-refractory components by C-ToF-AMS, BC by aethelometer, and metal oxides by XRF (plus associated oxygen estimated by SiO_2 , Al_2O_3 , Fe_2O_3 , and CaCO_3 , Usher et al., 2003) was on average $6.8 \mu\text{g m}^{-3}$ with a standard deviation of $4.6 \mu\text{g m}^{-3}$, with organic compounds dominating the submicron fraction (64%), followed by sulfate (20%), ammonium (6%), black carbon (5%), nitrate and metal oxides (2%) (Table 2). Total submicron organic mass (OM) measured by FTIR was $4.3 \pm 3.9 \mu\text{g m}^{-3}$, with the organic functional group composition dominated by alkane (37%) and carboxylic acid (28%) groups, followed by carbonyl (15%), alcohol (15%), and finally amine (5%) groups (Table 2).

The HUMPPA-COPEC campaign was punctuated by two types of high-OM events: sawmill activity and transported emissions from Russian wildfires (Eerdekens et al., 2009; Williams et al., 2011). Nearby sawmill (Korkeakoski, Finland, located 10 km SE of Hyytiälä) activity was identified by an enrichment of (+)- α -pinene over its (-)- α -pinene enantiomer, attributed to a metabolic response to wounding, coinciding with high nighttime monoterpene and isoprene concentrations (Williams et al., 2011; Yas-saa and Williams, 2007). Sawmill activity was detected at the Hyytiälä site on the nights of 17 July and 3 and 5 August, during which OM increased from 2.6 to $3.2 \mu\text{g m}^{-3}$ (as indicated by the bars on the top axis of Fig. 1). During the sawmill events, the OM had higher fractions of sulfate compared to the campaign average (Table 2). OM during sawmill events had more oxygenated organic functional groups (O-OFG), but those time periods were also characterized by a slightly higher fraction of alkane group mass compared to the campaign average, namely 40–44% rather than 37% (Table 2). The combustion associated with the sawmill operation and short transport time of fresh biogenic aerosol (< 1 h) are likely responsible for the higher alkane fraction. Organonitrate groups were near the campaign average ($0.02 \mu\text{g m}^{-3}$) during the sawmill periods, except for the night of 5 August ($0.09 \mu\text{g m}^{-3}$).

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Acetonitrile (CH_3CN) and carbon monoxide (CO) are gas-phase tracers used to identify periods influenced by regional biomass burning (Lobert et al., 1990), in addition to particle-phase tracers potassium and bromine (Andreae et al., 1996) (Fig. 1d and e). Increases in potassium (K) and bromine (Br) concentrations were observed on 26–28 July, 29–30 July, and 8–9 August, showing fire period averages of 380 and 8.6 ngm^{-3} , respectively, with percent increases over background (project minimum) concentrations of 1800% and 330% (Fig. 1e). Elevated concentrations of acetonitrile (0.45 ppb, 460%) and CO (220 ppb, 120%) were observed during these periods (Fig. 1e). Fire periods were dominated by O-OFG, with 2.1–4.1 μgm^{-3} carbonyl groups and 2.5–4.0 μgm^{-3} carboxylic acid groups (Table 2). OM during fire periods was two to five times greater than the campaign average OM, with the highest concentration (21 μgm^{-3}) on 9 August. The highest concentrations of black carbon 1.84 μgm^{-3} and metal oxides 0.25 μgm^{-3} were also observed when biomass burning emissions were advected to the field site.

3.1.2 OM and O/C comparison

FTIR OM and AMS OM showed strong agreement ($r = 0.94$, slope = 0.9), with the slight difference between the techniques falling within the FTIR and AMS uncertainties of 20–30% (Russell et al., 2009a,b) (Figure S1). Such strong agreement between the two independent techniques provides evidence of the accuracy and completeness of the OM quantification of both methods. Other field campaigns have shown lower correlation between the two methods ($r = 0.7$), likely due to OM contributions by refractory marine and dust particles (Hawkins et al., 2010; Liu et al., 2012), where this difference is consistent with the low AMS collection efficiency for refractory particles (Alfarra et al., 2004; Matthew et al., 2008). The high correlation between the two independent techniques suggests limited semi-volatile OM losses from FTIR filters and high collection efficiency of organic particles by the AMS due to the low dust and non-marine location.

Campaign average $\text{O}/\text{C}_{\text{FTIR}}$ was 0.56 ± 0.08 , with carboxylic acid (0.31) accounting for 55% of the total $\text{O}/\text{C}_{\text{AMS}}$. Sawmill periods were found to have lower $\text{O}/\text{C}_{\text{AMS}}$ values

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0.50 ± 0.06, while fire periods appeared to be more processed with an average O/C_{FTIR} of 0.67 ± 0.08 . O/C_{AMS} was slightly greater than O/C_{FTIR} , with a campaign average O/C_{AMS} of 0.76 ± 0.06 . When clean air masses originated over northern Scandinavian boreal forests, O/C_{FTIR} was greater than O/C_{AMS} . During these times, FTIR-measured alcohol functional group accounted for more than 50 % of the O/C_{FTIR} , which may be underestimated by the f_{44} (CO_2^+ fragment) that was used as a proxy for O/C_{AMS} . Sawmill periods were found to have lower O/C_{FTIR} values of 0.61 ± 0.13 , while fire periods appeared to be more processed with an average O/C_{FTIR} of 0.79 ± 0.15 . Both methods indicate that the aerosol at Hyytiälä is highly oxidized, with O/C ratios greater than 0.4 (Decarlo et al., 2008). However, despite this general agreement in high and low O/C events, there is a low correlation ($r = 0.20$) of O/C between the AMS and FTIR methods, which may result from the dependence of O/C on fragments other than $m/z44$, as well as other uncertainties in the AMS and FTIR measurements.

3.2 Source apportionment

Associating organic particles with their sources is important both for apportioning PM for regulatory purposes and for classifying the type of organic composition. Typically the major contribution to organic mass in populated areas is from fossil fuel combustion, primarily from motor vehicles (Liu et al., 2012). However, in forested areas, important seasonal contributions can come from both biogenic emissions and biomass burning events (Slowik et al., 2010; Takahama et al., 2011).

3.2.1 Clustering of FTIR spectra and organic tracers

Hierarchical Ward cluster analysis (Ward, 1963) was used to group 65 normalized FTIR spectra into four clusters (Fig. 2). More than four clusters resulted in cluster groups with few spectra (< 4). Particles in Cluster 1-IR had the largest fraction of carboxylic acid (28 %) and the lowest fraction of alcohol groups (13 %) of the four clusters, with alkane, carbonyl, and amine groups contributing to 35 %, 16 %, and 6 % of the OM. Cluster

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2-IR was found to have similar organic functional groups (OFG) to Cluster 1-IR, but with a higher alkane group fraction (41 %). Spectra of Cluster 3-IR were characterized by strong methylene peaks, but did not have the highest alkane fraction of the clusters. Cluster 3-IR had the largest OM ($12.6 \mu\text{g m}^{-3}$) and the highest O/C (0.68), in addition to the largest fractions of alcohol (23 %) and carbonyl (25 %) groups. Cluster 4-IR particles had the highest alkane group fraction (46 %) and contained the lowest O/C (0.49) of the four clusters. Additionally, Cluster 4-IR contained no carbonyl groups and had the lowest overall OM ($2.2 \mu\text{g m}^{-3}$). Spectral signatures of Cluster 4-IR include strong ammonium absorbance, and their spectral profiles closely resemble fossil fuel combustion factors identified at previous field campaigns (Russell et al., 2011). Amine group contributions were $< 5 \%$ for all four clusters, consistent with low mass fraction of amines for the entire campaign.

