Atmos. Chem. Phys. Discuss., 14, 12525–12553, 2014
www.atmos-chem-phys-discuss.net/14/12525/2014/
doi:10.5194/acpd-14-12525-2014

Atmospheric Chemistry and Physics
Discussions
Open Access

Hygroscopicity of aerosol and its organic component at a coastal location

J. D. Yakobi-Hancock[1], **L. A. Ladino**[1], **R. H. Mason**[2], **A. K. Bertram**[2], **C. L. Schiller**[3], **W. R. Leaitch**[4], **D. Toom-Sauntry**[4], **K. Jones**[3], **J. P. S. Wong**[1], and **J. P. D. Abbatt**[1]

[1]University of Toronto, Toronto, Ontario, Canada
[2]University of British Columbia, Vancouver, British Columbia, Canada
[3]Air Quality Science Unit, Environment Canada, Vancouver, British Columbia, Canada
[4]Climate Research Division, Environment Canada, Toronto, Ontario, Canada

Received: 22 April 2014 – Accepted: 24 April 2014 – Published: 16 May 2014

Correspondence to: J. D. Yakobi-Hancock (jyakobi@chem.utoronto.ca)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

As one aspect of the NETwork on Climate and Aerosols: Addressing Key Uncertainties in Remote Canadian Environments (NETCARE), measurements of the cloud condensation nucleation properties of 50 and 100 nm aerosol particles were conducted at Ucluelet on the west coast of Vancouver Island in August 2013. Additionally, the size-resolved chemical speciation of two particle size ranges (42–75 nm and 78–141 nm) was inferred using a combination of ion chromatography and particle size distributions. Together, this information was used to estimate the hygroscopicity parameter of the organic species contained within the ambient aerosol particles (κ_{org}). The overall hygroscopicity parameter of the aerosol (κ_{ambient}) exhibited a wide variation, ranging from 0.14 to 1.08, with the highest values arising when the organic to sulfate ratio of the aerosol composition was lowest and when the winds were from the west, i.e. off the ocean. Correspondingly, the aerosol's two-day average chemical speciation also showed variation but was consistently dominated by its organic (60 to 86 % by mass) and sulfate (10 to 34 % by mass) components. With derived values of κ_{org} from 0.3 to 0.5, it is illustrated that the organic component of marine-influenced aerosol can be viewed as quite hygroscopic, somewhat more than typical continental organics but not as much as soluble inorganic components.

1 Introduction

Atmospheric aerosol particles directly affect Earth's radiative budget by scattering and absorbing incoming solar radiation (Charlson et al., 1992). Additionally, these particles can also indirectly influence the radiative budget of Earth by acting as cloud condensation nuclei (CCN) in the formation of warm clouds (Albrecht, 1989). Warm clouds can trap the earth's outgoing infrared radiation, reflect incoming solar radiation, and influence Earth's hydrological cycle (Albrecht, 1989; Twomey, 1977b). More specifically, warm clouds in marine regions are significant contributors to the Earth's radiative flux due to their extensive coverage and large albedo in relation to the ocean's surface (Hartmann et al., 1992). It is well known that the indirect effects of these particles on climate constitute one of the largest uncertainties in understanding the present day climate sensitivity (IPCC, 2013). This large degree of uncertainty arises partially from an incomplete understanding of aerosol particles' abilities to act as CCN. Consequently, because of the resulting sensitivity of the earth's radiative budget to low-lying clouds, it is crucial to ensure that their CCN properties are well characterised.

Marine aerosol consists of two distinct types of particles: (1) primary sea-spray aerosol directly produced by breaking waves, consisting of inorganic salts and biogenic material such as surface-active microorganisms and exopolymer secretions; and (2) secondary aerosol formed by gas-to-particle conversion processes, mainly consisting of non-sea-salt (nss) sulfate and organic species (O'Dowd et al., 1997; Twomey, 1977a). However, in both coastal and marine locations it is also common for aerosol of anthropogenic and continental biogenic origin to be present, for instance, as a result of emissions by forests, populated areas, and shipping traffic. These sources can in turn result in high levels of substances of relevance to cloud formation, such as secondary organic aerosol (SOA) and sulfates, that are carried into the marine boundary layer by turbulence and convective mixing (Chang et al., 2010; Charlson et al., 1992; Coggon et al., 2012; Shantz et al., 2010).

While an enormous amount of effort has been applied to understanding and characterizing the aerosol hygroscopicity and CCN properties of continental biogenic, anthropogenic, and primary sea-spray aerosol (Andreae and Rosenfeld, 2008; Bigg, 2007; Chang et al., 2010; Coggon et al., 2012; Fuentes et al., 2011; Hegg et al., 2009; Kanakidou et al., 2005; Langley et al., 2010; Leck and Bigg, 2005a, b; Moore et al., 2011; Orellana et al., 2011; Ovadnevaite et al., 2011; Prather et al., 2013; Roberts et al., 2006; Shantz et al., 2010; Sun and Ariya, 2006), this has not been the case for coastal or marine aerosol (herein referred to as coastal/marine aerosol) that has been influenced by marine organics. In particular, past studies have resulted in a wide range in the CCN properties of measured coastal/marine aerosol, and making the direct comparison of results a challenge (Aalto and Kulmala, 2000; Allen et al., 2011; Ayers and Gras, 1991; Ayers et al., 1997; Bougiatioti et al., 2009; Good et al., 2010; Hegg et al., 1991; Hudson, 2007; Hudson et al., 2011; Kleinman et al., 2012; Lohmann and Leck, 2005; Meng et al., 2014; Moore et al., 2012; Ovadnevaite et al., 2011; Roberts et al., 2006, 2010; Shantz et al., 2008; Shinozuka et al., 2009; Sun and Ariya, 2006; Wang et al., 2008).

In addition to the poor characterisation of ambient coastal/marine aerosol, only a handful of studies have estimated the CCN properties of organics in such a setting, which have been reported to possess similar CCN abilities to organics in continental regions (Bougiatioti et al., 2009; Cavalli et al., 2004; Martin et al., 2011; Matsumoto et al., 1997; Meng et al., 2014; Novakov and Penner, 1993). However, the CCN properties of marine organics have not been consistently reported using a standardized method, which makes the relative ranking of their water droplet formation abilities a challenge.

Determination of the effective hygroscopicity parameter, κ, has been identified as a simple method to describe aerosol CCN activities, where the κ values of organic species of continental origins range from 0.02 to 0.2, and those of inorganic species such as $(NH_4)_2SO_4$ and NaCl vary from 0.6 to 1.3 (Petters and Kreidenweis, 2007, and references therein). By using this parameterization, the CCN abilities of aerosol particles, which depend on both their sizes and compositional characteristics (e.g. water solubility and surface activity), can be reported using a single standardized method (Petters and Kreidenweis, 2007, 2013; Twomey, 1977b).

In this study we use the hygroscopicity parameter approach to report the CCN activity of 50 nm and 100 nm ambient aerosol particles that were present on the west coast of Vancouver Island (Ucluelet, British Columbia) in August 2013. These experiments were conducted as part of a campaign to examine cloud formation properties of marine aerosol, as one component of NETCARE (the NETwork on Climate and Aerosols: Addressing Key Uncertainties in Remote Canadian Environments) project (http://www.netcare-project.ca/). This information is used in conjunction with the ambient aerosol's chemical speciation to provide one of the first estimates of the hygroscopicity parameter of organics contained within coastal ambient particles for two size bins (42–75 nm and 78–141 nm).

