



# First measurements of reactive $\alpha$ -dicarbonyl concentrations on PM<sub>2.5</sub> aerosol over the Boreal forest in Finland during HUMPPA-COPEC 2010 – source apportionment and links to aerosol aging

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**Abstract.** The first dataset for summertime boreal forest concentrations of two atmospherically relevant  $\alpha$ -dicarbonyl compounds, glyoxal (Gly) and methylglyoxal (Mgly) on PM<sub>2.5</sub> aerosol was obtained during the HUMPPA-COPEC-2010 field measurement intensive in Hyytiälä, Finland. Anthropogenic influences over the course of the campaign were identified using trace gas signatures and aerosol particle chemical composition analysis. The data evaluation allowed the identification of different events such as urban pollution plumes, biomass burning and sawmill emissions as sources of high Gly and Mgly concentrations. Mean aerosol concentrations during periods of biogenic influence were 0.81 ng m<sup>-3</sup> for Gly and 0.31 ng m<sup>-3</sup> for Mgly. Mgly was generally less abundant in PM<sub>2.5</sub>, probably due to its shorter photolysis lifetime and less effective partitioning into the particle phase due to its smaller effective Henry's Law constant compared to Gly. This is in contrast with previous urban studies which show significantly more Mgly than Gly. Peak concentrations for Gly coincided with nearby sources, e.g. high VOC emissions from nearby sawmills, urban pollution plumes from the city of Tampere located 50 km southwest of the sampling site and biomass burning emissions from wildfires. Calculated ratios of Gly in PM<sub>2.5</sub> and total organic matter in PM<sub>1</sub> aerosols indicate higher values in less aged aerosols. Irreversible processing of Gly in the particle

phase, e.g. via oxidation by OH radicals, organo sulfate or imidazole formation are processes currently discussed in the literature which could likely explain these findings.

## 1 Introduction

Atmospheric aerosols are a major source of uncertainty in estimations of the global radiative forcing (IPCC, 2007). Improving knowledge about sources, formation, growth and transformation processes of secondary organic aerosols (SOA) is necessary to reduce these uncertainties, as SOA makes up a large fraction of submicron atmospheric particles (Kanakidou et al., 2005; Zhang et al., 2007). Submicron or fine mode atmospheric particles influence global and regional climate due to their ability to scatter light and to act as cloud condensation nuclei (CCN) (Lohmann and Feichter, 2005). Biogenic emissions of volatile organic compounds (BVOCs) and their subsequent oxidation by atmospheric oxidants, such as hydroxyl (OH) radicals or ozone (O<sub>3</sub>), are major sources of SOA. The Boreal forest is known to be a major contributor to the global secondary organic aerosol (SOA) budget (Kulmala et al., 2004b; Tunved et al., 2006), since it represents over one quarter of the world's forest area (FAO, 2010). In contrast to tropical forests, where isoprene is the

most abundant BVOC in the boundary layer (e.g. Lelieveld et al., 2008), monoterpenes (e.g.  $\alpha$ - and  $\beta$ -pinene,  $\Delta_3$ -carene), especially  $\alpha$ -pinene, are often the most abundant gas phase compounds emitted by the Boreal forest (e.g. Ebben et al., 2011; Hakola et al., 2003).

During summer 2010 the HUMPPA-COPEC 2010 field measurement intensive was conducted from 12 July to 12 August at the SMEAR II measurement site in Hyytiälä (Hari and Kulmala, 2005), Finland. Key features of the station, land use near the site, predominant wind directions and meteorological conditions are described in detail by Williams et al. (2011). Briefly, the SMEAR II research station is located at  $61^{\circ}50'50.685''$  N and  $24^{\circ}17'41.206''$  E at 179 m above sea level (a.s.l.). The land within a radius of 50 km of the measurement site is dominated by coniferous and mixed forests with only one significant urban center (Tampere) to the southwest. During the campaign air masses originated primarily from southwestern (53.7 %) and southeastern (20.7 %) but also from northwestern (10.3 %) wind sectors. Generally high temperatures ( $T_{\max} = 32.4^{\circ}\text{C}$ ,  $T_{\text{ave}} = 20.0^{\circ}\text{C}$ ) and ozone concentrations (up to 70 ppb) were encountered during the campaign, but periods of lower temperatures and ozone concentrations, which coincided with wind from northwestern directions, also occurred. Aside from a few exceptions the precipitation was low ( $< 2 \text{ mm day}^{-1}$ ). One aim of the campaign was the identification and characterization of anthropogenic influences on European Boreal forest regions using backward trajectories, as well as aerosol particle and trace gas signatures (Williams et al., 2011). In this paper we will present detailed analysis of natural background concentrations of two prominent  $\alpha$ -dicarbonyl compounds; however, biomass burning, sawmill and urban pollution plume events, with regard to glyoxal (Gly) and methylglyoxal (Mgly) concentrations in particulate matter with aerodynamic diameters  $< 2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ), will also be investigated.