Particle types were also identified by clustering eight selected tracers, including anthropogenic tracers (SO_2 , NO_x , and black carbon), biogenic tracers (monoterpenes and methylvinylketone/methacrolein, MVK/MACR), sum of organic fragments measured by AMS (“AMS Org”), and temperature (Fig. 2). Tracers were filter-averaged and centered by their root-mean-square prior to clustering by Hierarchical Ward cluster analysis (Ward, 1963). Cluster 1-T had the highest cluster-averages for NO_x (65 ppb) and monoterpenes (580 ppt) and the lowest average temperature (16°C). Sawmill activity also coincided with Cluster 1-T on the nights of 17 July and 3 and 5 August. Tracer averages in Cluster 2-T were midrange, with the exception of elevated temperatures (24°C). The average tracer values were the highest in Cluster 3-T, including organic mass ($10.8 \mu\text{g m}^{-3}$), black carbon ($0.98 \mu\text{g m}^{-3}$), SO_2 (0.9 ppb), acetonitrile (0.23 ppb), MVK/MACR (0.5 ppt), and temperature (26°C). Cluster 3-T corresponded to arrival of biomass burning emissions on 26–28 July, 29–30 July, and 8–9 August. The lowest concentrations were observed for nearly all tracers in Cluster 4-T, including organic mass ($2.4 \mu\text{g m}^{-3}$) and monoterpenes (140 ppt). Organic mass in Cluster 3-T and monoterpene concentrations in Cluster 1-T were nearly 5 times greater than those in Cluster 4-T.

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Similar to fossil fuel combustion factors in other regions (Russell et al., 2011), $\text{FFC1}_{\text{FTIR}}$ contained most of the measured ammonium absorbance, followed by $\text{FFC2}_{\text{FTIR}}$, reinforcing the distinct separation of the two fossil fuel combustion sources. BIO_{FTIR} factor contained some ammonium absorbance. The attribution of ammonium to the BIO_{FTIR} factor is likely from nearby agricultural activities (including animal waste and soil fertilizer), as they are responsible for up to 90 % of the ammonia emissions in Finland (Grönroos et al., 2009). In order to compare organic functional groups in each factor, ammonium absorbance was removed from the factor spectra by scaling an ammonium sulfate reference spectrum to the absorbance at 3238 cm^{-1} and subtracting it from the baselined spectrum (Fig. 4b). The subtracted spectra illustrate the higher alcohol group absorbance by FFC2 and the difference in the alkane group absorbance.

3.2.3 Factors identified by AMS measurements

Three factors were identified from the AMS measurements. The 3-factor solution reconstructed 98 % of measured OM, with time series and normalized spectra of the AMS factors shown in Figs. 3 and 4c, with details of the PMF procedures given in the Supplement.

The first factor had an O/C ratio of 0.71 (estimated by the approximation given by Aiken et al., 2008) and had prominent fragments at m/z 29 (CHO^+) and m/z 43 ($\text{C}_2\text{H}_3\text{O}^+$). The fragments are consistent with α -pinene SOA from chamber experiments and biogenic SOA from plant chamber studies (Chhabra et al., 2011; Kiendler-Scharr et al., 2009; Shilling et al., 2009). The factor strength correlated moderately with temperature ($r = 0.6$), strongly with BVOC oxidation products (MVK/MACR) ($r = 0.8$), and strongly to numerous PTR-MS gas-phase organic compounds including acetone ($r = 0.9$), methanol ($r = 0.8$), and acetic acid ($r = 0.8$) (Figure S5). The time series of this factor peaked during sawmill events (early morning of 17 July, 4 August, and 6 August), consistent with this sporadic influence of biogenic-like SOA (Fig. 3). Additionally the factor was prominent during the first week of the campaign 12 July–19 July, when the local forests were undergoing a period of heat stress (Fig. 1). The factor

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also correlated strongly to BIO_{FTIR} ($r = 0.9$). Slowik et al. (2010) reported a factor ($\text{O}/\text{C} = 0.46$) identified in Egbert, Canada, that was associated with biogenic organic aerosol; however, the Egbert factor did contain a higher fraction of m/z 43. Previous springtime measurements at Hyytiälä have identified similar factors (OOA-2), but with much lower O/C (0.22 and 0.23), indicating these factors had undergone less atmospheric processing (Finessi et al., 2012; Raatikainen et al., 2010). Due to the correlation to MVK/MACR and BIO_{FTIR} , Factor 1 is referred to as $\text{OOA-1a}_{\text{AMS}}$, which likely has a strong biogenic influence.

The second factor was found to be the most oxidized of the three factors, with O/C ratio of 0.99 and f_{44} of 0.24. Factor 2 was spectrally similar to $\text{OOA-1a}_{\text{AMS}}$ (Fig. 4c); however, it contained a higher f_{44} to f_{43} ratio (4.0) than $\text{OOA-1a}_{\text{AMS}}$ (3.15), suggesting a more oxygenated organic aerosol (Ng et al., 2010). The time series of Factor 2 correlated strongly with biomass burning emission tracers: K ($r = 0.9$), Br ($r = 0.8$), acetonitrile ($r = 0.7$), CO ($r = 0.9$), and BC ($r = 0.9$), in addition to Pb ($r = 0.9$) (Figure S5). Due to the association with biomass burning emission tracers, high O/C value, and similar fragmentation pattern as $\text{OOA-1a}_{\text{AMS}}$, the second factor is identified as $\text{OOA-1b}_{\text{AMS}}$.

The $\text{OOA-1b}_{\text{AMS}}$ mass spectrum is chemically indistinguishable from $\text{OOA-1a}_{\text{AMS}}$, except that $\text{OOA-1b}_{\text{AMS}}$ has a larger m/z 44 signal and smaller signals for $m/z > 51$ (Fig. 4c). $\text{OOA-1a}_{\text{AMS}}$ and $\text{OOA-1b}_{\text{AMS}}$ factors were moderately correlated in time ($r = 0.6$), and $\text{OOA-1b}_{\text{AMS}}$ had highest concentrations during the FP1 and FP2 fire periods (Fig. 3) and correlated strongly with BB_{FTIR} ($r = 0.8$). Without biomass burning tracers (CO, acetonitrile, K, Br) that had clear time series correlations with the factor, $\text{OOA-1b}_{\text{AMS}}$ could not have been distinguished from $\text{OOA-1a}_{\text{AMS}}$. However, PMF factors have substantial uncertainty, especially when the chemical characteristics and time series have significant overlap. For this reason, we also present the same solution with the two similar factors (OOA-1a and OOA-1b) combined together in a factor named OOA-1 , which was found to correlate strongly ($r > 0.8$) with both biogenic and biomass burning tracers (Figure S5).

3.2.4 Comparison of FTIR and AMS Factors

The factors identified from AMS measurements are largely consistent with those from FTIR factors, in terms of both chemical speciation and temporal trends. OOA-1a_{AMS} and BIO_{FTIR} factors were strongly correlated to each other ($r = 0.9$). Both BIO_{FTIR} and OOA-1a_{AMS} had the largest concentrations during the stressed boreal and fire periods (as described in Sect. 3.2.2); however, OOA-1a_{AMS} was able to capture the sawmill events, as seen in the sawmill periods and those identified by Cluster 1-T shown in Fig. 3. This difference illustrates the ability of the higher time resolution of the AMS measurements to identify local sources (i.e. fresh biogenic OA from sawmill events). The O/C ratios of the two biogenic factors were both quite high relative to other reported ambient factors (Jimenez et al., 2009; Russell et al., 2011), with BIO_{FTIR} and OOA-1a_{AMS} having O/C ratios of 0.75 and 0.71, respectively (Table 3).