2 Experimental method

The field campaign took place in August 2013 at a coastal field site which was situated 20 m from shore and on the edge of the small town of Ucluelet (population 1800) on Vancouver Island, BC, Canada (48.92° N, 125.54° W), as shown in Fig. 1. The available instrumentation (Fig. 2) allowed for measurements of CCN activity, particle size distributions, ionic and organic aerosol composition, and gas phase SO_2, CO, NO_x, as described below.

The focus of this work is on data that were collected using a cloud condensation nuclei counter (CCN, DMT 100), which was used to directly calculate the κ of the ambient aerosol (κ_{ambient}). Experiments were conducted from 7–23 August on dry particles having mobility diameters of 50 nm and 100 nm that were size selected using a differential mobility analyzer (DMA, TSI 3081). After size selection, the monodispersed particle flow was split for measurement by the CCN counter as well as a Condensation Particle Counter (CPC, TSI 3010), which was used to measure the aerosol number concentrations. Experiments consisted of scanning supersaturations (0.07–1.2), where each supersaturation was held steady for 10 to 15 min, and resulted in experimental time resolution of 1.5 to 2 h for a full scan. All instruments sampled air through a main inlet in a trailer's roof, with intakes about 5 m above ground. The main inlets were stainless steel tubes (1/2" OD), which were connected to the instruments' inlets by 1/4" OD stainless steel tubing.

A scanning mobility particle sizer (SMPS, TSI 3081, 3782) measured dry aerosol size distributions of mobility diameters within the range of 19–914 nm every two min from 9–25 August, with some interruptions (Fig. 3) due to instrumental maintenance. The SMPS sampled from the same main inlet as the CCN counter and CPC.

A micro-orifice uniform deposition impactor (MOUDI, MSP 110R) sampled directly from a separate main inlet, with a sample flow of 24 L min^{-1}, to collect wet aerosol particles in five size bins corresponding to aerodynamic diameters of 56–100 nm, 100–180 nm, 180–320 nm, 320–560 nm, and 10–18 µm, where the bounds are for 50 % cut-off efficiency at 50 % relative humidity (RH). In order to obtain sufficient particle mass for ion chromatography (IC) to be conducted on the particles, the MOUDI sampled for two day time periods from 13–25 August. Cationic and anionic chromatography was conducted on the collected particles in order to obtain the size resolved two-day average concentrations of Na^+, K^+, NH_4^+, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, $C_2O_4^{2-}$, and methanesulfonic acid (MSA^-) (Phinney et al., 2006). Data from the two smallest size ranges (aerodynamic diameters 56–100 nm and 100–180 nm; i.e. mobility diameters 42–75 nm and 78–141 nm, respectively) will be discussed here. The uncertainty in the ionic concentrations is estimated to be ±20 % based on the MOUDI's collection efficiency, sample handling procedures, and analytical methods.

An aerosol chemical speciation monitor (ACSM, Aerodyne) (Ng et al., 2011) was located in a second trailer 11 m from the primary trailer, and sampled from its own main inlet. The ACSM measured the total organic, SO_4^{2-}, and NO_3^- mass concentrations of particles having wet aerodynamic diameters smaller than 1 µm every 25 min from 13–31 August, with a collection efficiency of 50 % (Ng et al., 2011). SO_2 (Thermo 42i), NO_x (Teledyne API 100TU), and CO (Thermo 48i-TL) monitors were also located in this trailer, where they shared a common inlet and sampled every minute.

3 Results and discussion

3.1 Air mass characteristics and origins

The NOAA Air Resources Laboratory HYSPLIT model was used to generate 72 h back trajectories, examples of which are shown in Fig. 1. Throughout the campaign, these trajectories indicate that air reaching the sampling site (red star) was the result of on-shore winds and was within the marine boundary layer (below ~ 1000 m) for significant periods of time prior to sampling (see Supplement, Fig. S1 middle). During the entire campaign there were three types of air masses that arrived in Ucluelet from (a) the north coast, including the Queen Charlotte Islands, (b) the south coast of USA, and (c) the Pacific Ocean. Consequently, while the winds were typically on-shore, they most likely carried a mixture of anthropogenic (e.g. marine shipping), biogenic continental, and marine aerosol, as was expected due to the sampling site's coastal location.

A characteristic clean marine ratio of MSA to nss-SO_4^{2-} varies from 0.07 to 0.4, depending on the study (Bates et al., 1992; Castebrunet et al., 2009; Chen et al., 2012; Norman et al., 1999; Phinney et al., 2006; Savoie and Prospero, 1989; Savoie et al., 2002). Because the measured two-day average ratios of the entire MOUDI size range (all particles greater than 56 nm), as calculated using the IC concentrations, range from 0.10 to 0.22, the aerosol associated with the air masses may contain a strong marine component. For reference, according to Savoie and Prospero (1989), who reported a characteristic marine ratio of 0.07, the aerosol would be classified as marine; however, according to Norman et al. (1999), who reported a characteristic marine ratio of 0.4, the aerosol would have some anthropogenic contribution. Because this ratio varies considerably with sea surface temperature, particle, size, season, and latitude it is difficult to say with a great deal of certainty whether or not the air masses were significantly marine in nature (Kerminen et al., 1998).

Figure 4 shows a time series (Pacific Daylight Savings Time, PDT) of the daily sea-surface temperature, SO_2 and NO_x mixing ratios, and CO mixing ratios. Based on the presence of NO_x, SO_2, and CO, it is clear that the air masses were anthropogenically influenced at times. These three species tended to increase between 11 a.m. and 11 p.m. on most days, with the maximum mixing ratios occurring between 5 p.m. and 8 p.m. (e.g. 12 and 15 August). As a result, in the cases when the air masses arrived at the sampling site from the Pacific Ocean (e.g. Fig. 1c), it is likely that these signals arise from boat traffic (e.g. whale watching, fishing, pleasure, and sight-seeing boats).

The maximum mixing ratios, which occurred in the late afternoon, were possibly due to these vessels entering the harbor and docking for the night.

When the air masses arrived in Ucluelet from coastal regions (e.g. Fig. 1a and b), the presence of NO_x, CO, and SO_2 may also be due to continental anthropogenic emissions, such as those originating from pulp and paper mills in the region. As well, forests may have acted as a biogenic source of SOA through their production of VOCs such as monoterpenes (e.g. Fig. 1a).

The average sulfate mass concentration as measured by the ACSM (Fig. 5) was $0.68 \pm 0.47\,\mu g\,m^{-3}$, where the uncertainty represents the measurement's standard deviation, with the majority (58–89 %) nss-SO_4^{2-} based on the levels of sodium measured by ion chromatography (Warneck, 1988). The NO_3^- levels as measured by the ACSM (Fig. 5) were typically very low in relation to the sulfate and organic mass concentrations, having an average mass concentration of $0.13 \pm 0.11\,\mu g\,m^{-3}$. Figure 3 (top) shows the total particulate volume concentrations from 9 to 25 August as measured by the SMPS, which correlate reasonably well with the total mass concentration measured by the ACSM (having an R^2 value of 0.3). Figure 3 (bottom) illustrates the wind speed from 9 August to 25. For the majority of August there was a clear diurnal trend in the wind speeds, with mid-day winds weaker than those occurring later in the day and into the night. Although this could be expected to cause a corresponding trend in the particle mass loadings, there was not a clear correlation with the total particulate volume concentrations shown in Fig. 3 (top).