The two simplest  $\alpha$ -dicarbonyl compounds have drawn much attention as potential SOA precursors over the last years. They are produced by a variety of biogenic (e.g. isoprene or monoterpenes) and anthropogenic (e.g. benzene, toluene, xylenes) sources (Volkamer et al., 2001, 2005). Even though their vapor pressures are too high to produce SOA with regard to traditional gas/particle partitioning theory (Odum et al., 1996; Seinfeld and Pankow, 2003) they are readily taken up by aqueous aerosols and water containing particles due to the high solubility of their mono- and di-hydrates in water. Subsequent aqueous phase chemistry yields products, which, at least partly, remain in the particle phase. The role of aqueous phase chemistry in SOA formation was recently reviewed by Lim et al. (2010). Briefly, radical reactions, including oxidation by aqueous OH radicals forming lower volatility products like oxalic and pyruvic acids (Carlton et al., 2007; Tan et al., 2009, 2010; Lim et al., 2010; Altieri et al., 2008), and non-radical reactions, including the formation of higher molecular weight compounds via

hemiacetal or acetal formation (Kalberer et al., 2004; Hastings et al., 2005; Liggio et al., 2005a, b; Loeffler et al., 2006; Zhao et al., 2006), aldol condensation (Schwier et al., 2010; Sareen et al., 2010; Yasmeen et al., 2010), imine formation (De Haan et al., 2009a, b, 2011; Noziere et al., 2009; Galloway et al., 2009; Shapiro et al., 2009; Yu et al., 2011; Kua et al., 2011) and organo sulfate formation (Liggio et al., 2005a; Surratt et al., 2007, 2008; Galloway et al., 2009), are involved in Gly/Mgly aqueous phase chemistry.

The Gly/Mgly measurements presented here analyze Gly/Mgly concentrations in  $\text{PM}_{2.5}$  particles as the sum of the monomeric  $\alpha$ -dicarbonyl, its hydrated forms and reversibly formed higher molecular weight compounds, using a derivatization technique as will be discussed in the measurements section. Thus, not the complete SOA formed via aqueous phase chemistry of Gly and Mgly in atmospheric particulates is measured. However, the compounds analyzed here specifically account for Gly/Mgly SOA, while some of the aforementioned compounds, e.g. oxalic or formic acid and other oxidation products, can have multiple precursors.

The purpose of this paper is the identification of non-natural Gly/Mgly influences and the quantification of background forest Gly/Mgly concentrations using aerosol and trace gas measurements during HUMPPA-COPEC 2010 in combination with backward trajectories. The aging state of ambient aerosols will be assessed through identification of specific aerosol sources and Gly/Mgly concentrations. Therefore, analysis of Gly and Mgly aerosol concentrations in combination with aerosol chemical composition analysis via FTIR, and trace gas measurements of carbon monoxide (CO), sulfur dioxide ( $\text{SO}_2$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ), n-pentane and important BVOC's ( $\alpha$ -,  $\beta$ -pinene,  $\Delta_3$ -carene, isoprene) will be used for the appointment of sources and investigations about the aging state of the respective aerosols. Additionally, biogenic pristine forest background concentrations of Gly and Mgly in Boreal aerosols are quantified.

## 2 Measurements

### 2.1 Gly/Mgly sample collection and HPLC-ESI-MS/MS analysis

A parallel set of two sampling devices was operated one platform below the top of the radiation tower (16 m above ground level) at the Boreal forest research station SMEAR II (Station for Measuring Ecosystem- Atmosphere Relation) in Hyytiälä, Finland, from 10 July to 10 August 2010. Each sampling device consisted of a size selective inlet (Digitel DPM  $\text{PM}_{2.5}$ , Riemer Messtechnik, Germany), which was operated at a flow rate of  $2.3 \text{ m}^3 \text{ h}^{-1}$  using a rotary vane vacuum pump (Becker VT 4.4, oil-free, air-cooled, Becker, Germany) and a stainless steel filter holder.  $\text{PM}_{2.5}$  particles were collected on 70 mm TFE-coated borosilicate glass fiber filters (Pallflex T60A20, Pall

Life Science, USA). Adsorption of water vapor and other polar gaseous compounds is minimized due to the hydrophobic surface of the filter material. Sampling periods of the first sampling device (A) were chosen to match forecasted trajectories (calculated using the NOAA HYSPLIT model) for the wind vectors northwest (N-W), northeast (N-E), southeast (S-E) and southwest (S-W). The second sampling device (B) was used as a backup and for additional experiments regarding the diurnal behavior of  $\alpha$ -dicarbonyl PM<sub>2.5</sub> concentrations. Sampling durations were 8 to 57 h. Loaded filters were stored in capped glass vessels covered with aluminum foil at  $-20^{\circ}\text{C}$  until analysis. HPLC-ESI-MS/MS analysis of glyoxal and methylglyoxal as their bis-2,4-dinitrophenylhydrazone derivatives was carried out using an Agilent 1100 series HPLC system (degasser, gradient pump, auto sampler, diode array detector, Agilent Technologies GmbH, Germany) equipped with a Varian Pursuit XRs 3 C8 (Varian, Germany) reversed phase analytical column and a Bruker HCT-Plus ion trap mass spectrometer (Bruker Daltonics, Germany) as described by Kampf et al. (2011). Briefly, loaded filters were extracted by means of ultra-sonication using methanol/water (1:1), concentrated under a gentle N<sub>2</sub>-stream and derivatized using a freshly cleaned acidic aqueous solution of 2,4-dinitrophenylhydrazine (DNPH). Reversibly formed higher molecular weight compounds are efficiently de-oligomerized due to the strong acidic conditions used. Hydration of  $\alpha$ -dicarbonyl monomers is a fast equilibrium reaction, thus constantly providing non hydrated carbonyl functional groups needed for the derivatization reaction. Therefore, under these conditions the  $\alpha$ -dicarbonyl compounds, their hydrated forms and reversibly formed oligomers yield one product upon derivatization, i.e. glyoxal-bis-2,4-dinitrophenylhydrazone (Gly-bis-DNPH) and methylglyoxal-bis-2,4-dinitrophenylhydrazone (Mgly-bis-DNPH), respectively. Specific fragments of the protonated ions were quantified for each target compound in multiple reaction monitoring mode (MRM) of the mass spectrometer.