To compare the sources of the OOA-1a_{AMS} and BIO_{FTIR} factors, PSCF were calculated for the mass fraction of each factor (Pekney et al., 2006; Russell et al., 2009b) and contours representing the potential source region of each factor were plotted over the European geographic distribution of vegetative biomes (Fig. 5a). Potential source regions of both OOA-1a_{AMS} and BIO_{FTIR} mass fractions overlap large regions of the Scandinavian boreal forests (Fig. 5a). Both BIO_{FTIR} and OOA-1a_{AMS} factors have large components from the southeast of Finland. This is consistent with BIO_{FTIR} and OOA-1a_{AMS} having moderate correlations with temperature ($r = 0.7$ and 0.6 , respectively), as temperatures were the highest when air masses arrived from the southeast, similar to the findings of Leaitch et al. (2011) that submicron biogenic organic mass in Whistler, Canada, increased exponentially with temperature. Figure 5a indicates that both factors represent contributions from large regional forest biomes.

Photochemical processing of biomass burning plumes can modify the chemical composition of submicron OM. AMS measurements with unit mass resolution (UMR) result in biomass burning mass spectra that look chemically similar to OOA after photochemical processing in the atmosphere (Grieshop et al., 2009). HYSPLIT

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backtrajectories, in addition to fire hotspot locations from FIRMS (fire hotspot data with > 90 % confidence: NASA FIRMS, 2012. MODIS Active Fire Detections. Available online <https://earthdata.nasa.gov/FIRMS>), indicated the biomass burning emissions had been transported more than 4 days prior to their arrival at Hyytiälä. OOA-1b_{AMS} had negligible contributions from levoglucosan mass fragments, m/z 57, 60, and 73, likely resulting from the extensive transport time of the plume (Lee et al., 2010; Schneider et al., 2006).

OOA-1b_{AMS} and BB_{FTIR} accounted for 39 % and 25 % of the OM (Table 3). PSCF calculated for mass fractions of OOA-1b_{AMS} and BB_{FTIR} indicate similar source regions for these two factors (Fig. 5b), overlapping in the regions heavily influenced by wildfires near Moscow and Ukraine in July and August 2010. Wildfire hotspots from 12 July – 12 August 2010 are nearly overlapped by the potential source regions of both biomass burning factors.

FFC2_{FTIR} had a weak correlation with OOA-2_{AMS} ($r = 0.4$) and showed geographic overlap in the potential source regions (Fig. 5d). FFC2_{FTIR} was found to have potential source regions near high SO_x (SO₂ + SO₃) emitting regions, specifically in Germany and Poland. The PSCF of OOA-2_{AMS} also depicted OOA-2_{AMS} originated near high SO_x emitting regions, in addition to northwestern Russia, which has significant industrial activity (Hole et al., 2009; Mira-Salama et al., 2008). OOA-2_{AMS} was found to have no correlation ($r = -0.1$) to FFC1_{FTIR}, which represents only a small OM contribution (12 %). FFC1_{FTIR}, which was correlated to Zn and V, had a small potential source region on the southern coastline of the Baltic Sea in moderately populated regions of Europe (Fig. 5c).

3.3 Single particle types from biomass burning emissions

46 particles from three days (26, 27, and 29 July) were sampled and analyzed by STXM-NEXAFS. All 46 particles were collected on days that had substantial OM contributions from biomass burning emissions that originated in western Russia. The majority of the sampled particles were 1–3 μm in diameter. The NEXAFS spectra had

clear absorption by carboxylic acid groups, which suggests the particles had substantial secondary organic mass components. The single-particle spectra were categorized by hierarchical Ward analysis (Ward, 1963) and compared to 14 types of single particles identified by Takahama et al. (2007) (Fig. 6).

Cluster 1 particles ($n = 21$) showed strong alkene/aromatic group (285.0 eV), carboxylic acid group (288.7 eV), and potassium (297.4 and 299.9 eV) absorption (Fig. 6a). Particles in Cluster 1 differed from the particle types identified by Takahama et al. (2007), as Type F particles were the only particles to contain strong K absorption. However, Type F particles also contained CO_3^{2-} (290.4 eV), a signature for dust particles that was not identified in Cluster 1 particles. Potassium is a typical tracer of primary pyrogenic emissions (Andreae, 1983), likely from volatilization and reactions within the vegetation during burning that results in the nucleation and condensation of potassium-salt particles (Gaudichet et al., 1995). Tarballs, spherical HULIS-like particles, have often been identified in biomass burning emissions (Posfai et al., 2003; Tivanski et al., 2007); however, no tarball-like particles were identified in the 46 particles sampled during biomass burning periods. Potassium-rich single particles have been identified in aged smoke plumes, including potassium-salt with amorphous organic coatings and organic particles with small potassium-salt inclusions (Li et al., 2003). These organic potassium-salt particles are believed to contain water-soluble organic compounds found in biomass smoke, making them important cloud condensation nuclei (Posfai et al., 2003), although other sources have also been identified (Pohlker et al., 2012).

The remaining clusters 2 and 3 resembled particle types identified by Takahama et al. (2007) (Fig. 6). Cluster 2 particles showed strong carboxylic acid group absorption at 288.7 eV and were the second-most dominant particle type ($n = 20$). Particles in Cluster 2 were spherical and spectra were similar to Type A particles, which are likely the result of atmospheric processing (Takahama et al., 2007) (Fig. 6b). Cluster 3 particles ($n = 5$) were characterized by strong alkene or aromatic group absorption at 285.0 eV and resembled Type H particles from Takahama et al. (2007), which likely

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have combustion origins (Fig. 6c) since the magnitude of the 285.0 eV peak is characteristic of high fractions of elemental or other pi bonded carbon.

4 Discussion of biomass burning and biogenic organic aerosol

Comparison of the biogenic and biomass burning factors for Hyytiälä OM measurements shows similarities in their composition (as measured by both AMS and FTIR), which are an expected consequence of their similar biological source material (Ahlm et al., 2012; Russell et al., 2011; Schwartz et al., 2010; Takahama et al., 2011): both biomass burning and biogenic OA can contain cellular material, rich in saccharide compounds that is lofted into the atmosphere and is typically rich in alcohol functional groups (Ahlm et al., 2012; Hawkins and Russell, 2010; Takahama et al., 2011). Both biogenic and biomass burning emissions include similar alkene VOCs that serve as SOA precursors, including monoterpenes, isoprene, and sesquiterpenes (Greenberg et al., 2006; Guenther et al., 1995; Simpson et al., 2011). Therefore they also contain similar oxidation products that are rich in O-OFG. Given these chemical similarities, is it possible to distinguish these two types of OM? Comparing the two techniques for measuring OM, we see that FTIR factor analysis is more sensitive to the small chemical differences between biogenic and biomass burning organic components, while AMS factor analysis has higher time resolution to allow identification of short-term events (such as local sawmill activities).

The fragmentation of organic aerosol in the AMS results in the majority of the organic mass fragments being associated with masses less than m/z 45, most of which have less than 2 carbons per fragment. For highly oxidized organic aerosol, the large fraction of m/z 44 outweighs the contributions of fragments that are more characteristic of their sources (Ng et al., 2011). For example, in rural regions like Hyytiälä, more than 90 % of OM can be highly oxygenated, making OOA the factor that accounts for a majority of OM in AMS factor analysis (Zhang et al., 2007). One key feature of AMS spectra is that as OM becomes increasingly photochemically processed, the OM mass fragment

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CA) (Hawkins and Russell, 2010; Takahama et al., 2011). In addition, we show here as a reference material for biomass burning a sample collected during a controlled burn of olive tree branches (Kostenidou et al., 2013). Even though the forest fires in Russia were not olive trees, the olive tree branch burning serves as a suitable reference for comparison to forest (mostly boreal and deciduous) BBOA since most vegetative material contains more than 80 % cellulose. BB_{FTIR} was found to correlate moderately with olive tree branch burning OM for all wavenumbers ($r = 0.6$). The only substantial difference in the spectra from these burning samples was the carbonyl region strong correlation was found when was excluded from the analysis ($r = 0.9$). Compared to other FTIR biogenic SOA factors, the Hyytiälä BIO_{FTIR} factor is very similar to the biogenic factor spectra identified for two different summertime studies at Whistler (Schwartz et al., 2010; Takahama et al., 2011). For comparison to a reference spectrum of biogenic SOA, the spectrum of SOA products from OH oxidation of α -pinene is shown (Chhabra et al., 2011), and the correlation of this FTIR spectrum to Hyytiälä BIO_{FTIR} was very strong ($r = 0.97$).