3.2 Determining the hygroscopicity of the ambient aerosol ($\kappa_{ambient}$) and its organic component (κ_{org})

The experimentally determined supersaturation required for 50 % of the ambient particles to be activated as CCN (S_c) is used to calculate $\kappa_{ambient}$ for 50 nm and 100 nm particles using Eq. (1), according to Petters and Kreidenweis (2007).

$$\kappa_{\text{ambient}} = \frac{4A^3}{27D_\text{d}^3\ln^2 S_\text{c}} \qquad (1)$$

$$A = \frac{4\sigma_{\text{s/a}}M_\text{w}}{\text{RT}\rho_\text{w}}$$

where D_d is the dry particle's mobility diameter, $\sigma_{\text{s/a}}$ is the surface tension of the solution/air interface (where the solution is assumed to be water), M_w is the molecular weight of water, R is the gas constant, T is the temperature, and ρ_w is the density of water. Based on the estimated uncertainties in the particle size (10 %) and instrumental supersaturations (5 %), the error in κ_{ambient} is calculated to be approximately 10 %.

As shown in Fig. 6, the time series of κ_{ambient} exhibits a large variability, ranging from 0.14 to 1.08. Because previous studies have indicated a size-dependency of the chemical composition of aerosol particles, it was expected that κ_{ambient} may differ between the 50 nm and 100 nm particles (Andreae and Rosenfeld, 2008). However, the difference was found to be insignificant, suggesting that the chemical composition of the two particle sizes was not significantly different. Interestingly, from 18 to 21 August the κ_{ambient} values were higher than at other times, and were associated with westerly air masses (see Supplement, Fig. S1 top). This indicates that the source of the highly hygroscopic particles may have been marine in nature.

While the correlations between the κ_{ambient} values for each of the two time periods and the air mass origins are not fully clear, there does appear to be a correlation with the average frequency of cloud-coverage in the area. Through qualitative field-site observations that were conducted several times a day, it was found that complete cloud coverage was present approximately 85 % of the time in the first period, and only 30 % of the time in the second period. As a result, the high κ_{ambient} values may be due to the enhancement of biological processes, resulting in emissions which occur in the presence of sunlight, such as the production of dimethyl sulfoxide (DMS) by phytoplankton

(Ayers and Cainey, 2007). Alternatively, it may be due to enhanced photochemistry, such as the photo-oxidation of DMS or SO_2 eventually to SO_4^{2-}.

A final possibility is that in the first time period, when there was a greater extent of cloud coverage, the majority of the more efficient CCN were removed through wet deposition. This would have skewed the results towards lower κ_{ambient} values in relation to those reported during the second time period.

Indeed, by inspection of Fig. 7, it is observed that some of the variability of the κ_{ambient} data are explained through a relationship with the organic to sulfate ratio of the aerosol, where increasing sulfate resulted in increasing κ_{ambient} values. The dependency of the CCN activity of coastal and marine aerosol on sulfate content is supported by previous studies that partially attributed the CCN properties of marine aerosol to the presence of biogenic and anthropogenic sulfate (Andreae and Rosenfeld, 2008b; Matsumoto et al., 1997; Quinn and Bates, 2011, and references therein).

The large range of κ_{ambient} values is comparable to measurements described in the handful of other studies that have reported the hygroscopicity parameters of ambient marine aerosol. For instance, Shantz et al. (2008) presented a case study in which CCN measurements conducted on an oceanographic vessel in the North Pacific Ocean were used to calculate an average κ range of 0.35 to 0.7. Shinozuka et al. (2009) assessed the CCN activity of ambient aerosol during an aircraft campaign over the West Coast of USA using the DMT CCN counter. It was reported that κ_{ambient} varied from 0.07 to 1.15, where the value decreased with increasing organic mass fractions. During a cruise in the tropical Atlantic, Good et al. (2010) reported that the κ of marine aerosol particles was between 1.15 and 1.40. This range was in contrast to the lower κ measured in more continental air masses, which varied from 0.75 to 0.89. Roberts et al. (2010) reported a κ of 0.21 in the northeastern Pacific marine boundary layer from an aircraft platform. This low value was attributed to the presence of a range of sources, including marine emissions, shipping emissions, long-range particle transport, and the downward mixing of particles from the free troposphere. CCN measurements were conducted with a DMT CCN counter by Moore et al. (2012) during flights over the eastern Pacific Ocean off southern Californian coast, where the range of continentally-influenced marine coastal κ values was reported to be 0.15–0.2, which agreed well with the κ of organic compounds reported by other studies (Petters and Kreidenweis, 2007). Finally, by conducting size-resolved CCN measurements at a coastal site in Hong Kong, Meng et al. (2014) determined that κ_{ambient} was 0.39, 0.31, and 0.28 for 116 nm, 56 nm, and 46 nm particles, respectively. The decrease in κ_{ambient} was attributed to increasing organic to inorganic volume ratios as particle size decreased.

In order to try to gain insight into the differing κ_{ambient} values, average two-day mass fractions of the aerosol's chemical species were determined (Fig. 8), with an estimated uncertainty of ±30 %. This was achieved using the size-resolved particle and ionic concentrations (measured by the SMPS and IC, respectively) to infer the organic fraction, and charge balance to infer the fraction of inorganic species (see Supplement, Sect. 1 for details).

As is shown in Fig. 8, the average aerosol composition in the CCN size range was consistently dominated by organic material, which made up 60–86 % of the mass. Of the inorganic species, $(NH_4)_2SO_4$ was the other consistently dominant component, making up 10–34 % of the mass. The organic to sulfate mass ratios of both the smaller size bin (ranging from 3.1 to 9.7) and the larger size bin (ranging from 1.6 to 5.7) agree well with the corresponding average mass ratios measured by the ACSM, which ranged from 1.8 to 3.9 for the same time periods.

As discussed previously, the observation that organic and sulfate species dominate the aerosol composition agrees well with previous studies of the chemical composition of marine aerosol (Good et al., 2010; Hawkins et al., 2008; Moore et al., 2012; O'Dowd et al., 2004; Phinney et al., 2006; Prather et al., 2013). However, it is difficult to conduct these measurements on sub-micron particles that are smaller than about 100 nm with a great deal of certainty (e.g. Moore et al., 2012; Prather et al., 2013). Consequently, the speciation of the smaller size range (42–75 nm) is relatively unique and notable in its similarity to that of the larger size bin since previous studies have reported a size-dependency of the organic fraction of aerosol particles (e.g.

O'Dowd et al., 2004; Prather et al., 2013). Whether the organic material is primary or secondary in nature is unknown; however, because the aerosol contains secondary inorganic species (14–40 % by mass), as opposed to primary sea salt, this highlights the potential importance of chemical processing influencing the aerosol composition. Furthermore, because a relationship was not found between κ_{ambient} and wind speed (Fig. 3, bottom and Supplement, Fig. S1 bottom) (having an R^2 value of 0.01), it is likely that the aerosol was more secondary in nature since primary marine aerosol emissions have been reported to correlate with wind speeds (O'Dowd et al., 1997).