## 2.2 Measurements of anthropogenic trace gases

Pentane measurements were obtained with the Fast Observation of Trace Organics System (FOTOS). The FOTOS consists of a custom, three-trap (water, enrichment, and cryofocusing) cryogenic sampling system, a fast GC (20 m  $\times$  0.25 mm  $\times$  1.0  $\mu\text{m}$ , PLOT-Al<sub>2</sub>O<sub>3</sub> "S"), and a MS quadrupole detector (Agilent 5973). For this campaign, the FOTOS was measuring at a height of 16.4 m above ground level with a sampling frequency of 5.5 min. Detection limits for both pentane isomers were below 3 pptv (Johnson, 2011).

The SO<sub>2</sub> and CO concentrations were measured from different levels (4.2, 8.4, 16.8, 33.6, 50.4 and 67.2 m) in the 73 m high tower of the SMEAR II site. For a description of the site and a more detailed description of the

instrumentation see Hari and Kulmala (2005) and Kulmala et al. (2001). SO<sub>2</sub> concentration was measured with a UV-fluorescence analyzer (TEI 43 CTL, Thermo Fisher Scientific, Waltham, MA, USA) in sequence from all the six levels. Time resolution was 1 min at 6 min intervals for each measurement level. Detection limit was 0.1 ppb and relative accuracy  $\pm 3\%$ . CO mixing ratios were measured on top of the HUMPPA tower (24 m) using a fast-response vacuum-UV resonance fluorescence instrument (Model AL-5002, Aero Laser, Germany) (Gerbig et al., 1999). The instrument was calibrated in the field every three hours with a secondary standard (260  $\pm$  2.1 ppbv CO in compressed air) traced to a NOAA reference standard. The time resolution of the original data is 1 s. Detection limit and total uncertainty were 1 ppbv and  $< 10\%$ , respectively.

## 2.3 GC-MSD analysis of BVOC concentrations (pinenes, carene, isoprene)

BVOCs were observed with an on-line sampling and TD-GC-MSD measurement system. The system consists of a flow controller and a thermal desorber (Markes International, Pontyclin, UK) connected to a gas chromatograph (GC 6890, Agilent, USA), equipped with a Mass Selective Detector (MSD 5973 inert, Agilent, USA). The sampling line was fixed on the HUMPPA tower (24 m), approximately 2–3 m above the canopy top. Ambient air was drawn continuously through a main sample line at about 71 min<sup>-1</sup> by a vacuum pump, the residence time of the inlet line was approximately 23 s. A sub stream of sampled air was drawn at about 38 ml min<sup>-1</sup> through a Teflon manifold connection to the main sample line, and concentrated directly on the cold, adsorbent filled trap kept at 10  $^{\circ}\text{C}$  of the thermal desorber by a membrane pump. The sampling time was 30 min. The cold trap was 2 mm in diameter and filled by a 60 mm long bed of sorbent (Tenax TA and Carbograph I) supported by quartz wool. The cold trap was then heated to 200  $^{\circ}\text{C}$  rapidly and then held there while the sample was transferred to the GC column (Cyclodex-B, 30 m, 0.256 mm I.D., 0.25  $\mu\text{m}$  film; J&W Scientific, CA, USA). Detection limits were below 10 pptv. A more detailed description of the instrument can be found in Williams et al. (2007).

## 2.4 FTIR sample collection and chemical composition analysis

Submicron particles were collected 4 m above ground, approximately mid-canopy level, in temperature controlled housing on 37 mm Teflon filters (Pall Inc., 37 mm diameter, 1.0  $\mu\text{m}$  pore size) located downstream of a 1  $\mu\text{m}$  sharp-cut cyclone (SCC 2.229 PM1, BGI Inc.). The aerosol was dried to  $< 75\%$  RH (Silica orange gel 13767, Sigma Aldrich, USA) prior to filter collection. Back filters were also collected to quantify VOC absorption and artifacts; however, absorption on all back filters was below limit of detection (LOD). Filter

sampling duration varied from 6, 9, and 12 h, including duplicate 24-h filters, which were used when mass loadings were low. To reduce evaporative losses, samples were stored and transported at 0 °C prior to analysis in San Diego, California, by a Tensor 27 spectrometer (Bruker, Billerica, MA). Spectra were interpreted to quantify organic functional groups by using calibration standards and a revised automated algorithm based on the linear response of absorption peak area to the number of moles of organic bond present on the Teflon filters (Russell et al., 2009; Gilardoni et al., 2007; Maria et al., 2003). Quantified organic functional groups included saturated aliphatic C-CH (alkane), unsaturated aliphatic C=CH (alkene), aromatic C=CH, non-acid organic hydroxyl C-OH (alcohol), primary amine C-NH<sub>2</sub>, non-acid carbonyl C=O (aldehyde and ketone), and carboxylic acid COOH groups. Alkene and aromatic groups were below the limit of quantification (LOQ) for the entirety of the field campaign. The sum of all measured FTIR organic functional groups (alcohol, alkane, amine, carbonyl, and carboxylic acid) is used to determine organic mass (OM) concentrations from each filter (Russell, 2003; Russell et al., 2009).

### 3 Results and discussion

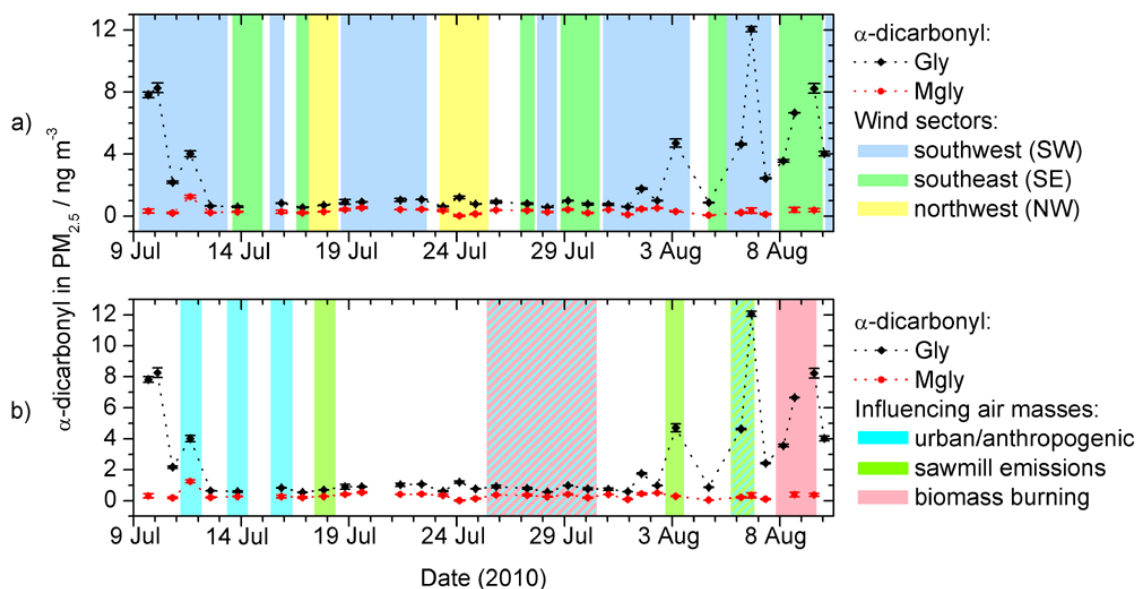
#### 3.1 Overview of $\alpha$ -dicarbonyl concentrations during HUMPPA-COPEC 2010

Field data concentrations of Gly and Mgly in PM<sub>2.5</sub> during HUMPPA-COPEC 2010 are provided from 10 July to 10 August. The concentrations ranged from 0.54 to 12.07 ng m<sup>-3</sup> for Gly and from below limit of detection (LOD) to 1.26 ng m<sup>-3</sup> for Mgly. Variation of Mgly concentration was much less pronounced as illustrated in Fig. 1a. Filter sampling according to the wind vectors as described in the previous section allowed the data to be analyzed for the potential sources of high Gly and Mgly concentrations. The highest concentrations of Gly and Mgly during the campaign were observed from southwestern (S-W) and southeastern (S-E) wind vectors, while northwestern (N-W) wind vectors did not show elevated concentrations. Land usage characteristics suggest a stronger anthropogenic influence in the south of the sampling site (Williams et al., 2011), whereas the N-W sector was deemed to be most representative of the boreal forest ecosystem. Several distinct sources for high  $\alpha$ -dicarbonyl concentrations are discussed in detail in the following section.

The mean concentration of Gly over the entire campaign was calculated to be 1.78 ng m<sup>-3</sup>  $\pm$  2.14 ng m<sup>-3</sup>. If the peak concentrations are considered to be of anthropogenic origin, as will be shown in the following section, the mean concentration attributed to the natural biogenic emissions of the surrounding coniferous forest was 0.81 ng m<sup>-3</sup>  $\pm$  0.23 ng m<sup>-3</sup>. Mgly concentrations were much lower; only 16 out of 35 filter samples showed concentrations

above the limit of quantification (LOQ), while from the remaining 19 filter samples 4 showed concentrations below the LOD. If the four samples below LOD are treated as zero concentrations and the samples with concentrations between LOD and LOQ are taken into account the mean Mgly concentration over the complete timescale of the campaign was 0.27 ng m<sup>-3</sup>  $\pm$  0.18 ng m<sup>-3</sup>. This value increases to 0.31 ng m<sup>-3</sup>  $\pm$  0.12 ng m<sup>-3</sup> when the timescale solely includes periods influenced by natural biogenic emissions. However, the observed Mgly concentrations are surprisingly low considering that major precursors for Gly and Mgly in this area are monoterpenes and isoprene. Both are abundant and possess a relatively high molar Mgly formation yield upon their atmospheric oxidation. Molar yields of 25 % (isoprene) and 4.2 % (monoterpenes) for Mgly, and 6.2 % (isoprene) and 2.8 % (monoterpenes) for Gly are reported by Fu et al. (2008). However, in the same study the modeled summertime mixing ratios of Gly and Mgly for southern Finland in 2006 are reported to be similar, i.e. 10–20 ppt for Gly and 5–20 ppt for Mgly (Fu et al. 2008). This is likely due to the shorter lifetime of Mgly with respect to photolysis and OH radical oxidation. Henry's Law constants ( $K_H$ ), describing the equilibrium of solutes between gas and aqueous phases (Betterton, 1992). Effective Henry's Law constants including hydration of the carbonyl groups ( $K_H^*$ ) reported for Gly and Mgly at room temperature are 3.6  $\times$  10<sup>5</sup> M atm<sup>-1</sup> and 3.7  $\times$  10<sup>3</sup> M atm<sup>-1</sup> (Zhou and Mopper, 1990; Betterton and Hoffmann, 1988), respectively, indicating uptake into the aerosol phase to be more important for Gly. Hence a shorter chemical lifetime may also contribute to the explanation of lower Mgly aerosol concentrations.

Other field data from boreal forest environments are very limited. Liggio and McLaren (2003) report Gly and Mgly PM concentrations in Vancouver and other rural and biogenic influenced sites (Sumas mountain) in Canada, ranging from 0.43 to 3.3 ng m<sup>-3</sup> in the case of Gly and from 0.03 to 1.2 ng m<sup>-3</sup> in the case of Mgly. These results are in good agreement with the concentrations encountered during HUMPPA-COPEC 2010. Gly peak concentrations are higher in the recent field campaign, owing to the diverse anthropogenic events occurring over the course of the campaign, as will be discussed in the following sections. Field data from major cities are reported by Kawamura and Yasui (2005), Li and Yu (2005) and Ho et al. (2007). The samples were collected in Hong Kong, other major Chinese cities and Tokyo, Japan. Gly and Mgly PM concentrations reported are one to two orders of magnitude higher than reported from boreal forest regions. Maximum concentrations of Gly and Mgly in these cities were up to 72.9 ng m<sup>-3</sup> and 218.4 ng m<sup>-3</sup>, respectively. Interestingly, the reported urban Mgly PM concentrations are high compared to Gly PM concentrations in major cities, while in the boreal forest environments Gly concentrations appear to be higher and more variable than Mgly concentrations. Kundu et al. (2010a) report seasonal



**Fig. 1.**  $\alpha$ -dicarbonyl concentrations centered at the middle of the respective sampling period. Dotted lines reflect linear interpolation of adjunct sampling periods. Error bars reflect measurement uncertainty. Colors in background correspond to: (a) wind vectors of air mass origins advected to the sampling site; (b) types of events influencing the sampling site.

$\alpha$ -dicarbonyl concentrations for an outflow region of Chinese pollutants (Gosan site, Jeju island, South Korea) and on average they find Mgly to be more abundant than Gly during the whole year. Mgly was also more abundant in a small field study conducted in southwest Germany at the Taunus Observatory, which is influenced by continental emission particularly from the highly industrialized Rhein-Main area (Kampf et al., 2011). Therefore, high concentrations of Mgly may suggest a stronger anthropogenic influence. However, this conclusion might not be applicable in strongly isoprene-emitting forests (e.g. Amazonian rain forests; Guenther et al., 2006) since atmospheric isoprene oxidation processes have been found to show a higher molar yield of Mgly (Fu et al., 2008). This should be addressed in future field studies.

### 3.2 Clean air, pollution events, sawmill activity and wildfires

Throughout the campaign several biomass burning, sawmill influence and urban/anthropogenic pollution events have been identified by tracer gases (Williams et al., 2011) and via chemical composition of the aerosol phase from FTIR. Biomass burning events, i.e. Russian wildfires which began from mid July 2010, were identified by sharp increases in the acetonitrile ( $\text{CH}_3\text{CN}$ ) and carbon monoxide (CO) mixing ratios, as well as high non-acid carbonyl and hydroxyl functional group concentrations in the aerosol phase. Sawmill influences were detected as peaks in BVOc concentrations accompanied by minima in the  $(-)/(+)\alpha$ -pinene ratio and urban/anthropogenic influences were identified as peaks in sulfur dioxide ( $\text{SO}_2$ ) and  $n$ -pentane time traces. Figure 1b

illustrates the influences of these events during the collection of the filter samples for Gly/Mgly analysis.

On several occasions high Gly and Mgly concentrations coincide with the aforementioned events. On 12 July an event with high submicron particle number counts was observed, which was deduced to be related to a pollution plume from the city of Tampere in the southwest of the sampling site (Williams et al., 2011). Gly and Mgly concentrations show a local maximum during this event. Ensemble 4 day back trajectories of other events attributed to have an urban/anthropogenic origin, i.e. on 14 July (St. Petersburg, Russia), 16 July (Poland and Germany), 26 July to 30 July (partly anthropogenic influence from St. Petersburg, Russia, coincident with Russian wildfire emissions) and 6 August (unclear origin, but identified as anthropogenic via peak in  $n$ -pentane mixing ratio), are available in the supporting material (Figs. S1–S5 in the Supplement). These events do not show elevated Mgly concentrations, which might be due to the greater distance of the respective sources from the sampling site. More distant sources result in longer transport times, thus increasing the chemical processing of  $\alpha$ -dicarbonyls to corresponding acids and other later generation reaction products in the aerosol phase. This potentially reduces the observable concentrations close to the background level and will be examined again in the following Sect. 3.3.

Two sawmill events on 3 August and 6 August show high Gly concentrations of 4.71 and 4.64  $\text{ng m}^{-3}$ . The highest concentration of Gly during the HUMPPA-COPEC 2010 field measurement intensive was measured a few hours after the sawmill event on 6 August. The sawmill event on 18 July

on the other hand is not visible with regard to increased Gly concentrations. Air masses, however, originated mainly from N-W wind vectors in this case, in contrast to S-W wind vectors during the events on 3 August and 6 August, thus originating from a different source.

The biomass burning event from 7 to 9 August resulted in increased Gly concentrations of up to  $8.23 \text{ ng m}^{-3}$ , while no such increase is visible in the period from 26 to 30 July. This indicates that a relatively fresh plume was directly transported to the sampling site from 7 to 9 August. Ensemble 4 day back trajectories and fire hotspot data for the August event are available in the supporting material (see Figs. S8–S10). On 7 August the transport time from the wildfires in the Russian Federation to the sampling site was around 3 to 4 days coinciding with the lowest Gly concentration for this event. On 8 August a wildfire with a transport time  $< 24 \text{ h}$  appears in the back trajectory plot, which potentially caused the high Gly concentrations observed on that day. The transport time from wildfires to sampling site on 9 August was around 2 days. While the transport times for the biomass burning events end of July were longer (4 to 5 days), also other parameters affecting the aging process of the aerosol potentially changed between the two periods of wildfire influencing the sampling site. Kundu et al. (2010b) report  $\alpha$ -dicarbonyl concentrations in biomass burning aerosols collected at the FNS (Fazenda Nossa Senhora Aparecida) site in Rondônia, Brazil, during the LBA-SMOCC campaign (2002). The reported Gly and Mgly concentrations are substantially higher in the fresh biomass burning aerosols studied during this extensive biomass burning period ( $9$  to  $54 \text{ ng m}^{-3}$  for Gly and  $13$  to  $43 \text{ ng m}^{-3}$  for Mgly). This finding can potentially be attributed to a very high source strength or little processing of  $\alpha$ -dicarbonyls in the young aerosols.

High Gly concentrations are also visible at the beginning of the campaign on 10 July. Unfortunately no data for the specific marker compounds are available for this time. However, we attribute these high concentrations to another pollution plume from the city of Tampere to the southwest of the sampling site, since the air mass backward trajectories calculated using the NOAA HYSPLIT model (see Fig. S7) indicate that the advected air masses went over Tampere. An increased vehicular activity at the measurement site itself associated with setting up instruments potentially may also contribute to the high Gly concentrations observed. Acetylene, which forms Gly and not Mgly and was presumably emitted by vehicles at the site, was identified as a potential SOA precursor by Volkamer et al. (2009). The pollution source seems to be different two days later (12 July), as on this day also an increase in Mgly concentration was observed.

Nucleation events are usually observed during spring and fall at the SMEAR II station, though some occasionally occur also during the summer season when air masses originate over the Arctic Ocean (Kulmala et al., 2004a; Sogacheva et al., 2005). On 23 July a nucleation event was observed during the HUMPPA-COPEC campaign (Williams et al., 2011).

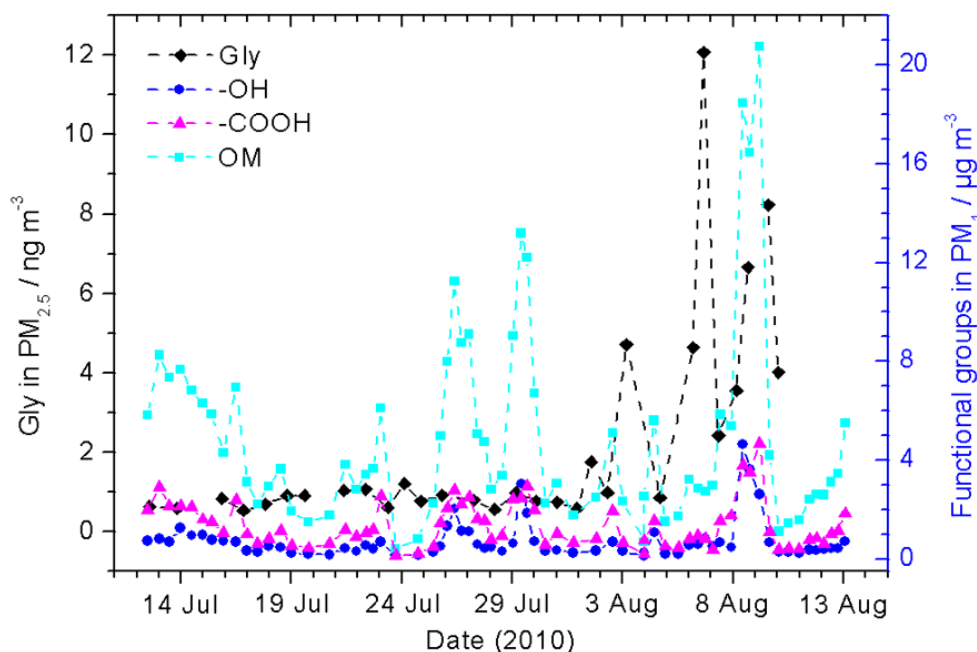
Interestingly, Gly concentrations show a local minimum on this day. This finding can potentially be attributed to the very clean air with a campaign minimum of total submicron particle counts ( $3$ – $1000 \text{ nm}$ ) at 06:00 local time.

### 3.3 Comparison with FTIR data

FTIR analysis was used to characterize the chemical composition of  $\text{PM}_{10}$  aerosols during HUMPPA-COPEC 2010. A comparison of organic matter (OM) characterized as hydroxyl ( $-\text{OH}$ ) functional groups and  $\alpha$ -dicarbonyl concentrations was investigated due to the following reasons. Gly and Mgly are present in the aerosol phase as their hydrated forms (mono- or di-hydrate) or oligomers formed via hemiacetal, acetal, imine, anhydride, ester, and sulfate ester formation and aldol condensation (see Lim et al., 2010 and references therein), thus drastically reducing free carbonyl functional groups related to Gly or Mgly and increasing hydroxyl functional groups at the same time. Concentrations of OM and hydroxyl functional groups in  $\text{PM}_{10}$  as well as Gly concentrations in  $\text{PM}_{2.5}$  are illustrated in Fig. 2.

During the biomass burning events from 26 to 30 July a significant amount of hydroxyl functional groups is present in the aerosol phase with a peak concentration of  $3.05 \mu\text{g m}^{-3}$  on 29 July. Only minor changes in Gly  $\text{PM}$  concentrations are visible during that time, suggesting that most of the reactive  $\alpha$ -dicarbonyl compounds have already been irreversibly processed. However, it cannot be ruled out that only little Gly was associated with these biomass burning events, resulting in the low concentrations observed. During the biomass burning event on 8 August high concentrations of Gly coincide with high  $-\text{OH}$  concentrations, pointing to a closer source for this event as already discussed in the previous section. The sawmill events on 3 August and 6 August resulted in strong increases of Gly  $\text{PM}$  concentrations, whereas only minor changes in  $-\text{OH}$  concentrations are visible. It should be noted that Gly concentrations are on a scale of  $\text{ng m}^{-3}$  and FTIR functional group concentrations are on a scale of  $\mu\text{g m}^{-3}$ . However, the distance of the source of the event to the sampling site is only around 10 km. Consequently, the aerosol is less aged and resulted in a campaign maximum for the fraction of Gly in OM. Gly/OM and Gly/ $-\text{OH}$  ratios at selected days are summarized in Table 1.

Maximum Gly/OM ratios were observed during the sawmill events on 3 August and 6 August. In these less aged aerosols Gly makes up 0.2 % and 0.41 % of the total OM respectively. Biomass Burning events on 26 July and 29 July were addressed as strongly aged aerosols in the previous discussion; this is also reflected here by low Gly/OM ratios of 0.01 %. On 8 August on the other hand the values are slightly higher, likely due to direct transport of a fresh plume during this event. At selected days without anthropogenic influences and wind vectors from S-W (21 July) and N-W (23 July and 25 July) directions the Gly/OM ratio ranged from 0.03 % to 0.14 %. The high value was observed on the day of the



**Fig. 2.** A comparison of Gly concentrations in  $PM_{2.5}$  and  $-OH$ ,  $-COOH$  as well as OM concentrations in  $PM_1$ .

**Table 1.** Fraction of Gly in OM and in hydroxyl functional groups at specific events during HUMPPA-COPEC 2010.

	Biomass Burning events / %			Sawmill events / %		Clean air / %		
	26 Jul	29 Jul	8 Aug	3 Aug	6 Aug	21 Jul	23 Jul *	25 Jul
Gly/OM	0.01	0.01	0.04	0.20	0.41	0.03	0.14	0.04
Gly/ $-OH$	0.04	0.03	0.16	1.43	1.78	0.27	0.38	0.32

\* nucleation event

nucleation event, thus again suggesting higher values in the Gly/OM ratio are related to less aged aerosols. However, the uncertainty of the measurements during the nucleation event is higher than for the other events mentioned here, because FTIR carbonyl functional group mass was below the limit of detection. Additionally, the relative importance of aerosol aging and source strength is subject to estimations based on backward trajectories and trace gas as well as particle composition analysis. Therefore, statements on the aerosol aging state are qualitative and are based on the parameters mentioned before.

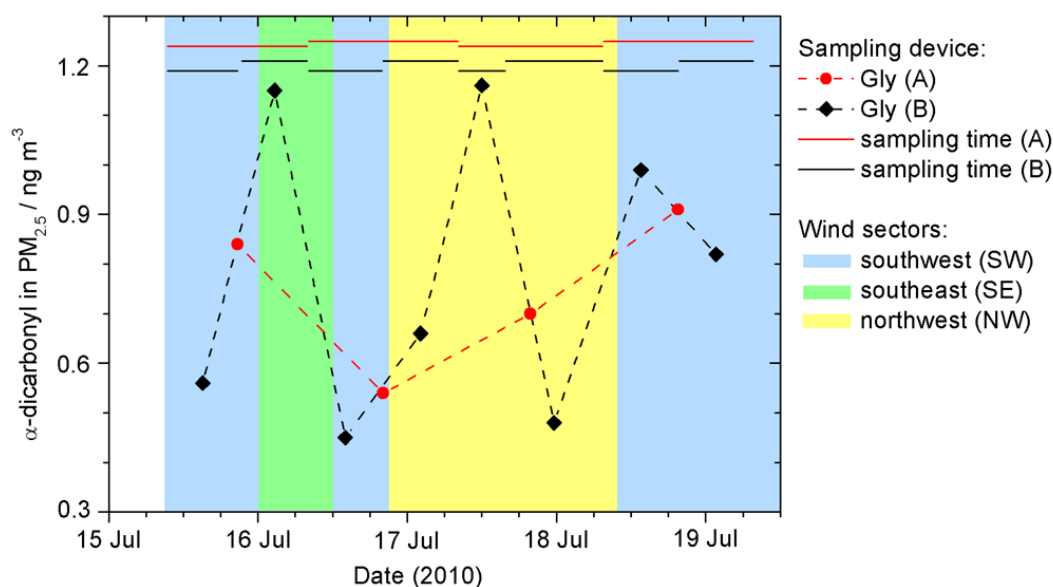
### 3.4 Time resolution and diurnal behavior of Gly in $PM_{2.5}$

In general filter sampling for Gly and Mgly was conducted related to air mass origins. While one of the sampling devices was used that way throughout the whole campaign, the other one was used to investigate the diurnal concentration behavior of Gly and Mgly in the week from 15 to 19 July. However, as mentioned before Mgly concentrations were very low resulting in total Mgly masses per filter below the LOD during

this week of experiments. Gly concentrations in  $PM_{2.5}$  for the week from 15 to 19 July are illustrated in Fig. 3.

A strong diurnal variation of the Gly PM concentrations is visible, however, without a clear trend. On 15 and 16 July the night time samples show higher concentrations than the day time samples, while the opposite is true for 17 and 18 July. Wind sectors changed quite frequently during that time (see Fig. 3). The analysis of air mass origins showed high day and low night time concentrations for Gly from the N-W wind sector, while the concentration behavior for Gly in air masses from southern wind sectors seems to be more complex. Comparisons between this temporal behavior and that of tracer measurements like aliphatic hydrocarbons (*n*-pentane), sulfur dioxide ( $SO_2$ ), carbon monoxide (CO) and nitrogen oxides ( $NO_x$ ) as anthropogenic tracers and BVOC's ( $\alpha$ -,  $\beta$ -pinene, isoprene,  $\Delta_3$ -carene and myrcene) as biogenic tracers, however, did not show significant correlation.

The Gly measurements with short and long sampling durations were found to be consistent with each other. Each ambient sample with a long sampling duration shows the mean concentration of the two corresponding ambient samples



**Fig. 3.** Gly measurements with different time resolutions are shown. Concentrations given are centered at the middle of the respective sampling period. Dotted lines reflect linear interpolation of adjunct sampling periods. Colored lines at the top reflect length of the respective sampling period. Colors in background correspond to wind vectors of air mass origins advected to the sampling site.

with short sampling durations with a maximum error of < 6 %, thus demonstrating the reliability of the analytical method applied and suggesting sampling artifacts to be minor. The drawback of a longer sampling duration, however, is obvious. Diurnal cycles in the concentration behavior are not observed due to longer averaging and short spikes or minima in concentration become invisible.

#### 4 Conclusions

HUMPPA-COPEC 2010 offered the opportunity to acquire the first set of data for PM<sub>2.5</sub> concentrations of the two most prominent  $\alpha$ -dicarbonyl compounds glyoxal and methylglyoxal in the boreal forest region of Finland. These concentrations were compared to a variety of other field data in order to appoint sources and investigate the relative abundance and relevance of  $\alpha$ -dicarbonyl compounds in the Boreal environment. Mean background concentrations of Gly and Mgly at the SMEAR II station in Hyytiälä, Finland, were 0.81 ng m<sup>-3</sup> and 0.31 ng m<sup>-3</sup>, respectively. However, local and regional events, e.g. biomass burning, sawmill emissions and urban/anthropogenic pollution, showed strong influences on  $\alpha$ -dicarbonyl aerosol concentrations and resulted in peak Gly concentrations of up to 12.07 ng m<sup>-3</sup>. From a mass perspective Gly and Mgly seem still not as relevant in boreal forest environments as in highly anthropogenic influenced urban centers. Volkamer et al. (2007) attributed at least 15 % of the SOA formation in Mexico City to glyoxal, which corresponds to several  $\mu$ g m<sup>-3</sup>. Mgly aerosol phase concentrations in the boreal forest are also low in comparison to previous

urban measurements. This may be due to a higher abundance of aromatic precursors with greater Mgly yields, e.g. xylenes, in urban environments. The relatively low Mgly concentration compared to Gly can be explained by the short photolysis lifetime and less pronounced uptake by water-containing SOA particles. Comparison with FTIR PM<sub>1</sub> chemical composition data allowed the aging state of aerosols advected from distinct events and sources to be assessed qualitatively by Gly/OM and Gly/–OH ratios. While short distanced events and events with very intensive sources had a strong influence and high Gly/OM ratios of up to 0.4 %, more distant and smaller events were not visible via increased  $\alpha$ -dicarbonyl concentrations and thus showed low Gly/OM ratios of 0.01 %. On background days, Gly/OM ranged from 0.03–0.14 %. Low Gly concentrations in aged aerosols can be explained by irreversible uptake of Gly and the formation of imidazoles and other high molecular weight compounds in ammonium containing aerosols (Galloway et al., 2009; Noziere et al., 2009; Shapiro et al., 2009; Lim et al., 2010; Yu et al., 2011). Furthermore, oxidative processing of Gly to glyoxylic acid, oxalic acid, formic acid and CO<sub>2</sub> through OH radical reactions will lower the Gly concentration in aged aerosols (Carlton et al., 2007).

**Supplementary material related to this article is available online at:** <http://www.atmos-chem-phys.net/12/6145/2012/acp-12-6145-2012-supplement.pdf>.



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