

**Characterization of
aerosol and cloud
water during WACS
2010**

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**Characterization of aerosol and cloud
water at a mountain site during WACS
2010: secondary organic aerosol
formation through oxidative cloud
processing**

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The water-soluble fractions of aerosol samples and cloud water collected during Whistler Aerosol and Cloud Study (WACS 2010) were analyzed using an Aerodyne aerosol mass spectrometer (AMS). This is the first study to report AMS organic spectra of re-aerosolized cloud water, and to make direct comparison between the AMS spectra of cloud water and aerosol samples collected at the same location. In general, the aerosol and cloud organic spectra were very similar, indicating that the cloud water organics likely originated from secondary organic aerosol (SOA) formed nearby. By using a photochemical reactor to oxidize both aerosol filter extracts and cloud water, we find evidence that fragmentation of aerosol water-soluble organics increases their volatility during oxidation. By contrast, enhancement of AMS-measurable organic mass by up to 30 % was observed during aqueous-phase photochemical oxidation of cloud water organics. We propose that additional SOA material was produced by functionalizing dissolved organics via OH oxidation, where these dissolved organics are sufficiently volatile that they are not usually part of the aerosol. This work points out that water-soluble organic compounds of intermediate volatility (IVOC), such as *cis*-pinonic acid, produced via gas-phase oxidation of monoterpenes, can be important aqueous-phase SOA precursors in a biogenic-rich environment.

1 Introduction

Organic materials are one of the major constituents of atmospheric particulates (Jimenez et al., 2009; Zhang et al., 2007). Their formation mechanisms and properties, however, have not been fully understood, thus introducing uncertainties into current global climate models (IPCC, 2007). In particular, atmospheric models that predict secondary organic aerosol (SOA) formation via traditional gas-phase oxidation of biogenic and anthropogenic precursors followed by gas-particle partitioning of semi-volatile products cannot match the observed SOA mass loadings (e.g., Heald et al.,

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2010; Johnson et al., 2006; Volkamer et al., 2006). Moreover, the oxidation state of ambient SOA is usually higher than that of SOA produced from smog chamber experiments (Aiken et al., 2008; Ng et al., 2010). These observations suggest that there are unrecognized SOA sources that have not been considered.

5 Atmospheric aerosols are usually hygroscopic and they can absorb water to become aqueous particles under humid conditions and activate to form cloud droplets upon water supersaturation. Because of the relatively high water content in cloud and fog droplets, water-soluble organic carbon (WSOC) compounds with high volatility which have not been considered as traditional SOA precursors, such as glyoxal, methylglyoxal and other less oxygenated organics, may partition into the aqueous solution (Fu et al., 10 2008, 2009; Volkamer et al., 2009). Oligomerization and functionalization of these organics via aqueous-phase oxidation may generate low volatility products that can remain in evaporated droplets, forming additional SOA material (Blando and Turpin, 2000; Ervens et al., 2011; Gelencser and Varga, 2005; Huang et al., 2011). Recent 15 laboratory studies have shown that the major particle-phase products of aqueous oxidation of glyoxal and methylglyoxal include small organic acids and high molecular weight products with high oxygen-to-carbon (O/C) atomic ratios (Carlton et al., 2007; Lim et al., 2010; Tan et al., 2009, 2010). Since the aerosol-cloud droplet conversions (i.e., cloud cycles) likely occur frequently within an air parcel, repeated repartitioning 20 of such WSOC between the gas, aqueous and particle phases in the presence of aqueous oxidative processing may be an important source of highly oxygenated SOA components.

25 Oxalic acid, formed via in-cloud processing (e.g., Ervens et al., 2004; Sorooshian et al., 2006, 2007), has been experimentally identified as an important aqueous oxidation product of many potential precursors under cloud-relevant concentrations (Perri et al., 2009; Tan et al., 2009, 2010). On the basis of aircraft measurements, Sorooshian et al. (2007) suggested that the source of oxalic acid in aerosol particles above cloud was a result of aqueous-phase processing, in which oxalic acid formation was more efficient relative to sulfate as the cloud water content increased. A recent modeling study

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mechanisms, especially the competition between the functionalization and fragmentation channels, of organic aerosols and cloud organics, and may help to identify potential aqueous-phase SOA precursors in a biogenic-rich environment.

2 Experiment

2.1 Aerosol and cloud water samples collection

Aerosol filter samples and cloud water were collected at Whistler, British Columbia, during summer 2010. The sampling site for aerosol collection was Raven's Nest (RN) which sits within a coniferous forest mountain area at an elevation of 1300 m a.s.l. The ambient aerosols passed through a cyclone with PM1 cut size (UGR, Model 463) and were collected on 47 mm Teflon filters (2.0 μm pores) for 24 h. A possible negative sampling artifact is that volatile and semi-volatile organic species in the aerosol phase may escape to the gas phase via evaporation. An Aerodyne High Resolution AMS (HR-AMS) was employed at the RN site to measure real-time aerosol chemical composition throughout the campaign for comparison with aerosol composition in filter samples. The cloud water samples were collected by automated versions of the Caltech Active Stand Cloudwater Collector (CASCC) (Hutchings et al., 2009; Macdonald et al., 2012) at RN and also at another site at the Whistler mountain peak, located at an elevation of 2182 m a.s.l. Particle volume monitors Gerber PVM-100 (Gerber, 1991) were used to measure the cloud liquid water content (LWC) at the two sites for automated triggering of cloud water collection. The cloud collection was initiated when the LWC reached a threshold value. Note that only one cloud water sample was analyzed from the peak site and hence the following discussion is primarily focused on RN data.