3.2.1 Inferring κ_{org}

The asymptotic value of the plot in Fig. 7 at high values of organic to sulfate ratio from the ACSM implies that the κ-value of the organics within the particles (κ_{org}) is between 0.2 and 0.4. However, the ACSM is sensitive to the total aerosol loading, with an upper size range close to 1 µm, i.e. much larger than the size of CCN. Instead, κ_{org} was estimated using the inferred chemical speciation and the overall aerosol hygroscopicity (see Supplement, Sect. 2 for details). From 13 to 23 August, the average κ_{org} of both 42–75 nm and 78–141 nm particles ranged from 0.3 to 0.5. A systematic uncertainty was estimated to be on the order of ±30 % based primarily on the uncertainties in κ_{ambient} (±10 %) and the composition measurements (±20 %). These κ_{org} values are in excellent agreement with the values inferred from the data in Fig. 7. Good agreement in the range of hygroscopicities indicates that the characteristics of the organic species did not differ significantly between the two size bins.

Because the ambient κ_{org} cannot be directly measured from CCN measurements, the few previous studies that have investigated this topic have used various techniques to infer this value. For instance, using CCN measurements taken at a remote marine site in the eastern Mediterranean, Bougiatioti et al. (2009) carried out a closure study in which a comparison was made between the predicted total CCN concentrations according to Köhler Theory and the measured concentrations. By assuming an organic density, molar mass, and van't Hoff factor for the aerosol's organic fraction, κ_{org} was found to be about 0.16, which is within the range of hygroscopicity parameters for highly aged or oxidized organic material (0.02–0.2) (Petters and Kreidenweis, 2007). This in turn resulted in an overall aerosol κ of about 0.3.

Similarly, Martin et al. (2011) conducted a CCN closure study on summer high Arctic aerosol, based on measurements that were conducted during the Arctic Summer Cloud Ocean Study. CCN concentrations were predicted using Köhler Theory and various permutations of the relevant variables (hygroscopicity parameters of organics and sulfate, density of organics, fraction of water insoluble organics). By comparing the predicted and measured concentrations κ_{org} was found to have a value of about 0.02 with an upper limit of 0.2, which resulted in an overall mean aerosol κ of 0.33 to 0.50. As was the case for Bougiatioti et al. (2009), this range in κ_{org} was comparable to the hygroscopicity parameters of oxidized organic material of continental origin (e.g. Dusek et al., 2010; Petters and Kreidenweis, 2007; Shantz et al., 2008).

Because the mean $\kappa_{\mathrm{ambient}}$ value reported in this study, 0.42 ± 0.15 (where the uncertainty is a one-sigma standard deviation), agrees well with the values reported by Bougiatioti et al. (2009) and Martin et al. (2011), it is intriguing that the corresponding range of κ_{org} indicates that the organic species in this study possess a relatively high degree of hygroscopicity. While this may be due to the differing κ_{org} estimation methodologies, it may also be the result of differing organic species characteristics on a molecular level. For instance, due to its maximum κ_{org} value of 0.5, the organic molecules appear to be, as an upper limit, smaller, more water soluble, or more surface active than the organic molecules investigated in prior studies, and therefore better able to promote water droplet formation (Petters and Kreidenweis, 2007).

We note that, in addition to inferring κ_{org} according to the rigorous method described in Sect. 2 of the Supplement, a simplified secondary method was also used to infer this value. To do this the aerosol was assumed to contain only organics and ammonium sulphate according to the ACSM measurements, using hygroscopicity values from Table S2. To agree with the ambient results, the κ_{org} values of both 42–75 nm and 78–

141 nm particles were found to range from 0.2 to 0.5, and were therefore in very good agreement with the more sophisticated method described above.

4 Summary and conclusions

A cloud condensation nucleus counter was used to investigate the hygroscopicity parameter, and therefore the CCN properties, of ambient aerosol particles on the west coast of Canada (Ucluelet, BC) in August 2013 as one aspect of NETCARE (the NETwork on Climate and Aerosols: Addressing Key Uncertainties in Remote Canadian Environments). These results were used in conjunction with the ambient aerosol's two-day average size-resolved chemical composition to assess the role of organics in promoting CCN behavior in a marine environment. Trajectory analysis and the presence of MSA in the particles is indicative of a significant marine origin to the air masses studied.

The hygroscopicity parameter of the ambient marine aerosol exhibits a large degree of variability, ranging from 0.14 ± 15 % to 1.08 ± 15 %, where the highest values arise when the organic to sulfate ratio of the aerosol is lowest. The two-day average aerosol composition in the 50 to 100 nm size range was consistently primarily composed of organic (60–86 % by mass) and sulfate species (10–34 % by mass). The dominant presence of secondary inorganic components highlights the importance of these secondary species in general, in addition to the primary components that have been considered to be drivers of the CCN properties of marine aerosol in the past.

The chemical speciation and overall aerosol hygroscopicity was used to estimate the hygroscopicity parameter of the organic species contained within the aerosol (κ_{org}), which was found to have an overall range of 0.3 to 0.5, regardless of particle size. Because these values are generally greater than those reported for both continental and marine organic species by previous studies, it may be hypothesized that the organic molecules contained within the aerosol were smaller, more water soluble, or more surface active than the organic species that have previously been investigated.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/12525/2014/acpd-14-12525-2014-supplement.pdf.

Acknowledgements. The authors thank R. Zhao (University of Toronto) and A. Lee (University of Toronto) for constructive comments regarding this project. NETCARE is funded by NSERC (Canada) through the Climate Change and Atmospheric Research Program. The Marine Boundary Layer site at Ucluelet is located at the coast guard site and we would like to thank the Department of Fisheries and Oceans and all the staff at the site for their help. The MBL site is jointly supported and maintained by Environment Canada, BC Ministry of the Environment and MetroVancouver.

References

Aalto, P. and Kulmala, M.: Using a cloud condensation nuclei counter to study CCN properties and concentrations, Boreal Environ. Res., 5, 349–359, 2000.

Albrecht, B. A.: Aerosols, cloud microphysics, and fractional cloudiness, Science, 245, 1227–1230, 1989.

Allen, G., Coe, H., Clarke, A., Bretherton, C., Wood, R., Abel, S. J., Barrett, P., Brown, P., George, R., Freitag, S., McNaughton, C., Howell, S., Shank, L., Kapustin, V., Brekhovskikh, V., Kleinman, L., Lee, Y.-N., Springston, S., Toniazzo, T., Krejci, R., Fochesatto, J., Shaw, G., Krecl, P., Brooks, B., McMeeking, G., Bower, K. N., Williams, P. I., Crosier, J., Crawford, I., Connolly, P., Allan, J. D., Covert, D., Bandy, A. R., Russell, L. M., Trembath, J., Bart, M., McQuaid, J. B., Wang, J., and Chand, D.: South East Pacific atmospheric composition and variability sampled along 20° S during VOCALS-REx, Atmos. Chem. Phys., 11, 5237–5262, doi:10.5194/acp-11-5237-2011, 2011.