The spectral similarities between Hyytiälä BB_{FTIR} and BIO_{FTIR} with factors from other regions and with the respective reference OM (namely olive tree burning BBOA and α -pinene chamber SOA) is striking. Such strong similarities indicate three important points: (1) The similarities in the alkane absorbance region indicate that the carbon backbones of both primary OM and secondary OM precursors are retained by the nondestructive aspect of FTIR spectroscopy. (2) The similarities in the ratios of carboxylic acid and carbonyl groups indicate that the relative amounts of oxidized functional groups produced from each type of precursor are relatively invariant, suggesting that region-specific differences in oxidants (e.g. OH, O_3 , and NO_3 levels) may have little effect on the OFG composition. (3) Oxidized OFG tend to dominate both biogenic and biomass burning OM. For biogenic OM, this high degree of oxygenation is the result of both oxygenated SOA and small submicron contributions of oxygenated POA from vegetative detritus. For biomass burning, the O-OFG may result largely from oxygenated combustion product POA and small increases in oxygenated OFG with transport time.

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One difference in the biomass burning factors is that Scripps Pier and Whistler (2009) had negligible amounts of alcohol group in the biomass burning factors (7 % and 2 %, respectively), whereas the Hyytiälä factor had a high alcohol group fraction (25 %). The higher alcohol group contribution at Hyytiälä may be because this campaign had fewer competing alcohol-group containing sources (i.e. biogenic marine or vegetative detritus) that could have caused misallocation in other factor analysis (Ahlm et al., 2012; Frossard et al., 2011; Hawkins and Russell, 2010; Hawkins et al., 2010; Liu et al., 2012). Even though BB_{FTIR} alcohol group fraction (25 %) was higher than the Scripps Pier and Whistler (2009) (2 % and 7 %, respectively), the olive tree burning reference OM has an even higher alcohol group fraction (30 %), indicating that the Hyytiälä fraction is well within the possible range of alcohol group fraction expected for biomass burning sources.

The chemical sensitivity of the FTIR method is partly explained by the nondestructive nature of FTIR spectroscopy, which retains a larger signal from the unbroken carbon backbone of source OM, allowing for easier separation of different types of oxygenated OM. In addition, FTIR provides information about both the degree of oxidation (O/C) and the type of O-OFG. The advantages of functional group composition over elemental ratios (O/C) are illustrated by Fig. 8, which shows the functional group equivalent of a Van Krevelen diagram, with the fraction of alkane groups analogous to H/C and the sum of the O-OFG group fraction analogous to O/C, and Fig. 8b separates the O/C by type of O-OFG (hydroxyl versus carbonyl-containing groups). Biomass burning and biogenic factors cover overlapping ranges on Fig. 8a because their O/C and H/C are not distinct; however, the two types are clearly separated in Fig. 8b.

Figure 8a and b also clearly illustrate that biomass burning factors identified in different regions have varying amounts of oxygenated carbon, likely associated with the transport time. Fresh olive tree burning emissions were less than 1 day old and had the lowest oxygenated group fraction (48 %), followed by biomass burning OM from Monterey measured at Scripps Pier (53 %) which was estimated to be between 2–4 days old (Hawkins and Russell, 2010), and finally Hyytiälä BB_{FTIR} with 4–5 day old

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biomass burning aerosol with the highest O-OFG fraction (73 %). The differences in O-OFG mass fractions and estimated transport times of BBOA are also evident in the varying molar ratios of carbonyl (non-acidic) group to alkane group (0.01–0.38), with lowest corresponding to the reference of olive tree burning OM and highest to the highly oxygenated Hyytiälä BB_{FTIR} factor. These differences were not evident in the nearly constant molar ratios of carboxylic acid group to alkane group (0.04–0.05) (Fig. 8b). Increasing molar ratios of carbonyl group to alkane group could indicate OH oxidation of long chain alkanes that form alkyl peroxides in first-generation monofunctional products (Russell et al., 2011). An additional source of carbonyls in carbonaceous particles includes OH oxidation of aromatics (Lee and Lane, 2009, 2010; Wang et al., 2007; Webb et al., 2006), a common precursor found in biomass plumes (Reid et al., 2005). The other difference between the O-OFG for the biomass burning reference (i.e. olive tree branches) and the other factors is that the olive tree burning reference OM has the highest alcohol group fraction (30 %) and the lowest carbonyl and carboxylic acid group (COR' + COOH) fraction (18 %).

The differences in the factor and reference spectra for biogenic OM were smaller, with alkane group fraction varying from 25 % to 40 % and O-OFG varying from 53 % to 64 % (Fig. 8a). The same is true when looking at the fraction of alcohol (12–23 %) and (COR' + COOH) (35–52 %) groups. The consistency of molar ratios of carbonyl group to alkane group (0.08–0.13) and of carboxylic acid group to alkane group (0.10–0.11) for both biogenic factors and α -pinene SOA is also shown in Fig. 8b.

During July and August 2010, OM at Hyytiälä was $4.4 \mu\text{g m}^{-3}$ on average with a maximum concentration of $21 \mu\text{g m}^{-3}$, higher than OM measured in previous springtime (1.20 to $1.24 \mu\text{g m}^{-3}$, Finessi et al., 2012; Raatikainen et al., 2010) or summertime (1.7 – $2.2 \mu\text{g OC m}^{-3}$, Kourttchev et al., 2009; Yttri et al., 2011) campaigns. Consistent with our results, these studies have found that biogenic OM makes up approximately one-third of submicron OM in Hyytiälä. During HUMPPA-COPEC, the majority of the remaining OM was from transported emissions (i.e. biomass burning and fossil fuel combustion), making rural Hyytiälä not as pristine or remote in character as one might

temperature-driven increases in BVOC emissions have been shown to result in substantially enhanced concentrations of biogenic OM (Leaitch et al., 2011).

In addition to the biogenic and biomass burning sources, the remaining 39 % OM was largely associated with fossil fuel emissions from motor vehicles or other fossil fuel combustion sources. A unique intermittent local source of biogenic-like emissions was a nearby sawmill operation (Korkeakoski, Finland, located 10 km SE of Hyytiälä), which contributed 60 % of OM when the wind was from the southeast during nighttime hours (midnight–4 a.m.). The short dark periods of high latitude summer nights meant that photochemical reactions could continue throughout much of the night.

Distinguishing the chemical differences between biomass burning and biogenic sources is challenging, since both the primary and secondary contributions originate from terrestrial vegetation. As a consequence, primary components of both sources include cellulose-breakdown products, and secondary components include oxidation products of monoterpenes and other terpenoid compounds. These inherent chemical similarities were more clearly identified in the FTIR spectra than in the mass fragment spectra, with the differences evident in (1) the higher non-acidic carbonyl groups present in the biomass burning organic factor, possibly a characteristic of their further oxidation by higher temperatures in plume conditions and (2) the presence of methylene peaks characteristic of longer-hydrocarbon chain waxes that are lofted in greater amounts in windy conditions commonly associated with wildfires. Mass fragments in the OOA-1b_{AMS} factor spectra did not include characteristic BB fragments reported by other studies and greatly resembled those found in OOA-1a_{AMS}, likely due to atmospheric processing of the biomass burning plume which was transported for 4–5 days prior to arriving at Hyytiälä. However, AMS factor analysis could separate sources by temporal correlation with particle and gas-phase tracers, even though there were only negligible differences in mass fragments within the factor spectra. In past studies that lacked such tracers, biogenic and oxidized biomass burning organic aerosol may have been considered to be inseparable, since its chemical characteristics were not evident in mass-fragment-based O/C retrievals. This study demonstrates that SOA transported

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multiple days from different sources may have indistinguishable AMS mass fragment spectra but different FTIR spectra, showing that functional group absorption provides more information than mass fragment spectra (at 600 C) for distinguishing types of highly oxidized SOA.