In addition, a ground-based counter-flow virtual impactor (CVI) from the University of Stockholm was installed at the peak site (Noone et al., 1988; Macdonald et al., 2012). This ground-based CVI selects droplets based on their inertia, created by a high vacuum intake flow, relative to a warm dry counter flow volume of air. In this

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case, droplets/particles larger than about 5 μm diameter were sampled by the CVI and smaller cloud droplets and interstitial particles were expelled. The sampled droplets were dried in the CVI inlet and the non-refractory composition of cloud residuals was measured by AMS with unit mass resolution (CToF-AMS). The CVI only operated during cloud events and another inlet was used to sample ambient aerosol particles during pre- and post-cloud periods. In this study, the AMS organic spectra of cloud residual (09:06–10:51) and aerosol particles during pre- and post-cloud period (02:36–03:48 and 13:15–13:45) on 22 July are discussed.

2.2 AMS characterization and photo-oxidation of aqueous samples

The aerosol filter samples were extracted in about 30 ml of 18 M Ω water and the cloud water was filtered before analysis. The water-soluble fraction of ambient aerosols in aqueous extracts and filtered cloud water samples were atomized by compressed air on site using a TSI atomizer (Model 3076). The aqueous particles passed through a diffusion dryer and were subsequently analyzed by the CToF-AMS for determination of their non-refractory composition including sulfate, nitrate, ammonium and organics. The working principle of AMS has been reviewed by Canagaratna et al. (2007). The standard fragmentation table with the corrected air fragment volume for our carrier gas and the default values of relative ionization efficiency were used in the AMS data analysis (Squirrel, version 1.50b). Some of the aqueous samples were oxidized for 10 min using a custom-made photochemical reactor (Lee et al., 2011a,b). Photolysis of H₂O₂ with initial concentration of about 70 mM was used to produce aqueous OH radicals. Because the reaction vessel allows atomization during the photo-oxidation processing, the composition changes of the reacting solution were monitored continuously by the CToF-AMS. With the aerosol drying process prior to the AMS measurement, the experimental setting qualitatively simulates aqueous oxidation in the bulk aerosol or cloud droplets followed by evaporation of water and volatile organics to form SOA.

To determine the background organic level contributed from water that was used for filter extraction, we atomized a few blank water samples and quantified its organic level

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using the experimental approach described above. Because of the low organic aerosol loading within the pre-biogenic period, a few aerosol filter extracts with total organic levels comparable to the background organic level of blank water were excluded from our data analysis.

3 Results and discussion

3.1 Chemical composition of aerosol and cloud water

The daily average composition profiles (sulfate, nitrate and organic mass fraction) of ambient particulate matter measured by HR-AMS at RN are shown in Fig. 1a. The details of aerosol characteristics and meteorological conditions at both sampling sites have been reported in the overview paper of the WACS 2010 campaign (Macdonald et al., 2012). In brief, the filter sample collection period can be roughly divided into three different phases namely pre-biogenic (21 June–6 July), biogenic (6–11 July, yellow shaded region in Fig. 1a) and post-biogenic (11–22 July) period. Note that the WACS 2010 also covered another biogenic event with a significant biomass burning influence (23–29 July), which is outside our filter sampling period. The biogenic period was well defined by a sustained high-pressure system over the region with cloud-free and high temperature conditions. During the biogenic period, SOA increased to a maximum of $\sim 6 \mu\text{g m}^{-3}$ at RN mainly due to photochemical oxidation of gas-phase biogenic precursors such as α -pinene and isoprene emitted from the regional forest area (Macdonald et al., 2012). The in-cloud days at RN are shaded in grey as shown in Fig. 1a.

Figure 1a,b demonstrate that the overall chemical composition of the water-soluble fraction of aerosol filter samples is in good agreement with that measured simultaneously by HR-AMS at RN. Although the evaporative loss of semi-volatile species during sample collection, filter extraction, and droplet evaporation prior to AMS analysis was possible, this observation implies that most of the PM1 organics at RN were water extractable and able to be detected by the AMS after re-atomization. The average

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compositions of aerosol filter extracts are shown in Fig. 1c. In the pre-biogenic period, inorganic components accounted for 50 wt% of the water-soluble materials with sulfate as the main contributor. The WSOC compounds rapidly increased to over 85 wt% within the biogenic period. Extremely low sulfate content in aerosol extracts (< 5 % in general) indicates that the aerosol composition was not significantly influenced by anthropogenic sources. During the post-biogenic period, the organic fraction was sustained at about 70 wt% of the water-soluble materials, which was much higher than that observed in the pre-biogenic period, indicating that biogenic SOA production may have influenced the organic aerosol composition during this period.

Organics contributed about 50 wt% of cloud water constituents but this is likely a lower limit because of the presence and potential loss of volatile organics. The high water content in cloud droplets favors partitioning of water-soluble, volatile species into the aqueous phase. A portion of them however may not be retained in the evaporated droplets and hence may not be fully detected by the AMS. For example, C1–C5 carbonyls including formaldehyde, acetaldehyde, glyoxal, methylglyoxal, propionaldehyde and isovaleraldehyde already accounted for between 8–30 % of water-soluble organic carbon in cloud samples collected at Whistler based on the results of offline analysis (Wang et al., 2012). Small carboxylic acids such as formic and acetic acid are also commonly found in cloud water (e.g., Munger et al., 1989). In addition to small carbonyls and organic acids, a predominance of pinonaldehyde, one of the major gaseous products of monoterpenes oxidation, was observed in rainwater at central Japan (Satsumabayashi et al., 2001), providing evidence that cloud droplets can also absorb biogenic volatile organic compounds (VOC) with limited solubility in water. In the following discussion, low-volatility cloud water organics (LV-CWO) refer to AMS-measurable cloud organics and volatile cloud water organics (V-CWO) refer to high vapor pressure cloud organics that are not retained in the residuals of evaporated droplets for AMS detection.