Andreae, M. O. and Rosenfeld, D.: Aerosol–cloud–precipitation interactions, Part 1. The nature and sources of cloud-active aerosols, Earth-Sci. Rev., 89, 13–41, doi:10.1016/j.earscirev.2008.03.001, 2008.

Ayers, G. P. and Cainey, J. M.: The CLAW hypothesis: a review of the major developments, Environ. Chem., 4, 366–374, doi:10.1071/EN07080, 2007.

Ayers, G. P. and Gras, J. L.: Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air, Nature, 353, 834–835, 1991.

Ayers, G. P., Cainey, J. M., Gillett, R. W., Ivey, J. P., Smith, M. H., and Lenton, T.: Atmospheric sulphur and cloud condensation nuclei in marine air in the Southern Hemisphere, Philos. T. Roy. Soc. B, 352, 203–211, doi:10.1098/rstb.1997.0015, 1997.

Bates, T. S., Calhoun, J. A., and Quinn, P. K.: Variations in the methanesulfonate to sulfate molar ratio in marine aerosol particles over the South Pacific Ocean, J. Geophys. Res., 97, 9859–9865, 1992.

Bigg, E. K.: Sources, nature and influence on climate of marine airborne particles, Environ. Chem., 4, 155, doi:10.1071/EN07001, 2007.

Bougiatioti, A., Fountoukis, C., Kalivitis, N., Pandis, S. N., Nenes, A., and Mihalopoulos, N.: Cloud condensation nuclei measurements in the marine boundary layer of the Eastern Mediterranean: CCN closure and droplet growth kinetics, Atmos. Chem. Phys., 9, 7053–7066, doi:10.5194/acp-9-7053-2009, 2009.

Castebrunet, H., Martinerie, P., Genthon, C., and Cosme, E.: A three-dimensional model study of methanesulphonic acid to non sea salt sulphate ratio at mid and high-southern latitudes, Atmos. Chem. Phys., 9, 9449–9469, doi:10.5194/acp-9-9449-2009, 2009.

Cavalli, F., Facchini, M. C., Decesari, S., Mircea, M., Emblico, L., Fuzzi, S., Ceburnis, D., Yoon, Y. J., O'Dowd, C. D., Pataud, J.-P., and Dell'Acqua, A.: Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic, J. Geophys. Res., 109, D24215, doi:10.1029/2004JD005137, 2004.

Chang, R. Y.-W., Slowik, J. G., Shantz, N. C., Vlasenko, A., Liggio, J., Sjostedt, S. J., Leaitch, W. R., and Abbatt, J. P. D.: The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: relationship to degree of aerosol oxidation, Atmos. Chem. Phys., 10, 5047–5064, doi:10.5194/acp-10-5047-2010, 2010.

Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley, Jr, J. A., Hansen, J. E., and Hofmann, D. J.: Climate forcing by anthropogenic aerosols, Science, 255, 423–430, 1992.

Chen, L., Wang, J., Gao, Y., Xu, G., Yang, X., Lin, Q., and Zhang, Y.: Latitudinal distributions of atmospheric MSA and MSA/nss-SO_4^{2-} ratios in summer over the high latitude regions of the Southern and Northern Hemispheres, J. Geophys. Res., 117, D10306, doi:10.1029/2011JD016559, 2012.

Coggon, M. M., Sorooshian, A., Wang, Z., Metcalf, A. R., Frossard, A. A., Lin, J. J., Craven, J. S., Nenes, A., Jonsson, H. H., Russell, L. M., Flagan, R. C., and Seinfeld, J. H.: Ship impacts on the marine atmosphere: insights into the contribution of shipping emissions to the properties of marine aerosol and clouds, Atmos. Chem. Phys., 12, 8439–8458, doi:10.5194/acp-12-8439-2012, 2012.

Dusek, U., Frank, G. P., Curtius, J., Drewnick, F., Schneider, J., Kürten, A., Rose, D., Andreae, M. O., Borrmann, S., and Pöschl, U.: Enhanced organic mass fraction and decreased hygroscopicity of cloud condensation nuclei (CCN) during new particle formation events, Geophys. Res. Lett., 37, L03804, doi:10.1029/2009GL040930, 2010.

Fuentes, E., Coe, H., Green, D., and McFiggans, G.: On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol – Part 2: Composition, hygroscopicity and cloud condensation activity, Atmos. Chem. Phys., 11, 2585–2602, doi:10.5194/acp-11-2585-2011, 2011.

Good, N., Topping, D. O., Allan, J. D., Flynn, M., Fuentes, E., Irwin, M., Williams, P. I., Coe, H., and McFiggans, G.: Consistency between parameterisations of aerosol hygroscopicity and CCN activity during the RHaMBLe discovery cruise, Atmos. Chem. Phys., 10, 3189–3203, doi:10.5194/acp-10-3189-2010, 2010.

Hartmann, D. L., Ockert-Bell, M. E., and Michelsen, M. L.: The Effects of cloud type on earth's energy balance: global analysis, J. Climate, 5, 1281–1304, 1992.

Hawkins, L. N., Russell, L. M., Twohy, C. H., and Anderson, J. R.: Uniform particle-droplet partitioning of 18 organic and elemental components measured in and below DYCOMS-II stratocumulus clouds, J. Geophys. Res., 113, D14201, doi:10.1029/2007JD009150, 2008.

Hegg, A., Radke, F., and Hobbs, V.: Measurements of Aitken nuclei and cloud condensation nuclei in the marine atmosphere and their relation to the DMS-Cloud-Climate Hypothesis, J. Geophys. Res., 96, 18727–18733, 1991.

Hegg, D. A., Covert, D. S., Jonsson, H. H., and Woods, R.: Differentiating natural and anthropogenic cloud condensation nuclei in the California coastal zone, Tellus B, 61, 669–676, doi:10.1111/j.1600-0889.2009.00435.x, 2009.

Hudson, J. G.: Variability of the relationship between particle size and cloud-nucleating ability, Geophys. Res. Lett., 34, L08801, doi:10.1029/2006GL028850, 2007.

Hudson, J. G., Noble, S., and Jha, V.: On the relative role of sea salt cloud condensation nuclei (CCN), J. Atmos. Chem., 68, 71–88, doi:10.1007/s10874-011-9210-5, 2011.

IPCC: Summary for Policymakers, in: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.

Kerminen, V., Hillamo, R. E., and Wexler, A. S.: Model simulations on the variability of particulate MSA to non-sea-salt sulfate ratio in the marine environment, J. Atmos. Chem., 30, 345–370, 1998.

Kleinman, L. I., Daum, P. H., Lee, Y.-N., Lewis, E. R., Sedlacek III, A. J., Senum, G. I., Springston, S. R., Wang, J., Hubbe, J., Jayne, J., Min, Q., Yum, S. S., and Allen, G.: Aerosol concentration and size distribution measured below, in, and above cloud from the DOE G-1 during VOCALS-REx, Atmos. Chem. Phys., 12, 207–223, doi:10.5194/acp-12-207-2012, 2012.

Langley, L., Leaitch, W. R., Lohmann, U., Shantz, N. C., and Worsnop, D. R.: Contributions from DMS and ship emissions to CCN observed over the summertime North Pacific, Atmos. Chem. Phys., 10, 1287–1314, doi:10.5194/acp-10-1287-2010, 2010.