5 **Supplementary material related to this article is available online at:**
**[http://www.atmos-chem-phys-discuss.net/13/16151/2013/
acpd-13-16151-2013-supplement.pdf](http://www.atmos-chem-phys-discuss.net/13/16151/2013/acpd-13-16151-2013-supplement.pdf)**

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Table 1. Summary of biogenic and biomass burning apportionment from previous studies influenced by forest OM.

Reference Factor Analysis	Project	Key Findings
This Study	HUMPPA-COPEC12	BIO _{FTIR} and BOA _{AMS} were separated from aged BB aerosol and captured local sawmill operations. BIO _{FTIR} had a strong correlation to temperature and the factor spectra correlated strongly to α -pinene oxidation products from OH oxidation.
Takahama et al. (2011)	Whistler, Canada; Summer 2009	BIO _{FTIR} was separated from BB _{FTIR} , and contained high fractions of alcohol and carbonyl organic functional groups. PSCF analysis indicated BIO _{FTIR} factor originated from forested regions in northern Canada.
Schwartz et al. (2010)	Whistler, Canada; Summer 2008	PMF attributed 65 % of OM to biogenic sources. BIO _{FTIR} was dominated by oxygenated species: carbonyl, carboxylic acid, and alcohol organic functional groups, and correlated strongly to monoterpenes and MVK/MACR.
Setyan et al. (2012)	CARES, Sacramento Valley; Summer 2010	A more-oxygenated organic aerosol (MO-OOA _{AMS}) component was associated with BSOA. Correlations to MVK/MACR and enhanced m/z 29 (CHO ⁺) signature confirm the biogenic influence on this factor. MO-OOA _{AMS} was enhanced when anthropogenic emissions increased and BVOCs were abundant.
Finessi et al. (2012)	Hyytiälä, Finland; Spring 2007	Clean, marine influenced, air masses were linked to a less oxygenated aerosol (OOA2 _{AMS}) and carbonyl/carboxylic enhanced aerosol (Terpene-SOA _{NMR}). Terrestrial biogenic secondary organic aerosol (BSOA) accounted for 30 % of OA.
Slowik et al. (2007)	Egbert, Ontario; Summer 2007	An OOA2 _{AMS} factor was found to correlate strongly with MACR/MVK tracers and temperature, suggesting influence from BSOA. Model calculations and remote sensing measurements indicate BSOA impacted regional aerosol loadings.
Raatikainen et al. (2010)	Hyytiälä, Finland; Apr 2005	Factor analysis and back trajectories attributed an OOA2 _{AMS} factor to local VOC oxidation (e.g. BSOA). Volatility study found that OOA2 _{AMS} was much more volatile than the more oxidized OOA1 _{AMS} factor.
Williams et al. (2007)	ICARTT, Chebogue Pt; Summer 2004	Factor analysis, back trajectories, and correlations to BVOC oxidation products helped identify two biogenic components: Isoprene _{TAG} and Terpene _{TAG} oxidation, accounting for 20 % of OM. Both factors had high organic mass fractions (> 75 %).
Organic Tracer Analysis		
Offenberg et al. (2011)	RTP, North Carolina; 2006	Isoprene SOA accounted for up to 40 % of OM in the summer months and was highly temperature dependent.
Fu et al. (2010)	MTX2006; East China	Isoprene derived secondary organic carbon (SOC) was 7 times greater than monoterpene derived SOC. Biogenic SOC accounted for 10 % of OC, and 60 % of SOC.
¹⁴ C and OC/EC Analysis		
Szidat et al. (2009)	Goteborg, Sweden; 2005 & 2006	OC _{BIO} was the dominant OM source during summer months (40%). The presence of BSOA during the winter months in Sweden suggests that POA from wood burning could contribute to this aerosol fraction.
Lewis et al. (2004)	Summer 1999	Biogenic contribution to organic carbon was identified; however, it was undetermined what fraction was primary and what fraction was secondary.
Classification Analysis		
Chen et al. (2009)	AMAZE-08; Manaus, Brazil	Class of aerosol consistent with low sulfate concentrations, high organics, in-Basin flow, and correlation to isoprene and monoterpenes was determined to be BSOA.

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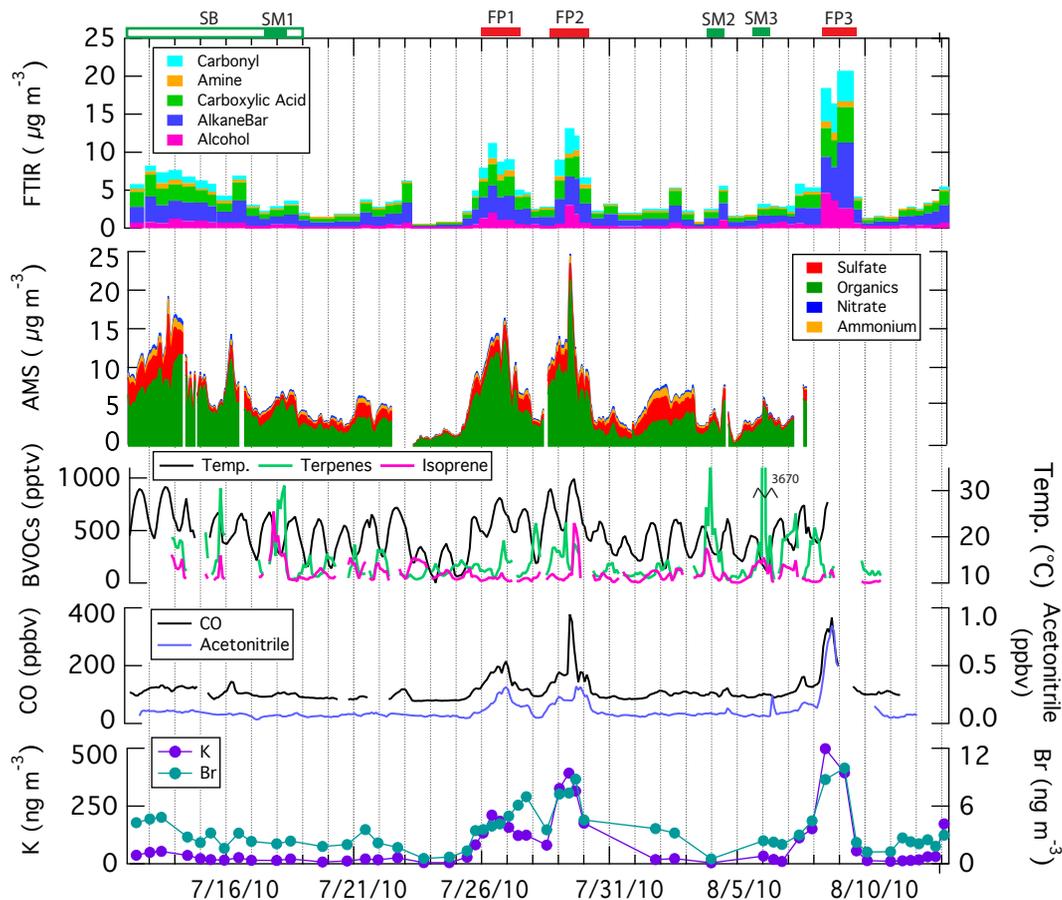
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Table 3. Summary of concentration, OM fraction (shown in parentheses), O/C, and composition (organic functional group composition of FTIR factors and prevalent m/z signatures of AMS factors) for FTIR and AMS factors. Organic functional groups from FTIR, including alcohol (pink), alkane (blue), carboxylic acid (green), amine (orange), and carbonyl (teal).