The AMS results show that nitrate mass was comparable to sulfate mass in the cloud water samples, consistent with the results obtained from conventional

analytical methods (Wang et al., 2012), whereas sulfate was the dominant inorganic in the aerosol filter samples collected within the non-biogenic period. The averages of nitrate-to-sulfate ($[\text{NO}_3^-]/[\text{SO}_4^{2-}]$) mass ratios of cloud water and aerosol filter extracts collected within the non-biogenic period were approximately 1.4 and 0.2, respectively.

5 Similarly, Hayden et al. (2008) reported that the $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ mass ratios of bulk cloud water (ranged from 0.6 to 7.1) were much higher than those of the below-cloud aerosols (ranged from 0.02 to 0.69) based on summer aircraft measurements near Cleveland, Ohio as part of ICARTT 2004.

3.2 Spectral characteristics of aerosol and cloud water organics

10 The average AMS organic spectra of WSOC in aerosol filter samples are shown in Fig. 2a–c. The spectral features observed throughout the campaign are almost identical, reflecting a common, biogenic source of particles. The main exception is that the fresh biogenic SOA formed during the biogenic episode (Fig. 2b) has a relatively higher mass fraction intensity at m/z 43 (f43) and lower f44 than the SOA collected in the pre- and post-biogenic periods (Fig. 2a,c). While the organic fragment at m/z 44 (CO_2^+) is primarily due to the fragmentation of organic acids, m/z 43 mostly originates from $\text{C}_2\text{H}_3\text{O}^+$ (Ng et al., 2010), indicating the presence of less oxygenated functional characteristics. Figure 3a, showing the time series profiles of f43 and f44 of the aqueous filter extracts, demonstrates that the biogenic time period is characterized by lower f44-to-f43 ratios, indicating these particles are less oxygenated than the aged SOA in the pre- and post-biogenic period at Whistler. This supports the hypothesis that atmospheric aging increases the degree of oxygenation of organic aerosol.

15 Figure 2d,f show the average AMS organic spectra of LV-CWO in cloud water collected at RN (except the sample collected on 12 July) and peak sites, respectively. The spectral characteristics of LV-CWO collected at both sites are similar to each other and to those of WSOC compounds in aerosol filter samples collected during the non-biogenic period (R^2 of the linear regression between the organic spectra > 0.9). Nevertheless, the cloud water collected immediately after the biogenic episode (12 July)

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at RN has noticeably stronger f29 (CHO⁺) intensity and a lower f44-to-f43 ratio than the other cloud samples, as shown in Figs. 2e and 3a. This is likely due to the increased concentration of carbonyl functional groups. Physical uptake of water-soluble gaseous carbonyls, actively produced in the biogenic episode, and oxidative aging of cloud organics could give rise to this observation (see later discussion). For example, based on our lab studies, glyoxal, methylglyoxal and propionaldehyde, all highly water-soluble carbonyls commonly found in cloud water, can give strong organic signals at *m/z* 29 and/or 43 but low organic signals at *m/z* 44 and other large fragments in their AMS spectra. Pyruvic acid, a product of aqueous oxidation of methylglyoxal (Tan et al., 2010), has comparable organic intensities at *m/z* 43 and 44 in its AMS spectrum.

Our real-time AMS measurement also shows that the organic spectra of cloud residuals sampled by the CVI are very similar to those of ambient aerosol particles analyzed during pre- and post-cloud period at the peak site (R^2 of the linear regression between the organic spectra > 0.9) as shown in Fig. 2g,h (22 July). Similar to the re-atomization process of cloud water, sampling cloud residuals via the CVI would result in evaporation of V-CWO from the cloud droplets and hence, only LV-CWO would be retained in the condensed-phase and subsequently measured by the AMS. On the basis of all organic spectra obtained in this study (Fig. 2a–h), it can be concluded that the overall spectral features of aerosol and cloud droplets at Whistler are very similar to each other, indicating that the cloud organics likely originated from secondary organic aerosol (SOA) formed nearby.

To better understand the characteristics of atmospheric organic aerosol, Ng et al. (2010) analyzed a worldwide AMS dataset on an f44 vs. f43 space. The global ambient organic aerosol predominately cluster inside a triangular region in the space, which is indicated by the dashed line bounded area in Fig. 3b. While semi-volatile oxygenated organic aerosols (SV-OOA or less oxidized OOA) mainly reside in the lower half of the triangular region, low-volatility OOA (LV-OOA or more oxidized OOA) concentrate in the upper half. The WSOC compounds in the filter samples and the LV-CWO mainly fall in the transition zone of ambient SV-OOA and LV-OOA components.

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Based on the correlation established by Aiken et al. (2008), the f44 value can be used as a surrogate to estimate the O/C ratio of ambient organic aerosols. The estimated O/C ratios of the WSOC in aerosol filter samples ranged from 0.44 to 0.50 and from 0.50 to 0.55 in the biogenic and non-biogenic periods, respectively. The estimated O/C ratios of LV-CWO were between 0.52 and 0.59, but it is not known whether the Aiken et al. (2008) relationship is valid for all products from aqueous-phase processing.

3.3 Aqueous oxidation of aerosol and cloud water organics

Figure 3b also shows the results for aqueous OH oxidation of filter extracts and cloud water as described. All the resulting organics have a higher degree of oxygenation (estimated O/C ratios ranged from 0.79 to 0.98) than the original samples and have coordinates closer to that of global LV-OOA on the f44 vs. f43 space. This observation suggests that aqueous-phase chemistry is potentially important to produce atmospheric LV-OOA, in addition to traditional gas-phase chemistry and heterogeneous oxidation (Ng et al., 2010). The typical f44, f43 and f29 kinetic profiles of the oxidizing filter extracts are shown in Fig. 3c as an illustration. During the aqueous oxidation, the f44 intensity of filter extracts and cloud water rise continuously, caused by increasing contribution of organic acids to total organic mass. The two-step kinetic behavior of f43 and f29 for both sample types suggest that less oxygenated carbonyls are likely condensed-phase intermediates that are subsequently converted to organic acids and volatile species in the reacting solution (Lambe et al., 2011; Lee et al., 2011a; Lim et al., 2010). Note that aqueous oxidation of *cis*-pinonic acid and laboratory-generated α -pinene SOA give similar kinetic profiles of these organic fragments (Lee et al., 2011a).