Leck, C. and Bigg, E. K.: Biogenic particles in the surface microlayer and overlaying atmosphere in the central Arctic Ocean during summer, Tellus B, 57, 305–316, 2005a.

Leck, C. and Bigg, E. K.: Source and evolution of the marine aerosol – A new perspective, Geophys. Res. Lett., 32, L19803, doi:10.1029/2005GL023651, 2005b.

Lohmann, U. and Leck, C.: Importance of submicron surface-active organic aerosols for pristine Arctic clouds, Tellus B, 57, 261–268, 2005.

Martin, M., Chang, R. Y.-W., Sierau, B., Sjogren, S., Swietlicki, E., Abbatt, J. P. D., Leck, C., and Lohmann, U.: Cloud condensation nuclei closure study on summer arctic aerosol, Atmos. Chem. Phys., 11, 11335–11350, doi:10.5194/acp-11-11335-2011, 2011.

Matsumoto, K., Tanaka, H., Nagao, I., and Ishizaka, Y.: Contribution of particulate sulfate and organic carbon to cloud condensation nuclei in the marine atmosphere, Geophys. Res. Lett., 24, 655–658, doi:10.1029/97GL00541, 1997.

Meng, J. W., Yeung, M. C., Li, Y. J., Lee, B. Y. L., and Chan, C. K.: Cloud condensation nuclei (CCN) and HR-ToF-AMS measurements at a coastal site in Hong Kong: size-resolved CCN activity and closure analysis, Atmos. Chem. Phys. Discuss., 14, 9067–9107, doi:10.5194/acpd-14-9067-2014, 2014.

Moore, M. J. K., Furutani, H., Roberts, G. C., Moffet, R. C., Gilles, M. K., Palenik, B., and Prather, K. A.: Effect of organic compounds on cloud condensation nuclei (CCN) activity of sea spray aerosol produced by bubble bursting, Atmos. Environ., 45, 7462–7469, doi:10.1016/j.atmosenv.2011.04.034, 2011.

Moore, R. H., Cerully, K., Bahreini, R., Brock, C. A., Middlebrook, A. M., and Nenes, A.: Hygroscopicity and composition of California CCN during summer 2010, J. Geophys. Res.-Atmos., 117, D00V12, doi:10.1029/2011JD017352, 2012.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol, Aerosol Sci. Tech., 45, 780–794, doi:10.1080/02786826.2011.560211, 2011.

Norman, A. L., Barrie, L. A., Sirois, A., Krouse, H. R., Li, S. M., and Sharma, S.: Sources of aerosol sulphate at Alert: apportionment using stable isotopes, J. Geophys. Res., 104, 11619–11631, 1999.

Novakov, T. and Penner, J. E.: Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, Nature, 365, 823–826, 1993.

O'Dowd, C. D., Smith, M. H., Consterdine, I. E., and Lowe, J. A.: Marine aerosol, sea-salt, and the marine sulphur cycle: a short review, Atmos. Environ., 31, 73–80, 1997.

O'Dowd, C. D. O., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676–680, doi:10.1038/nature02959, 2004.

Orellana, M. V, Matrai, P. A., Leck, C., Rauschenberg, C. D., and Lee, A. M.: Marine microgels as a source of cloud condensation nuclei in the high Arctic, P. Natl. Acad. Sci. USA, 108, 13612–13617, doi:10.1073/pnas.1102457108, 2011.

Ovadnevaite, J., Ceburnis, D., Martucci, G., Bialek, J., Monahan, C., Rinaldi, M., Facchini, M. C., Berresheim, H., Worsnop, D. R., and O'Dowd, C.: Primary marine organic aerosol: a dichotomy of low hygroscopicity and high CCN activity, Geophys. Res. Lett., 38, 1–5, doi:10.1029/2011GL048869, 2011.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961–1971, doi:10.5194/acp-7-1961-2007, 2007.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity – Part 3: Including surfactant partitioning, Atmos. Chem. Phys., 13, 1081–1091, doi:10.5194/acp-13-1081-2013, 2013.

Phinney, L., Richard Leaitch, W., Lohmann, U., Boudries, H., Worsnop, D. R., Jayne, J. T., Toom-Sauntry, D., Wadleigh, M., Sharma, S., and Shantz, N.: Characterization of the aerosol over the sub-arctic north east Pacific Ocean, Deep-Sea Res. Pt. II, 53, 2410–2433, doi:10.1016/j.dsr2.2006.05.044, 2006.

Prather, K. A., Bertram, T. H., Grassian, V. H., Deane, G. B., Stokes, M. D., Demott, P. J., Aluwihare, L. I., Palenik, B. P., Azam, F., Seinfeld, J. H., Moffet, R. C., Molina, M. J., Cappa, C. D., Geiger, F. M., Roberts, G. C., Russell, L. M., Ault, A. P., Baltrusaitis, J., Collins, D. B., Corrigan, C. E., Cuadra-Rodriguez, L. A., Ebben, C. J., Forestieri, S. D., Guasco, T. L., Hersey, S. P., Kim, M. J., Lambert, W. F., Modini, R. L., Mui, W., Pedler, B. E., Ruppel, M. J., Ryder, O. S., Schoepp, N. G., Sullivan, R. C., and Zhao, D.: Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol., P. Natl. Acad. Sci. USA, 110, 7550–7555, doi:10.1073/pnas.1300262110, 2013.

Quinn, P. K. and Bates, T. S.: The case against climate regulation via oceanic phytoplankton sulphur emissions, Nature, 480, 51–56, doi:10.1038/nature10580, 2011.

Roberts, G., Mauger, G., Hadley, O., and Ramanathan, V.: North American and Asian aerosols over the eastern Pacific Ocean and their role in regulating cloud condensation nuclei, J. Geophys. Res., 111, D13205, doi:10.1029/2005JD006661, 2006.

Roberts, G. C., Day, D. A., Russell, L. M., Dunlea, E. J., Jimenez, J. L., Tomlinson, J. M., Collins, D. R., Shinozuka, Y., and Clarke, A. D.: Characterization of particle cloud droplet activity and composition in the free troposphere and the boundary layer during INTEX-B, Atmos. Chem. Phys., 10, 6627–6644, doi:10.5194/acp-10-6627-2010, 2010.

Savoie, D. L. and Prospero, J. M.: Comparison of oceanic and continental sources of non-sea-salt sulphate over the Pacific Ocean, Lett. to Nat., 339, 685–687, 1989.

Savoie, D. L., Arimoto, R., Keene, W. C., Prospero, J. M., Duce, R. A., and Galloway, J. N.: Marine biogenic and anthropogenic contributions to non-sea-salt sulfate in the marine boundary layer over the North Atlantic Ocean, J. Geophys. Res., 107, 4356, doi:10.1029/2001JD000970, 2002.

Shantz, N. C., Leaitch, W. R., Phinney, L., Mozurkewich, M., and Toom-Sauntry, D.: The effect of organic compounds on the growth rate of cloud droplets in marine and forest settings, Atmos. Chem. Phys., 8, 5869–5887, doi:10.5194/acp-8-5869-2008, 2008.