Factor	Campaign Avg. ($\mu\text{g m}^{-3}$)	O/C	Composition
BOA _{FTIR}	1.7 (35 %)	0.75	
BB _{FTIR}	1.2 (25 %)	0.53	
FFC1 _{FTIR}	0.6 (12 %)	0.14	
FFC2 _{FTIR}	1.3 (27 %)	0.27	
OOA-1 _{AMS}	3.0 (70 %)	0.87	m/z : 28, 44, 50, 51, 53, 55, 65, 69
OOA-1a	1.3 (30 %)	0.71	m/z : 50, 53, 55
OOA-1b	1.7 (39 %)	0.99	m/z : 44, 28, 18
OOA-2 _{AMS}	1.3 (30 %)	0.60	m/z : 41, 43, 55, 67

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Fig. 1. Time series of submicron aerosol components and gas phase tracers with stressed boreal (green outline), sawmill (green box) and fire (red box) periods denoted at figure top. **(A)** Organic functional groups from FTIR, including alcohol (pink), alkane (blue), carboxylic acid (green), amine (orange), and carbonyl (teal). **(B)** Non-refractory organic aerosol from C-ToF-AMS including: organics (green), sulfate (red), ammonium (orange), and nitrate (blue). **(C)** 2 h average sum of monoterpenes (light green), isoprene (pink), and temperature (black). **(D)** 2 h average CO (black) and acetonitrile (violet). **(E)** XRF potassium (purple) and XRF bromine (teal) for subset of FTIR filters analyzed by XRF. Stressed boreal periods were identified by several weeks of unusually high temperatures prior to and during the first week of the campaign (Bäck et al., 2013) and sawmill periods by their enrichment of (+)- α -pinene over its (-)- α -pinene enantiomer, coinciding with abnormally high nighttime spikes in monoterpene and isoprene concentrations (Williams et al., 2011). Fire periods were defined as times that exhibited acetonitrile, CO, potassium, and bromine concentrations, with percent increases of greater than 100 % above background concentrations.

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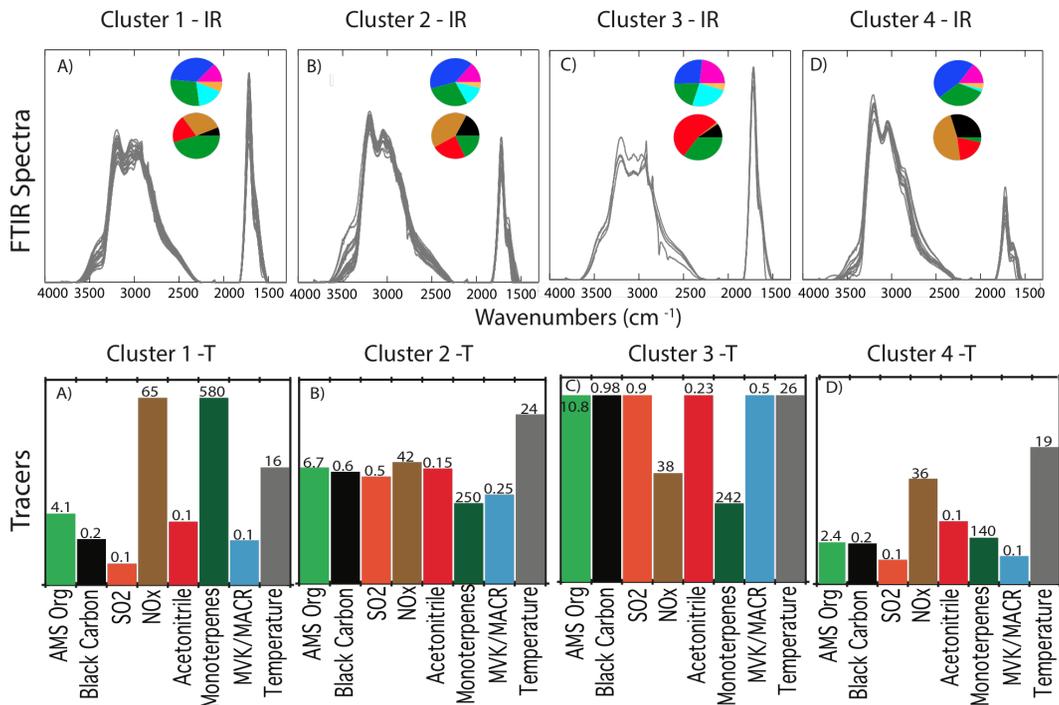


Fig. 2. (Top) FTIR spectral clusters from Ward algorithm **(A)** Cluster 1-IR (23 spectra), **(B)** Cluster 2-IR (22 spectra), **(C)** Cluster 3-IR (5 spectra), and **(D)** Cluster 4-IR (11 spectra). Top pie chart in each panel shows average organic functional composition for each cluster: alcohol (pink), alkane (blue), carboxylic acid (green), nonacid carbonyl (teal), and primary amine (orange). Bottom pie chart in each panel represents the average contribution of each FTIR PMF factor in each of the four clusters: FFC1_{FTIR} (black), FFC2_{FTIR} (tan), BB_{FTIR} (red), and BIO_{FTIR} (green). (Bottom) Clustering of organics, gas phase, particle phase, and meteorological data. **(A)** Cluster 1-T, high monoterpenes (580 ppt) and NO_x (65 ppb). **(B)** Cluster 2-T, low organics (6.7 μg m⁻³). **(C)** Cluster 3-T, high organics (10.8 μg m⁻³), SO₂ (0.9 ppb), MVK/MACR (0.5 ppt), and temperature (26 °C). **(D)** Cluster 4-T, low organics (2.4 μg m⁻³) and moderate temperatures (19 °C). Cluster averages of each tracer are normalized to the maximum value of each tracer to show relative differences between cluster groups. Average values of each tracer are listed on the bar plot: AMS Organics and black carbon (μg m⁻³), SO₂, NO_x, and acetonitrile (ppb), monoterpenes and MVK/MACR (ppt).

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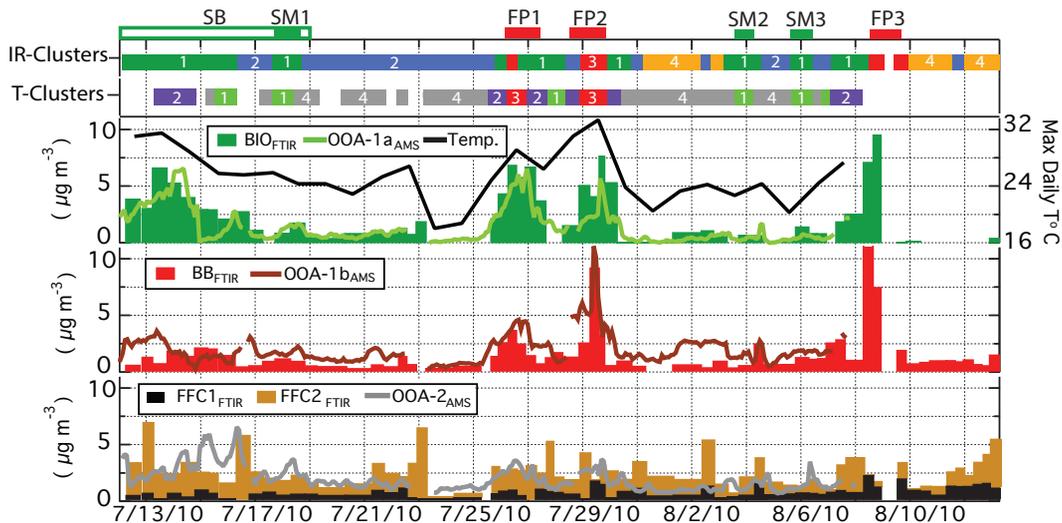


Fig. 3. Time series of submicron OM reconstructed from PMF analysis on AMS and FTIR spectra and clusters of FTIR spectra (IR-Clusters) and tracers (T-Clusters). (Top) Times series of IR-Clusters: Cluster 1-1R (green), Cluster 2-IR (blue), Cluster 3-IR (red), Cluster 4-IR (orange) and T-Clusters: Cluster 1-T (light green), Cluster 2-T (purple), Cluster 3-T (red), and Cluster 4-T (grey). Bars horizontally span sampling periods for each filter (or filter-averaged period). (Bottom) Time series of AMS and FTIR factors grouped by factor source: biogenic (which includes maximum daily temperature), combustion, and biomass burning. Color bars on top of figure indicate periods of stressed boreal conditions (green outline), sawmill (green box), and fire periods (red box).