Figure 4a,d display the organic spectra of an aerosol filter extract (10 July) and also cloud water (12 July) measured at the end of aqueous oxidation, and they also look similar to each other. The spectral differences between the AMS organic spectrum of an unoxidized sample from that of the corresponding oxidized sample for both sample types are shown in Fig. 4b,e. The differences of both sample types are almost identical. Most of the organic mass fragment signals decline with oxidation (displayed as

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negative differences), due to the consumption of starting material whereas only the strong positive differences are at m/z 44 and some other related fragments (e.g. m/z 18 and m/z 28), indicating that organic acids are the predominant condensed-phase products retained in the evaporated droplets within the timescale of our oxidation experiments.

Note that the organic intensities at m/z 28 and m/z 18 are directly estimated from m/z 44 signals using the standard fragmentation table in Squirrel so that their changes cannot provide extra information for identifying the functional characteristics of oxidation products.

The spectral differences obtained by comparing spectra normalized to total AMS organics does not reflect the absolute changes in organic composition and their mass loadings. Assuming inorganic sulfate does not react and is not produced significantly in the oxidizing aqueous samples, the organic mass spectra normalized by sulfate mass can be used to determine the absolute changes of individual organic fragments, as presented in Fig. 4c,f. For the case of aerosol filter extracts, the majority of organic fragments were consumed with only a minor production of m/z 44 (or even a small reduction in some samples). By contrast, a significant mass production of m/z 44 and consumption of other organic fragments are observed in cloud water. Note that oxidation of S(IV) species may produce inorganic sulfate in cloud water samples, and hence the sulfate normalized results likely represent a lower limit of m/z 44 production. This observation suggests that the organic composition of total cloud organics (LV-CWO + V-CWO) is different to that of WSOC in aerosols, but their differences cannot be easily distinguished by our technique of atomization and subsequent AMS detection. In particular, we believe that there is a considerable amount of V-CWO in cloud water, which is not AMS-measurable. As described in the next section, this material is involved in aqueous oxidation chemistry to produce additional, lower volatility organic materials in the evaporated droplets.

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3.4 Aqueous oxidation mechanisms: functionalization vs. fragmentation

Functionalization, fragmentation and oligomerization processes have been recently proposed to describe how aging controls the volatility of aerosol organics and thus their mass loadings in the atmosphere (Jimenez et al., 2009; Kroll et al., 2009). Briefly, oxidative functionalization reduces vapor pressure and enhances O/C ratios of organics through addition of oxygenated functional groups to a molecule without breakage of its carbon skeleton. In contrast, fragmentation refers to cleavage of the skeleton and therefore enhances volatility of organic species. Fragmentation and functionalization usually take place together during oxidative processing so that the vapor pressure of products greatly depends on the chemical structure of original molecules as well as the branching ratio of the two oxidative pathways (Kroll et al., 2009). Lastly, oligomerization or formation of high molecular weight organic compounds involves association reactions resulting in an increase of carbon chain length and reduction of volatility.

Figure 5a shows that organic mass profiles (normalized by sulfate mass) of some filter extracts keep decreasing throughout the reaction time regardless of their collection period. From the observed increasing O/C ratio (or f_{44}) during aqueous oxidation of filter extracts, it can be concluded that significant fragmentation and functionalization of aerosol organics occur simultaneously to produce high-volatility oxygenates that lead to continuous mass loss through evaporation. The general decreasing trend of sulfate-normalized organic signals at m/z 29, 43 and 44 (Fig. 5b–d) suggests that the total evaporative loss of oxygenated species is faster than their production via aqueous-phase oxidation. The remaining condensed-phase products are mostly organic acids as discussed above. In the WACS 2010 campaign, the Toronto Photo-Oxidation Tube (TPOT) was used to oxidize ambient aerosol particles with a high level of gas-phase OH radicals at Whistler. It was found that heterogeneous oxidation also enhanced the O/C ratio of organic aerosols and reduced the aerosol mass loading by 10% (Wong et al., 2011). Overall, the above findings suggest that the fragmentation pathway plays a dominant role in both aqueous and heterogeneous oxidation to control the overall

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volatility of atmospheric organic aerosols at Whistler.

For the cloud water samples, organic mass loadings (normalized by sulfate mass) initially increase by 10–30 % and then decline, as shown in Fig. 5a. In principle, functionalization of LV-CWO may explain the initial increase of organic mass and O/C ratio if most of the intermediates are non-volatile in nature (i.e., insignificant fragmentation). However, the similarity of the AMS spectra of WSOC in filter extracts and LV-CWO suggests that LV-CWO may mainly originate from cloud activation of SOA. If so, LV-CWO would be expected to display a similar mass change response to aerosol WSOC during aqueous oxidation. Recall that, as described above, a few identified small carbonyls account for about 8–30 % of water-soluble organic carbon in cloud water collected at Whistler. The contribution of all V-CWO to total cloud organic mass should be higher than this lower limit. Therefore, low-volatility products formed via simultaneous functionalization and fragmentation of V-CWO (i.e., conversion of V-CWO to AMS-measurable organics) may be the major mechanism to compensate for the mass loss due to oxidation of LV-CWO, leading to the observed net mass enhancement at intermediate stages of oxidation. If this is the case, the functionalization reaction of V-CWO plays a major role to control the overall volatility of cloud organics at the early stage of oxidation (Fig. 5a).