Shantz, N. C., Chang, R. Y.-W., Slowik, J. G., Vlasenko, A., Abbatt, J. P. D., and Leaitch, W. R.: Slower CCN growth kinetics of anthropogenic aerosol compared to biogenic aerosol observed at a rural site, Atmos. Chem. Phys., 10, 299–312, doi:10.5194/acp-10-299-2010, 2010.

Shinozuka, Y., Clarke, A. D., DeCarlo, P. F., Jimenez, J. L., Dunlea, E. J., Roberts, G. C., Tomlinson, J. M., Collins, D. R., Howell, S. G., Kapustin, V. N., McNaughton, C. S., and Zhou, J.: Aerosol optical properties relevant to regional remote sensing of CCN activity and links to their organic mass fraction: airborne observations over Central Mexico and the US West Coast during MILAGRO/INTEX-B, Atmos. Chem. Phys., 9, 6727–6742, doi:10.5194/acp-9-6727-2009, 2009.

Sun, J. and Ariya, P.: Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): a review, Atmos. Environ., 40, 795–820, doi:10.1016/j.atmosenv.2005.05.052, 2006.

Twomey, S.: Atmospheric Aerosols, Elsevier, Amsterdam, 1977a.

Twomey, S.: The influence of pollution on the shortwave albedo of clouds, J. Atmos. Sci., 34, 1149–1152, 1977b.

Wang, J., Lee, Y.-N., Daum, P. H., Jayne, J., and Alexander, M. L.: Effects of aerosol organics on cloud condensation nucleus (CCN) concentration and first indirect aerosol effect, Atmos. Chem. Phys., 8, 6325–6339, doi:10.5194/acp-8-6325-2008, 2008.

Warneck, P.: Chemistry of the Natural Atmosphere, edited by: Dmowska, R. and Holton, J. R., Academic Press, London, 1988.

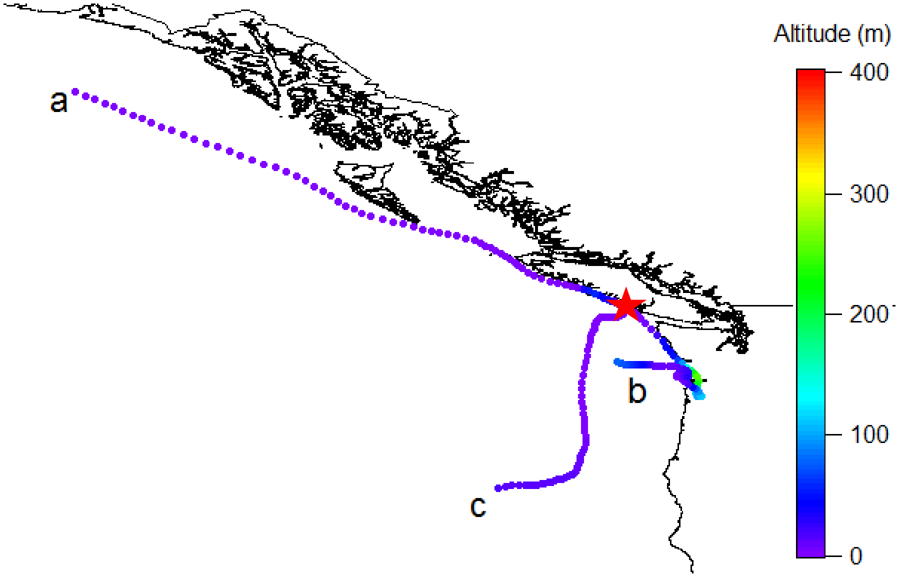

Fig. 1. Examples of the three types of air masses that were seen throughout the entire campaign, generated using the NOAA Air Resources Laboratory-HYSPLIT program. The three types arrived in Ucluelet (star) after passing **(a)** down the north coast and near or over the Queen Charlotte Islands (4 August, 06:00 PDT), **(b)** up the south coast (17 August, 14:00 PDT), or **(c)** directly from the Pacific Ocean (15 August, 00:00 PDT).

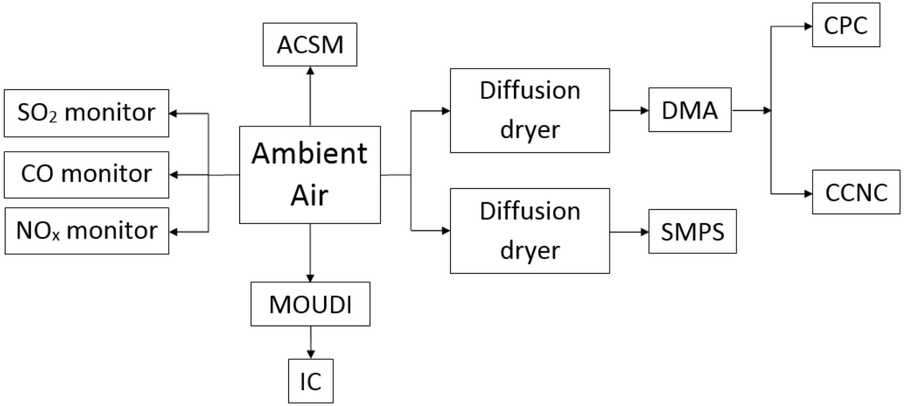

Fig. 2. Schematic of the main components of the experimental setup, which included SO_2, CO, and NO_x monitors, an aerosol chemical speciation monitor (ACSM), micro-orifice deposit impactor (MOUDI), ion chromatograph (IC), differential mobility analyzer (DMA), condensation particle counter (CPC), cloud condensation nuclei counter (CCNC), and a scanning mobility particle sizer (SMPS). The ACSM, and SO_2, CO, and NO_x monitors were in a neighbouring trailer.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀| |▶

◀ ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

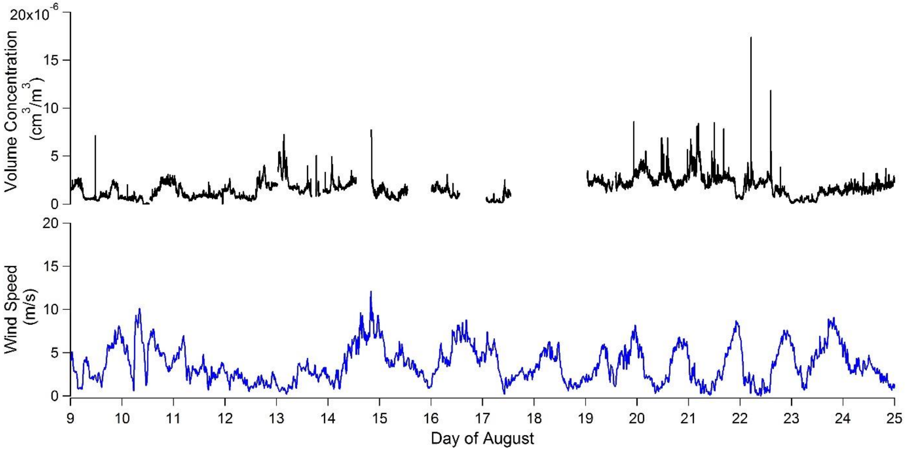

Fig. 3. Time series for 9–25 August of SMPS total volumetric concentrations (top) and wind speed (bottom).