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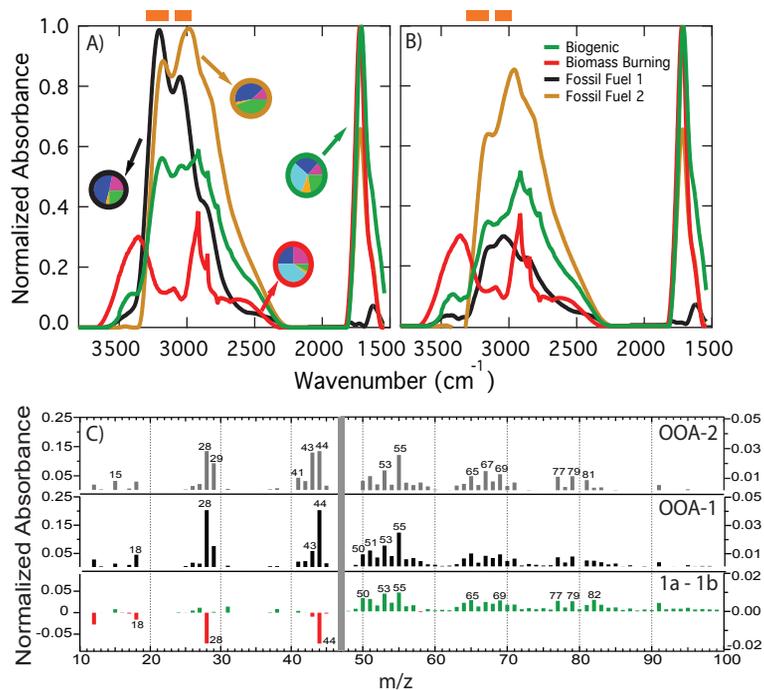


Fig. 4. Normalized FTIR and AMS spectra from the 4-factor (FPEAK = 0, seed = 1) and 3-factor (FPEAK = -0.4, seed = 1) PMF solutions. **(A)** FTIR factors: FFC1_{FTIR} (black), FFC2_{FTIR} (tan), BB_{FTIR} (red), and BIO_{FTIR} (green). Pies show average organic functional group composition for each factor: alkane (blue), alcohol (pink), amine (orange), carbonyl (teal), and carboxylic acid (green). Factor spectra include organics and ammonium. **(B)** FTIR Factor spectra after subtraction of ammonium absorbance so that only organic absorbance is shown (factors were smoothed by a 5-point box algorithm). Orange bars on top denote region of ammonium absorbance. **(C)** Normalized mass spectra for the 3-factor PMF solution: OOA-1_{AMS}, OOA-2_{AMS}, and the difference mass spectra of OOA-1a_{AMS} and OOA-1b_{AMS}. Vertical grey bar indicates change in axis for fragments greater than m/z 47.

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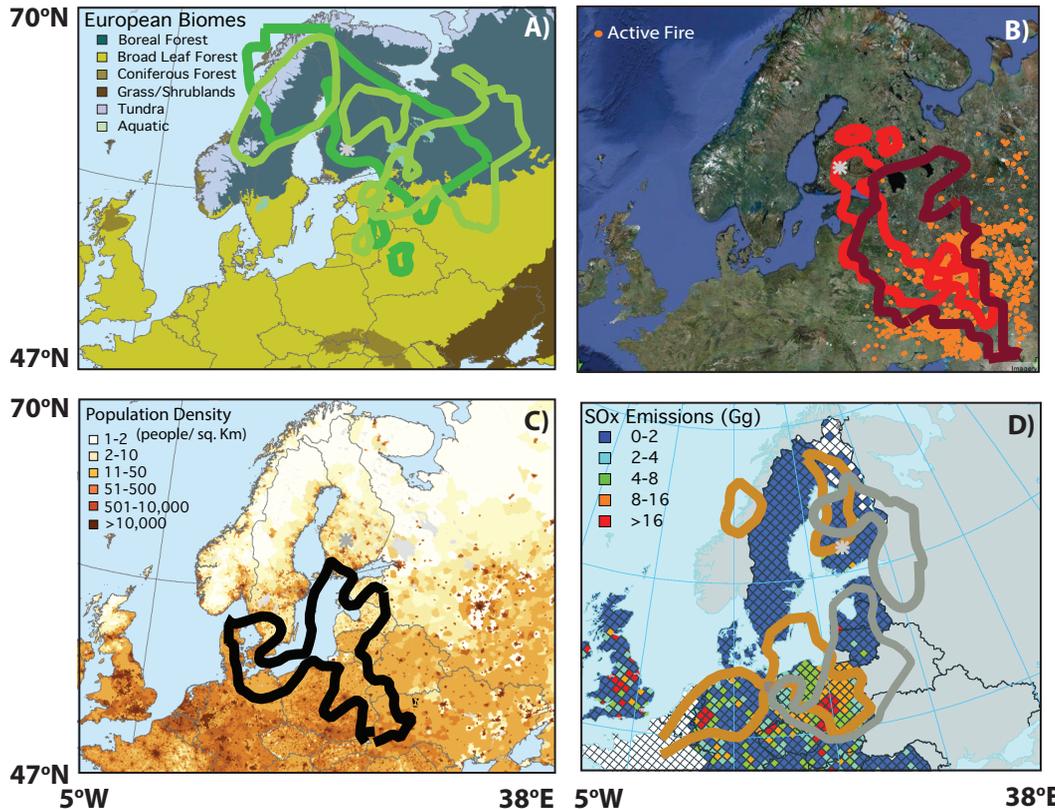
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Fig. 5. PSCF of AMS and FTIR factor fractions with contours indicating 0.4 probability of potential source region in each map. **(A)** BIO_{FTIR} (green) and $\text{OOA-1a}_{\text{AMS}}$ (light green) contours showing proximity to regional vegetative biomes (map: PLACE III – Europe Biomes, <http://sedac.ciesin.columbia.edu/data/set/nagdc-population-landscape-climate-estimates-v3>). **(B)** BB_{FTIR} (red) and $\text{OOA-1b}_{\text{AMS}}$ (dark red) contours and active wildfire hotspots (12 July – 12 August 2010) in Eastern Europe and Russia, for fires with > 90 % confidence (fire data: NASA FIRMS, 2012. MODIS Active Fire Detections. Available online <https://earthdata.nasa.gov/FIRMS>). **(C)** $\text{FFC1}_{\text{FTIR}}$ (black) contours and population density for Europe and western Russia (map: PLACE III – Population Density 2010, Europe, <http://sedac.ciesin.columbia.edu/data/set/nagdc-population-landscape-climate-estimates-v3>). **(d)** $\text{FFC2}_{\text{FTIR}}$ (brown) and $\text{OOA-2}_{\text{AMS}}$ (grey) contours with 2005 SO_x emissions (no SO_x data is shown in white and grey regions indicate outside of the study area) (map: EEA, www.eea.europa.eu/data-and-maps/figures/emissions-of-sox-in-2005). Hyytiälä is denoted by a grey asterisk in each map.

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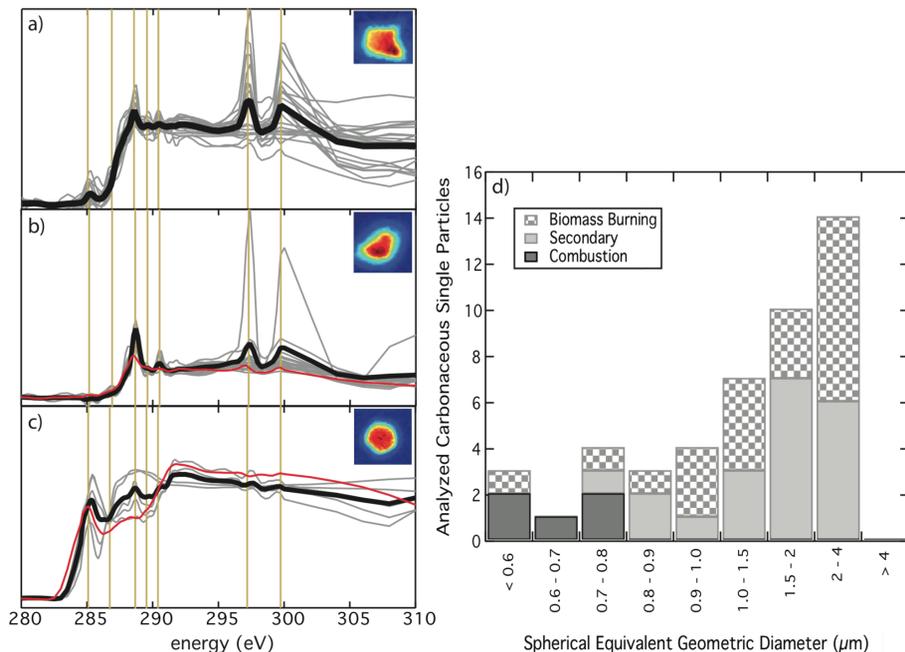


Fig. 6. Normalized single-particle spectra clustered into three categories: **(A)** Cluster I, **(B)** Cluster II, and **(C)** Cluster III. Black line indicates cluster average and grey lines represent individual particle spectra. Red lines represent type “a” and “h” (identified in Takahama et al., 2007) particles for Cluster II and III respectively. Yellow vertical lines indicate absorptions of specific organic and inorganic functional groups: 285.0 eV alkene/aromatics, 286.7 eV ketonic carbonyl, 287.7 eV carboxylic carbonyl, 289.5 eV alcohol, 290.4 eV carbonate, and 297.4 and 299.9 eV for potassium. **(D)** Distribution of 46 organic-containing single particles binned by spherical equivalent geometric diameter. Images inset in **(A–C)** show absorbance images at 288.85 eV and represent typical single-particle geometries of each cluster.

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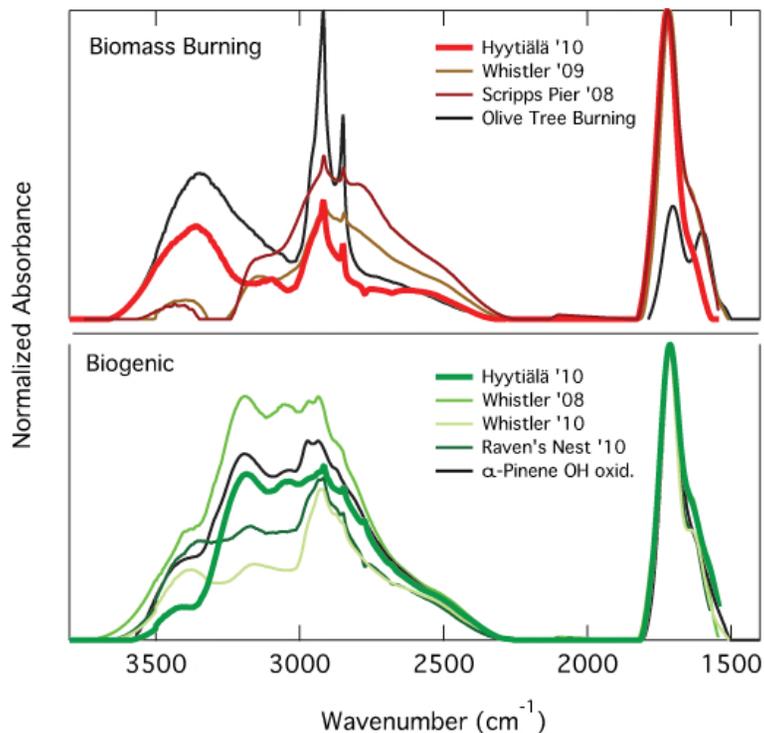


Fig. 7. Normalized biomass burning (top) and biogenic factors (bottom) from Whistler, Canada, and Scripps Pier (La Jolla, CA) (Schwartz et al., 2010; Takahama et al., 2011; Ahlm et al., 2012; Hawkins and Russell, 2010), in addition to SOA formed from aged Olive Tree burning emissions (Kostenidou et al., 2013) and SOA products from smog chamber oxidation of α -pinene (OH) (Chhabra et al., 2011).

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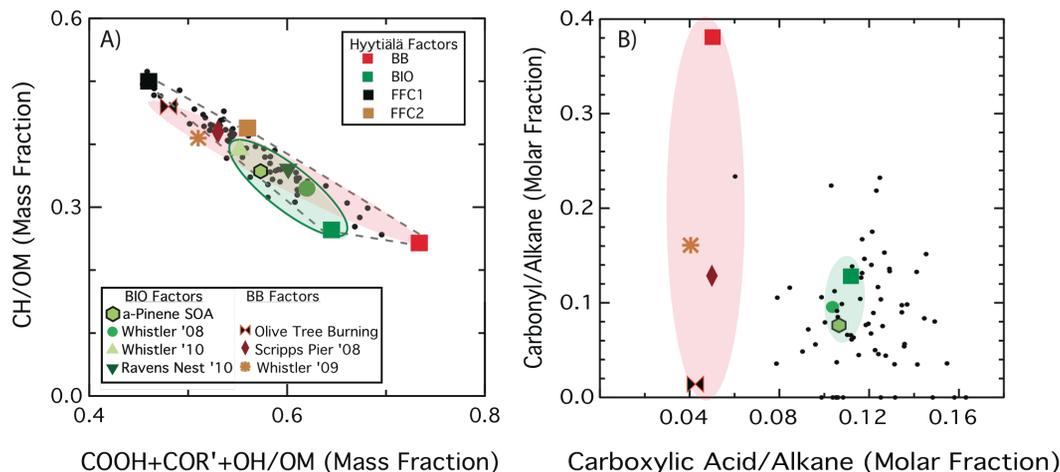


Fig. 8. (A) Distribution of oxygenated functional groups in ambient aerosol (black circles) and PMF factors in terms of mass fractions for biogenic and biomass burning factors: Hyttiälä, Whistler, 2008 (Schwartz et al., 2010), Whistler, 2009 (Takahama et al., 2011), Whistler, 2010 (including Raven's Nest) (Ahlm et al., 2012), Scripps Pier, 2008 (Hawkins and Russell, 2010), POA formed from aged Olive Tree burning emissions (Kostenidou et al., 2013) and SOA from α -pinene oxidation (Chhabra et al., 2011). (B) Molar fractions of carbonyl (non-acid carbonyl) and carboxylic acid. Markers correspond to those presented in legend found in (A). Red and green shaded regions correspond to typical distributions of biomass burning and biogenic factors, respectively.

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