Oxidation of less volatile intermediates, which were produced via aqueous-phase oxidation of V-CWO, further enhances their degree of oxygenation and leads to significant fragmentation at later stages of OH exposure, resulting in the observed mass reduction (Fig. 5a). Continuous production of less volatile organic acids in the oxidizing cloud water is supported by the growing trend of sulfate-normalized signals at m/z 44 (Fig. 5d). Their formation rate, however, slows at the later stage of OH exposure, possibly due to the increasing importance of fragmentation reactions of the organic acids. Lastly, note that the sulfate-normalized intensity profiles of m/z 29 and 43 (Fig. 5b,c) agree with the changes in organic mass loadings throughout the whole period of aqueous oxidation (Fig. 5a). This observation suggests that less oxygenated carbonyl species also contribute to the enhanced organic mass.

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3.5 Laboratory SOA formation via aqueous oxidation of model organics

The hypothesis that additional SOA is formed through aqueous-phase oxidation of V-CWO can be demonstrated using *cis*-pinonic acid as a model compound. *Cis*-pinonic acid, a major first-generation product of α -pinene ozonolysis, is a moderately water-soluble organic acid with a vapor pressure within the category of intermediate volatile organic compounds (IVOC) (Donahue et al., 2011; Jimenez et al., 2009). Therefore, it likely exists in both the gas and particle phase and upon oxidation may give rise to SV-OOA and LV-OOA formation in the atmosphere (Donahue et al., 2012; Jimenez et al., 2009). In our approach, *cis*-pinonic acid solution droplets were generated by atomization and a large portion of *cis*-pinonic acid was expected to repartition from solution droplets to the gas phase when they were dried, before passing to the AMS for measurement. In this way, it would behave similarly to some V-CWO in our cloud water samples. The aqueous-phase OH oxidation of *cis*-pinonic acid was performed in the same photochemical reactor and ammonium sulfate salt was added to the reacting solution as an internal standard for normalization of organic signals. Other experimental details can be found in our previous publication (Lee et al., 2011a,b).

Figure 6a shows the AMS organic mass profiles (normalized by sulfate mass) of the *cis*-pinonic acid solution as it is oxidized. The organic mass initially increased and then decayed, a similar behavior to that observed in the case of cloud water oxidation. Since the organic mass increased by a factor of 2.2 at its maximum, this cannot be realistically achieved by addition of functional groups to *cis*-pinonic acid molecules only (e.g., this would require addition of about 10 OH groups, without fragmentation occurring), even assuming *cis*-pinonic acid is non-volatile and is fully retained in the dried aerosol particles that the AMS measures. However, due to the fact that only a fraction of *cis*-pinonic acid remains in the evaporated droplets, extra organic material can accumulate in the aerosol measured by the AMS, given that the first- and/or second-generation oxidation products have vapor pressures much lower than *cis*-pinonic acid (Jimenez et al., 2009). The second hypothesis more reasonably explains the large increase of

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organic mass observed. The kinetic profiles of sulfate-normalized organic intensities at m/z 29, 43 and 44 are also consistent to those observed in the cloud water oxidation (Fig. 6a). The high similarity between the case of *cis*-pinonic acid and cloud organics implies that water-soluble IVOC (e.g., pinonaldehyde, pinic acid and *cis*-pinonic acid) produced via gas-phase oxidation of monoterpenes may be important aqueous-phase SOA precursors in a biogenic-rich environment.

Glyoxal and methylglyoxal have been considered as major SOA formation precursors via aqueous chemistry (e.g., Ervens and Volkamer, 2010; Fu et al., 2008; Lim et al., 2010), and thus aqueous-phase OH oxidation of glyoxal and methylglyoxal were also performed to examine whether extra organic mass can be produced via oxidation. Figure 6b shows that large organic mass reductions were observed for both dicarbonyls, indicating that fragmentation reactions dominated throughout the whole period of oxidative processing to produce more volatile species such as formic acid (Lee et al., 2011b). The small increase of organic mass at the latter period of glyoxal oxidation was due to the presence of hydroxyhydroperoxide that is produced by the reaction between glyoxal and H_2O_2 in the early stages of the oxidation experiment (see details in Lee et al., 2011b). Although glyoxal and methylglyoxal can lead to formation of highly oxygenated OOA components (Lambe et al., 2011; Lee et al., 2011b; Tan et al., 2010), aqueous oxidation of these two dicarbonyls cannot explain the organic mass enhancement observed in the oxidized cloud organics. This is consistent with the offline analytical measurement that glyoxal and methylglyoxal only contributed about 5 % of water-soluble organic carbon in our cloud water samples (Wang et al., 2012).

4 Conclusions and atmospheric implications

The chemical characteristics of aerosol filter extracts and cloud water samples collected at WACS 2010 campaign were analyzed on site using an Aerodyne aerosol mass spectrometer. We report AMS organic spectra of re-aerosolized cloud water and make a direct comparison between the AMS spectra of cloud water and aerosol

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samples collected at the same location. Sulfate was the major inorganic component in the aerosol samples collected in the non-biogenic period whereas the mass fraction of inorganic nitrate and sulfate were comparable in cloud water, indicating that there was an additional source of inorganic nitrate via cloud processing or absorption from the gas phase such as partitioning of nitric acid (HNO_3) and hydrolysis of N_2O_5 . The AMS spectral features of aerosol filter organics show that the fresh biogenic SOA produced in the Whistler forest area was generally less oxygenated than the cloud organics and aged SOA collected in the non-biogenic period, supporting the hypothesis that atmospheric aging enhances the oxidation state of condensed-phase organics.

Fragmentation is the predominant pathway to enhance the overall volatility of organic aerosols throughout the entire aqueous oxidation period. Heterogeneous oxidation of organic aerosols suggests a similar aging mechanism (Donahue et al., 2012; George and Abbatt 2010; Kroll et al., 2009). Therefore, aqueous and heterogeneous oxidation of biogenic SOA can generate highly oxidized ambient LV-OOA but do not necessarily lead to formation of additional SOA mass. We also present evidence that a highly oxidized SOA mass can be produced via aqueous oxidative processing of volatile cloud water organics (V-CWO). In the atmosphere, the SOA formation first involves the conversion of V-CWO to low volatility CWO (LV-CWO) followed by the evaporative loss of water and volatile organics. Although the total mass of cloud organics declined at the end of our oxidation experiment, the OH exposures used in our experiment are likely much higher than that in atmospheric aqueous droplets. The oxidative cloud processing of V-CWO is likely represented by the data observed at the low OH exposure region. Since the ambient aerosol particles may experience numerous aerosol-cloud cycles within their lifetime, oxidative cloud processing of V-CWO can be potentially important to produce SOA in the atmosphere.

This is the first study to oxidize atmospheric water-soluble samples and, by contrast to the aerosol case, we demonstrate that functionalization is the dominant pathway to produce additional SOA mass at the earliest stages of cloud water organic oxidation whereas fragmentation leads to organic mass reduction at a later stage. Kroll

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et al. (2009) and Donahue et al. (2012) recently suggested that functionalization reactions dominate oxidative aging of reduced organic materials with fragmentation being a minor channel. Fragmentation dominates for moderately oxidized organics (e.g., $O/C > 0.6$). This provides an insight that the majority of V-CWO that contributed to extra organic mass formation may be the less oxidized materials having high to moderate molecular weight. In particular, the water-soluble IVOC produced via gas-phase oxidation of monoterpenes such as pinonaldehyde, pinic acid and *cis*-pinonic acid may be important aqueous-phase SOA precursors in our cloud water samples collected at Whistler and perhaps other biogenic-rich environments. For example, Gelencser and Varga (2005) have suggested that organics having Henry's law constant greater than 10^3 Matm^{-1} , such as pinonaldehyde ($9 \times 10^3 \text{ Matm}^{-1}$), can lead to significant SOA formation via aqueous processing. Nevertheless, V-CWO usually consists of short chain carbonyls with high O/C ratio such as glyoxal and methylglyoxal and their oxidation products are usually highly oxygenated and/or volatile. The observed mass increase of cloud water oxidation is possibly the net result of the co-oxidation of small carbonyls and IVOC (Lee et al., 2011a). More detailed chemical characterization of cloud organics and laboratory studies of aqueous oxidation of potential V-CWO will be needed to further improve our understanding of SOA formation via oxidative cloud processing.

Acknowledgement. This work was funded by Environment Canada, Canadian Foundation for Climate and Atmospheric Science (CFCAS) and Natural Science and Engineering Research Council (NSERC). Environment Canada funded the Whistler Aerosol and Cloud Study 2010 through the Clean Air Regulatory Agenda (CARA). Funding was provided through Environment Canada's Grants and Contribution program for JPDA and AKYL (G&C 1004932). PH acknowledges partial funding from NSF grant AGS#0847710. Co-operation and support from Whistler-Blackcomb is gratefully acknowledged.

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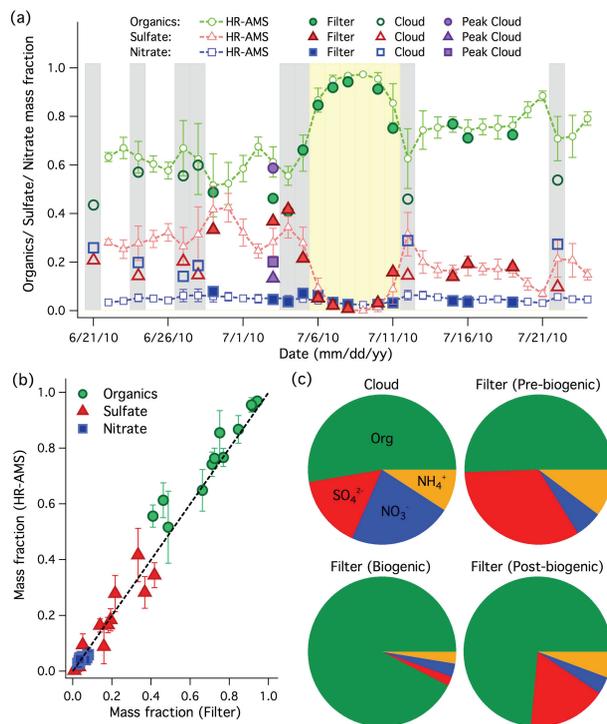


Fig. 1. (a) Chemical composition (sulfate, nitrate, and organics mass fraction) profile of ambient aerosol measured by online HR-AMS, aerosol filter samples at RN, and cloud water samples collected at both RN and peak sites. The biogenic episode is indicated by the yellow shaded region (6–11 July). The in-cloud days at RN are indicated by the grey shaded regions. (b) Correlations between chemical compositions of ambient aerosol measured by online HR-AMS at RN and those of re-aerosolized filter aerosol extracts at the same site. (c) Average chemical compositions of cloud water and water-soluble fraction of aerosol filter samples collected during the pre-biogenic, biogenic and post-biogenic periods at RN.

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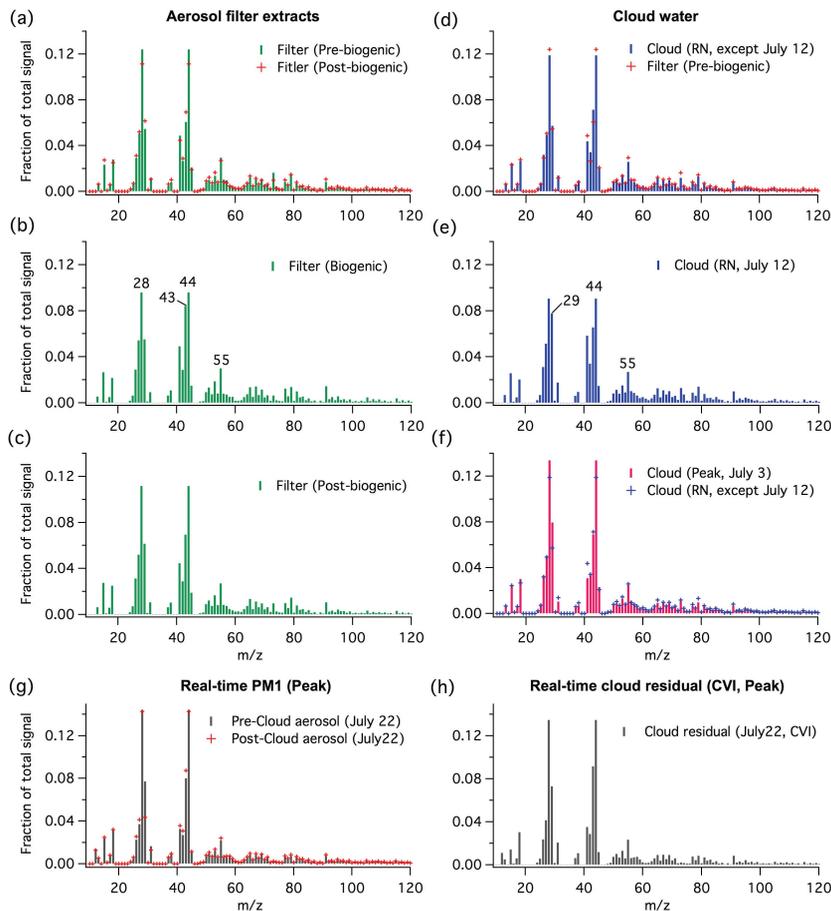


Fig. 2. AMS organic spectra (normalized by AMS organic mass) of aerosol filter extracts (a–c), cloud water (d–f), real-time PM1 in pre- and post-cloud period (g) and real-time cloud residuals at the peak sites (h).

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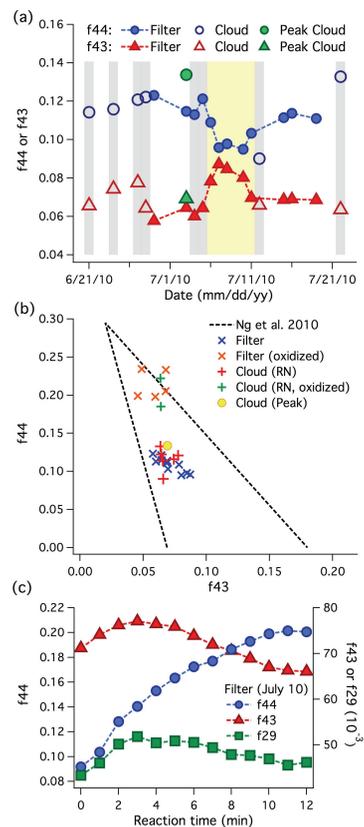


Fig. 3. (a) The f44 and f43 profiles of aerosol filter extracts and cloud water samples, (b) Coordinates of aerosol filter and cloud water samples before and after aqueous-phase OH oxidation on the f44 vs. f43 space. The worldwide ambient datasets mainly distributed within the dash line bounded triangular region (Ng et al., 2010). (c) The typical f44, f43, and f29 profiles of filter aerosol extracts during oxidation (10 July sample).

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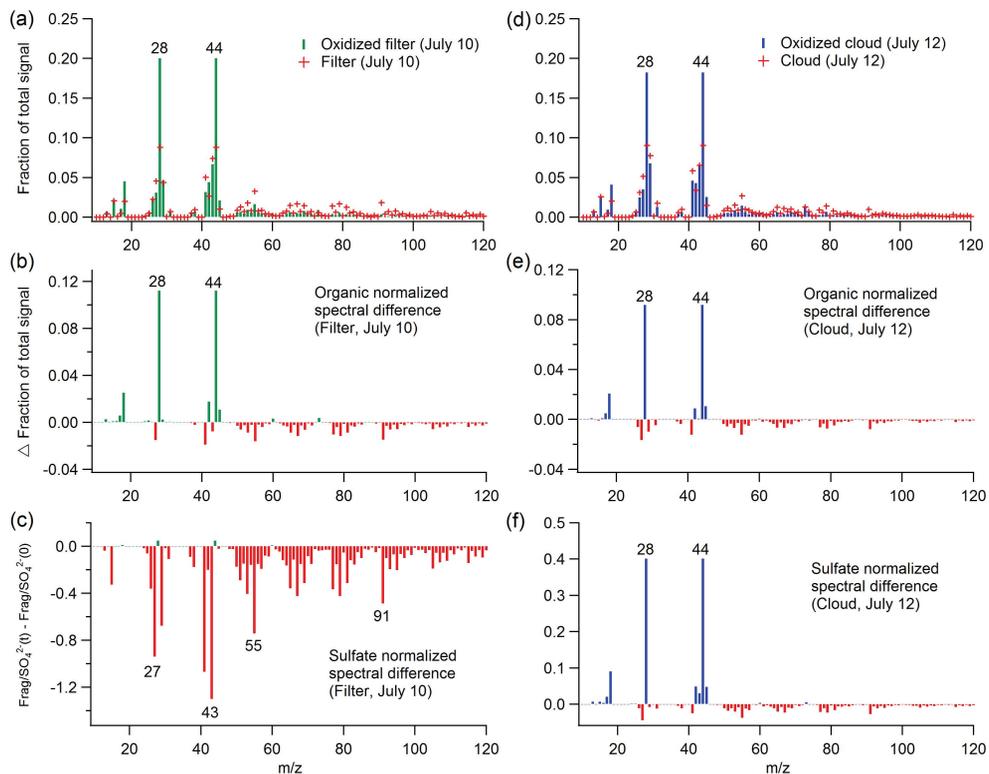


Fig. 4. Top spectra: AMS organic spectra of (a) aerosol filter extracts and (d) cloud water before and after aqueous-phase OH oxidation. Middle spectra: Spectral difference between the AMS organic spectra (normalized by AMS organics mass) of oxidized and un-oxidized (b) aerosol filter extracts and (e) cloud water. Bottom spectra: spectral difference between the AMS organic spectra (normalized by sulfate mass) of oxidized and un-oxidized (c) aerosol filter extracts and (f) cloud water. Negative values (red) shown in (b), (c), (e) and (f) indicate that the mass fragments were consumed due to aqueous-phase OH oxidation.

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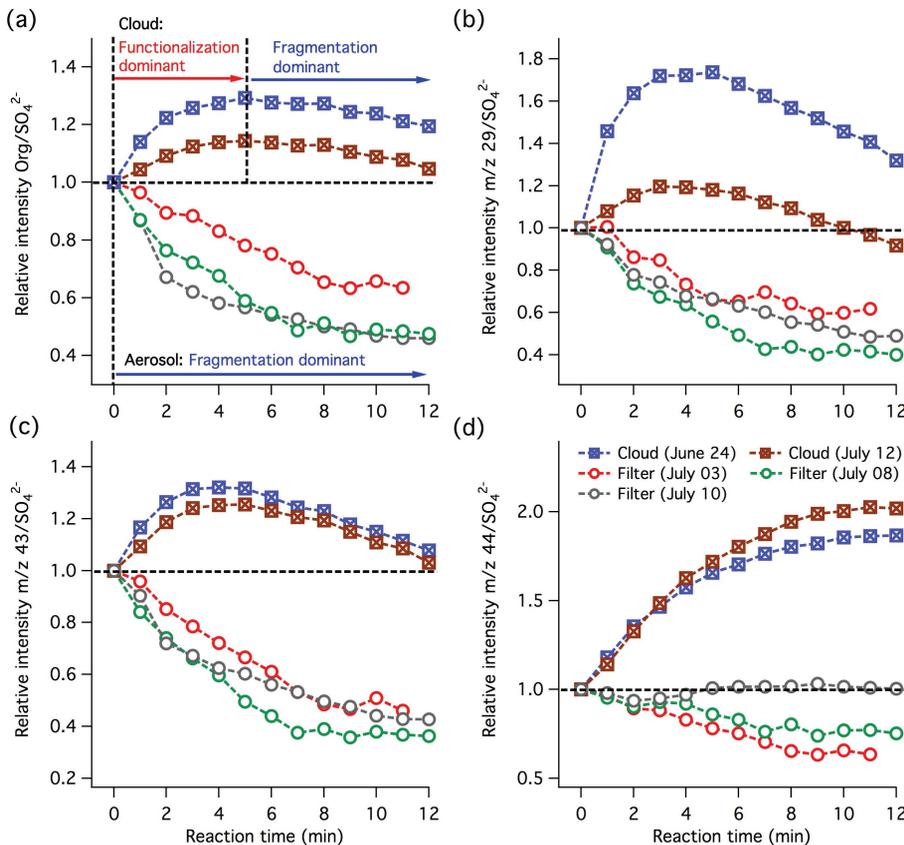


Fig. 5. Time series profiles of sulfate-normalized (a) Org/SO₄²⁻, (b) m/z 29/SO₄²⁻, (c) m/z 43/SO₄²⁻, and (d) m/z 44/SO₄²⁻ of filter aerosol and cloud water samples due to aqueous-phase OH oxidation.

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Characterization of aerosol and cloud water during WACS 2010

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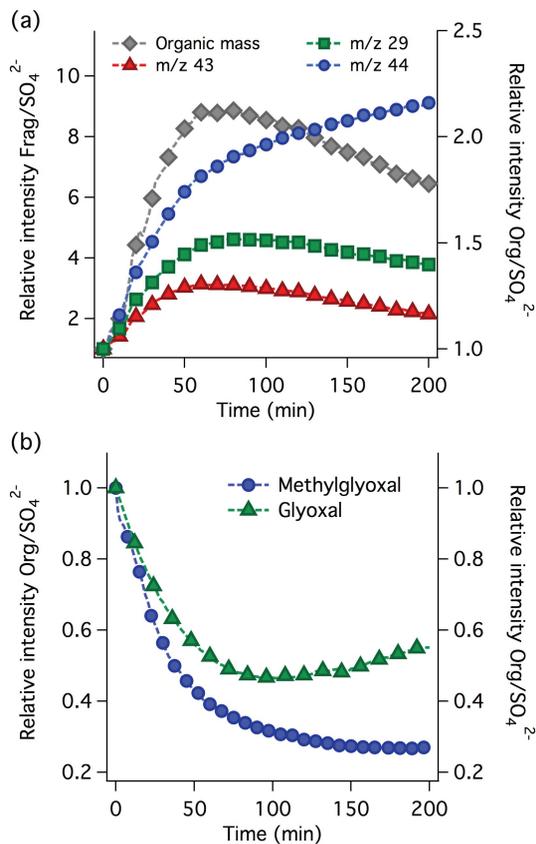


Fig. 6. (a) Time series profiles of sulfate-normalized $\text{Org}/\text{SO}_4^{2-}$, $m/z\ 29/\text{SO}_4^{2-}$, $m/z\ 43/\text{SO}_4^{2-}$, and $m/z\ 44/\text{SO}_4^{2-}$ of *cis*-pinonic acid (500 μM) due to aqueous-phase OH oxidation. (b) Time series profiles of sulfate-normalized $\text{Org}/\text{SO}_4^{2-}$ of glyoxal (3 mM) and methylglyoxal (3 mM) throughout the aqueous-phase oxidation period.