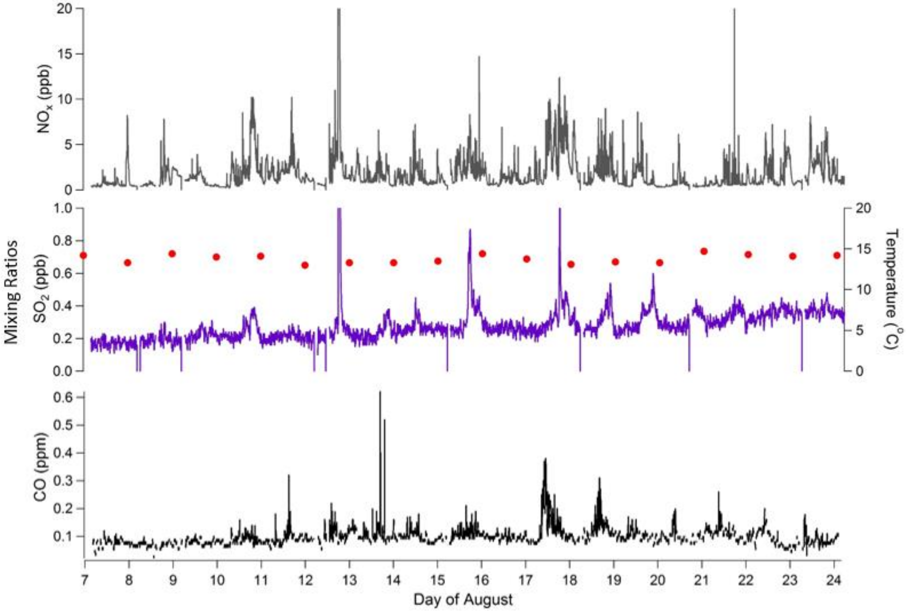

Fig. 4. Time series for 7–24 August of sea surface temperature (red circles), NO$_x$ (top), SO$_2$, and CO (bottom) mixing ratios.

ACPD

14, 12525–12553, 2014

Hygroscopicity of aerosol and its organic component

J. D. Yakobi-Hancock et al.

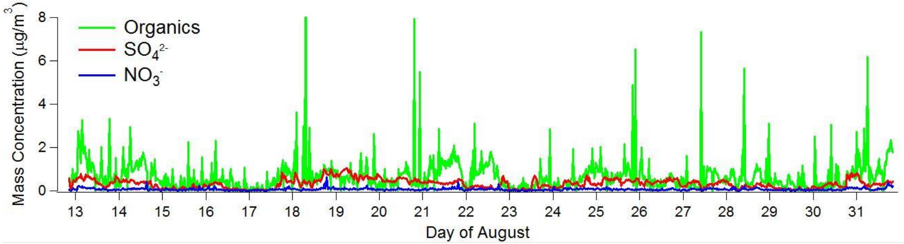

Fig. 5. Time series for 13–31 August of ACSM organics (green), SO_4^{2-} (red), and NO_3^- (blue).

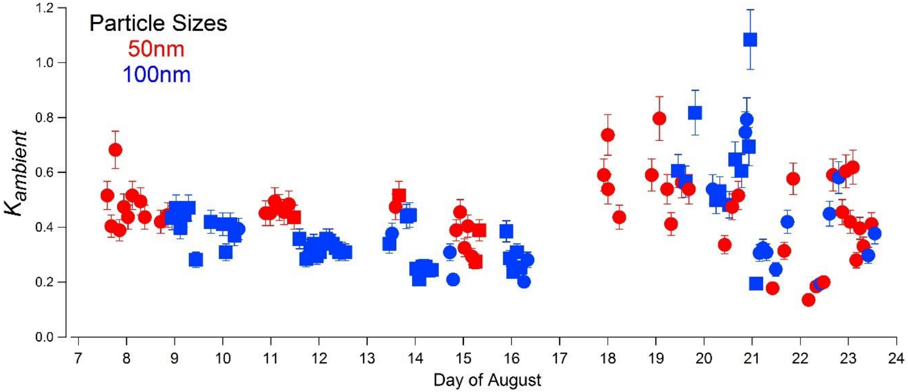

Fig. 6. Time series for 7–24 August of CCN-derived κ_{ambient} of monodispersed ambient aerosol having dry mobility diameters of 50 nm (red circles) and 100 nm (blue squares). The error bars represent a systematic error of ±10 %.

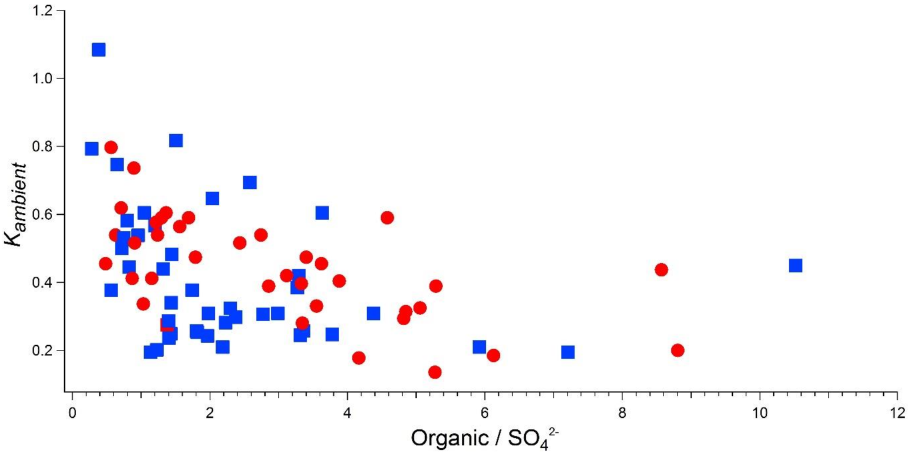

Fig. 7. CCN-derived $\kappa_{\mathrm{ambient}}$ of monodisperse ambient marine aerosol having dry mobility diameters of 50 nm (red circles) and 100 nm (blue squares) as a function of the organic to sulfate ratio measured by the ACSM.

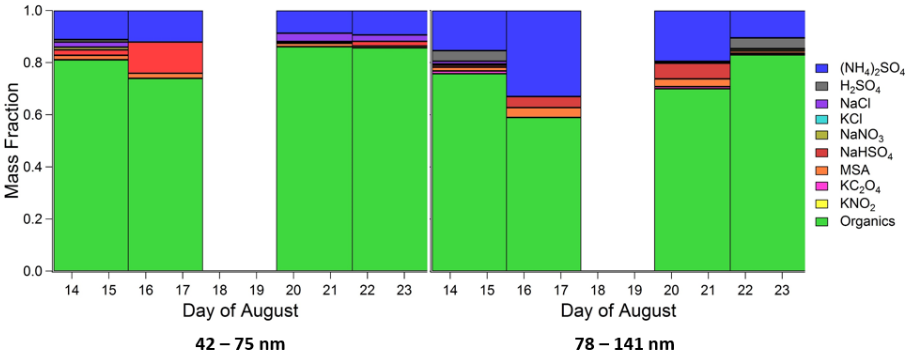

Fig. 8. Mass fractions of ambient aerosol particle species during 13–17 August and 19–23 August for dry mobility diameter ranges of 42–75 nm and 78–141 nm.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion