Hygroscopicity of particles at two rural, urban influenced sites during Pacific 2001: Comparison with estimates of water uptake from particle composition


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Abstract

Hygroscopicity of particles was measured at Langley (rural) and Eagle Ridge (semi-rural) as part of the Pacific 2001 field campaign. The measured growth factors at the two sites were comparable. However, differences in particle composition as measured by an Aerosol Mass Spectrometer were evident at these two sites. Sulphate mass concentration was found to be similar at the two sites, while higher nitrate and organic mass were observed at Eagle Ridge. Higher growth factors were observed when the air mass was impacted by SO2 sources, while lower growth factors were observed when the air mass was affected by urban emissions. To examine the hygroscopic role of the different particle components, expected growth factors were calculated from the composition data and compared to measured growth factors. Calculations were done using the Zdanovskii, Stokes and Robinson (ZSR) mixing rule. Sulphate fraction played a dominant role in particle hygroscopicity at both sites. Calculated growth factors were within the uncertainty of the measurements, except when the nitrate fraction was high. The results imply that particulate nitrate takes up much less water than ammonium nitrate, indicating that the ZSR mixing rule fails for nitrate. Small variations of organic growth factors with source regions suggest that secondary organic matter is more hygroscopic than primary organic matter.

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1. Introduction

The hygroscopicity of a particle affects its interaction with atmospheric gases, its ability to act as a cloud condensation nucleus, and its potential to
degrade visibility. Sub-micrometer particles are commonly found in the atmosphere as internal mixtures of inorganic and organic material, and their ability to sorb water can be highly variable (Cocker et al., 2001; Swietlicki et al., 1999; Väkevä et al., 2002). While the contributions of the inorganic fraction to particle hygroscopicity are well characterised, this is not the case for the organic fraction. In some previous field studies, authors have assumed that the organic fraction is inert with respect to water uptake (Pitchford and McMurry, 1994; Swietlicki et al., 1999; Hameri et al., 2001; Busch et al., 2002). However, recent studies have shown that organics can alter water uptake.

Laboratory studies using small carboxylic and multi-functional acids have shown that organic particles are able to take up water (Prenni et al., 2001; Peng et al., 2001). Within a mixed particle, organics can contribute to water uptake (Cruz and Pandis, 2000; Choi and Chan, 2002; Prenni et al., 2003), albeit they play a smaller role than the inorganic fraction at higher relative humidity. At lower relative humidity, the presence of soluble organics can appreciably influence the water content of a particle (Dick et al., 2000; Prenni et al., 2003). Field measurements support the assertion that organics can contribute to water uptake in certain particle types; for example, Dick et al. (2000) and Saxena et al. (1995) found evidence of organic associated water within atmospheric particles sampled at a non-urban site. In contrast, the organic fraction can also reduce the water sorbing ability of the inorganic fraction for certain particle types (Choi and Chan, 2002; Cruz and Pandis, 2000; Saxena et al., 1995), such as particles in an urban environment (Saxena et al., 1995). Differences in the hygroscopic behaviour of the organic fraction may result from increased atmospheric processing and the presence of polar organics in the non-urban particles. Alfarra et al. (2004) found that the organic fraction of particles at the rural sites was composed of highly oxidised organic compounds, while a mixture of saturated and unsaturated hydrocarbons dominated the particle organic fraction at urban sites.

Measurements of the hygroscopic growth of submicrometer particles were made during the PACIFIC 2001 field study at a forested, a rural and a semi-rural site. The overlying goal of PACIFIC 2001 was to provide a better understanding of the sources, formation, and distribution of particulate matter in the Lower Fraser Valley, British Columbia. Due to its large population and geographic location, the valley is exposed to emissions from a variety of sources, and particulate matter is likely to be composed of a mixture of natural and anthropogenic material. A description of the study can be found in Li (2004) and hygroscopic growth measurements from two of the sampling sites have been previously discussed (Shantz et al., 2004; Aklilu and Mozurkewich, 2004). Here, we extend our study of the hygroscopic properties and focus on water uptake due to the organic fraction of particles. During PACIFIC 2001, organics represented 34–44% of the total particle mass (<1 μm) at rural and semi-rural sites (Boudries et al., 2004); this fraction was even higher for smaller sized particles. This provided an appropriate environment for investigating the effect of the organic fraction on the hygroscopicity of atmospheric particles.

Humidified tandem differential mobility analysers (hTDMA) were used to measure hygroscopicity. Particle composition was measured using an aerosol mass spectrometer (AMS), Micro Orifice Uniform Deposition Impactor (MOUDI) and optical instruments. These methods allow characterisation of the aerosol with good time resolution. A comparison of the measured particle hygroscopicity between the two sites was performed. Using compositional data and the Zdanovskii, Stokes and Robinson (ZSR) approach, the role of the organic fraction in particle hygroscopicity was investigated.

2. Experimental

2.1. Sampling sites

Particles were sampled at Eagle Ridge and Langley, both of which are located in the Lower Fraser Valley, British Columbia, Canada. The Langley site was located in a rural setting, 90 m above sea level (asl) and 6 km from the nearest urban centre (population 24,000). The Eagle Ridge site was about 20 km further inland, located on a sparsely forested ridge. This site was at an elevation of 300 m asl and 3 km from the city of Abbotsford (population 120,000); it was often above the nocturnal boundary layer. A detailed description of the sites can be found in Li (2004). Particles at the two sites were expected to be aged and/or secondary particles. Eagle Ridge, being located in a sparsely forested area, was expected to be impacted by biogenic emissions. A large fraction of the particulate matter at these sites was aged and predomi-
nantly affected by regional factors (Boudries et al., 2004).

The main study took place between 13th and 31st of August 2001. However, a complete data set for the entire period was not available; thus, the data discussed here are from the last segment of the study, 25th to 31st August. This period was relatively dry, although partly cloudy skies were the norm for many of the sample days. The dominant daytime flow pattern was into the valley, making Eagle Ridge downwind of Langley. Detailed analysis of meteorological patterns can be found in Snyder and Strawbridge (2004).

2.2. Sampling method

hTDMAs were used to measure particle hygroscopicity at the two sites. An hTDMA makes use of two DMAs to examine particle diameter increases due to water sorption. Ambient particles were first dried, and then a narrow size range was selected using the first DMA. The near-monodisperse particles were then exposed to a desired relative humidity and the second DMA was used to measure the growth of the humidified particles. Using the dried and humidified diameters, a growth factor (\(D_p\) wet/\(D_p\) dry) was calculated for a given relative humidity. Particles at Eagle Ridge were dried to \(~15\%\) RH using a multi-tube Perma Pure dryer (model PD-625-24SS). The size-selected particles were humidified to a range of relative humidities from 50\% to 85\%. The humidification system comprised of two Perma Pure tubes (model MH-070-24P and model MD-110-24F). Aklilu and Mozurkewich (2004) give a more detailed description of the hTDMA at Eagle Ridge. At Langley, the particles were dried to \(~5\%\) RH using diffusion dryers. Perma Pure tubing (model MD-110-48S) was used to humidify the size selected particles to two discrete relative humidities, 80\% and 90\%. The hTDMA at Langley was kept at a temperature of 30\(^\circ\)C. Prenni et al. (2001) provide a detailed description of the hTDMA used at Langley. The two hTDMAs were both used at Golden Ears Provincial Park prior to the main segment of the study (Shantz et al., 2004). Although sampling was done at different sizes (100 and 75 nm), the results obtained using the two instruments were in very good agreement with an average difference of less than 2\%.

In addition to the hygroscopicity measurements, size resolved particle composition was measured using an AMS and a MOUDI. The AMS provides on-line quantitative measurements of the size and chemical composition of the non-refractory fraction of submicron particles. Jayne et al. (2000) and Jimenez et al. (2003b) provide a description of the AMS and its operation, while Allan et al. (2003, 2004) describe the data analysis techniques used. AMS measurements provided total loadings of sulphate, nitrate, ammonium and organics, but cannot provide data on the refractory fraction, in particular black carbon. Size-resolved data was only available for sulphate, nitrate and organics. The average uncertainty of the AMS measurement at both sites was 30\% (Boudries et al., 2004). Mass concentrations of inorganic sulphate and nitrate were measured using the MOUDI. The Teflon filters from the MOUDI samplers were analysed using ion chromatography. Size resolved black carbon measurements were not available, therefore PM 2.5 measurements were used for estimates. PM 2.5 black carbon concentrations were measured using a Particle Soot Absorption Photometer (PSAP) at Eagle Ridge and an aethalometer at Langley. The 2.5 \(\mu\)m cut-off for these instruments was determined using cyclones. Samples were taken about 4m above the ground using \(\frac{1}{4}\) stainless steel tubing. Both instruments used the same method of collection with some differences in the optical absorption method. The PSAP measures at a wavelength of 565 nm whereas the aethalometer measures at 880 nm. The major difference is that PSAP has a built in algorithm to correct for the multiple scattering due to the quartz fibre matrix. The two instruments were compared in the laboratory prior to the field study and were found to agree within 15\% of each other.

3. Particle hygroscopicity and composition at the two sites

3.1. Particle composition

The AMS samples particles in the size range of 0.05–1 \(\mu\)m (vacuum-aerodynamic diameter) (Boudries et al., 2004). For an average particle density of 1.5 \(g\) \(m^{-3}\), an AMS size interval of 100–160 \(nm\) corresponds to an equivalent mobility diameter range of 67–107 \(nm\), the approximate size measured by the hTDMAs. The average mass concentration of sulphate, nitrate and organic for this size range are 0.12, 0.13 and 0.61 \(\mu\)g m\(^{-3}\) at Eagle Ridge, and 0.11, 0.05 and 0.36 \(\mu\)g m\(^{-3}\) at Langley. The AMS
detection limits for Eagle Ridge were 0.04 \( \mu \text{g m}^{-3} \) for nitrate and sulphate mass and 0.1 \( \mu \text{g m}^{-3} \) for organics. At Langley, the AMS detection limits were 0.02 \( \mu \text{g m}^{-3} \) for nitrate and sulphate mass and 0.05 \( \mu \text{g m}^{-3} \) for organics. Size resolved ammonium data was not available; however, total mass measurements with the AMS showed that submicrometer particles at these sites were fully neutralised. Most of the mass was in larger particles than the ones considered here, but it is to be expected that smaller particles are neutralised more rapidly due to their larger surface to volume ratio.

The AMS provides the total sulphate and nitrate mass; a check on these measurements was made by comparing them with the MOUDI measurements. The MOUDI particle diameter range used for these comparisons was limited to particles on the stage 10 of the MOUDI (100–170 nm aerodynamic diameter) which roughly corresponds to a vacuum-aerodynamic diameter bin range of 126–215 nm. For the size range in study, the two diameters are related by the square root of the particle effective density. Particle composition for this size range was very similar to that chosen for comparison with hTDMA measurements.

For sulphate, agreement between the AMS and MOUDI measurements was excellent as shown in Fig. 1. Linear correlation coefficients were 0.91 for both Langley and Eagle Ridge and slopes were within experimental error of unity for best fit lines forced through the origin. However, nitrate mass from the MOUDI was much lower than that of AMS; this was especially true at Eagle Ridge, where average concentrations were 0.01 \( \mu \text{g m}^{-3} \) (MOUDI) and 0.14 \( \mu \text{g m}^{-3} \) (AMS). The MOUDI detection limit for nitrate mass was 0.003 \( \mu \text{g m}^{-3} \). At Langley the MOUDI and AMS nitrate masses correlated significantly with a linear correlation coefficient of 0.60, while at Eagle Ridge, a linear correlation coefficient of 0.42 was found not to be significant at confidence level of 90%. Some of the discrepancy between the two types of measurements could be due to evaporative losses (Wang and John, 1988; Singh et al., 2003). Thus, the results are consistent with all of the nitrate being inorganic, but we cannot exclude the possibility that a portion of the ultrafine particle nitrate may have been organic.

The AMS did not measure the black carbon mass concentration. An estimate of the black carbon concentrations at 100–160 nm vacuum-aerodynamic diameter was made using total mass (<1 \( \mu \text{m} \)) as measured by the AMS and PM 2.5 black carbon measurements. We assume that the black carbon measurement is a good measure of the total elemental carbon. At Eagle Ridge black carbon mass concentrations hovered around 0.5 \( \mu \text{g m}^{-3} \) until 28th August, after which concentrations at this site showed a similar trend to Langley and ranged between 0.2 and 2 \( \mu \text{g m}^{-3} \) (Fig. 2). Low black carbon concentrations were observed on the 27th, 30th and 31st of August, when concentrations were lower than 0.5 \( \mu \text{g m}^{-3} \). The detection limits for the PSAP and the aethalometer were 2 and 5 \( \text{ng m}^{-3} \), respectively. Black carbon concentrations at Langley were higher than at Eagle Ridge at most times. The ratio of PM 2.5 black carbon mass to total AMS mass was used to estimate the black carbon contribution in the size range of 100–160 nm (vacuum-aerodynamic). This estimation assumes that a significant portion of the PM 2.5 lies below

![Graph](image1.png)

Fig. 1. Sulphate mass correlation between MOUDI and AMS measurements. (a) Eagle Ridge: the Pearson correlation coefficient is 0.91 \((n = 8)\) and the slope is 1.10±0.09. (b) Langley: the Pearson correlation coefficient is 0.91 \((n = 25)\) and the slope is 1.04±0.06. Both correlations were found to be significant at 95% confidence. Average uncertainties for AMS measurements were ±30%.
1 μm (PM 1.0–PM 2.5) and that black carbon fraction is independent of size. Black carbon size distributions have shown that a large fraction of the mass exists below 1 μm (Hitzenberger and Tohno, 2001; Neusüß et al., 2002). These distributions can be bimodal with a mode at 0.15 and 0.37 μm or unimodal with mass median diameter at 0.38 μm (Hitzenberger and Tohno, 2001). Therefore, our assumption is reasonable, though of uncertain accuracy. The average ratio of black carbon mass to AMS mass was higher at Langley (0.2) than at Eagle Ridge (0.06). This was primarily due to larger AMS total mass at Eagle Ridge rather than a significantly lower black carbon concentration.

3.2. Particle hygroscopicity

Hygroscopicity measurements were carried out for 50 and 100 nm (mobility diameter) particles at Langley and 30, 75 and 110 nm (mobility diameter) particles at Eagle Ridge. Compositional data were not available for 30 and 50 nm particles. Therefore, only data for the larger sizes will be discussed. Hygroscopic growth factors at the two sites ranged from 1.00 to 1.48 at 80±1% relative humidity. At Eagle Ridge, where hygroscopic growth was measured over a range of relative humidities, particles were observed to pickup small amounts of water at relative humidities as low as 50%. This phenomenon has been observed in a number of hTDMA studies and has been attributed to the presence of soluble organics (Dick et al., 2000). Humidification of near-monodispersed particles resulted in a single humidified mode or in a bimodal distribution with ‘less’ and ‘more’ hygroscopic modes. The presence of multi-modal humidified distributions is an indication of external mixing; this has been observed in a number of previous studies of atmospheric particles (for e.g. Pitchford and McMurry, 1994; Swietlicki et al., 1999; Cocker et al., 2001). At 80% RH, particles typically showed a single humidified mode. The frequency of bimodal humidified distribution increased with relative humidity above 80%. For example, at Langley, 43% of the measurements indicated bimodal distributions at 90% RH, while only 15% showed bimodal distributions at 80% RH. Our observations indicate that both internally and externally mixed particles were present at these sites. For the purpose of comparison with AMS data, growth factors for bimodal distributions were combined using the particle concentration in each peak.

Fig. 3 shows the measured growth factors at Eagle Ridge and Langley. Growth factors at the two sites were similar. A close look at these data reveals a time delay between observations at the two sites. This delay ranged from 1.5 h (27th August) to 5 h (30th August). Eagle Ridge would be expected to lag behind Langley if both sites were influenced by the same air mass, since Eagle Ridge is about 20 km to the northeast of Langley. No consistent diurnal patterns were observed for this period. Higher growth factors on the 27th, 30th and 31st of August correspond to increased sulphate volume fraction, as implied by the correlation shown in Fig. 4, and lower black carbon concentrations. Trajectory analysis (Boudries et al., 2004) showed that during these periods of higher growth factors, the air mass at the two sites was primarily impacted by SO2 sources from refineries located southwest of Langley in the state of Washington.

3.3. Correlation between growth factors and composition

The compositional volume fraction, rather than mass fraction, is required to relate particle hygroscopicity to composition. For this purpose, sulphate, nitrate and organic mass concentrations were converted to volumes, assuming the particles were fully neutralised. This is discussed in more detail in the following section on estimating growth factors. The volume fractions were compared with the measured growth factors. Comparing the sulphate fractions with hygroscopic growth factors resulted in linear correlation coefficients of 0.83 for 100 nm particles at Langley. At Eagle Ridge the correlation
Fig. 3. Growth factors at Langley and Eagle Ridge. Growth factors were measured at 80% relative humidity. Growth factors for the few bimodal humidified distributions were combined using the fraction of particles in each mode.

Fig. 4. Correlation of hygroscopic growth factors with sulphate volume fraction. Panel (a) shows correlation at Langley; the linear correlation coefficient was 0.83 (n = 68). Panel (b) shows correlation for 110 nm particles at Eagle Ridge, a linear correlation coefficient of 0.83 (n = 62) was obtained. Panel (c) shows correlation for 75 nm particles at Eagle Ridge, a linear correlation coefficient of 0.78 (n = 102) was obtained.
coefficients were 0.83 and 0.78 for 110 and 75 nm particles, respectively. Fig. 4 illustrates the results. All the correlations were found to be significant at confidence level of 99%. The correlation between the sulphate fraction and growth factor indicates that hygroscopicity at these sites was primarily driven by the sulphate fraction during this time period. The linear correlation between growth factors and the combined fraction of sulphate and nitrate was weaker for both Langley (R = 0.81) and Eagle Ridge (R = 0.72 and R = 0.58 for 110 and 75 nm, respectively).

The nitrate fraction alone indicates no significant correlation with particle water uptake even at a confidence level of 90%. The linear correlation coefficient between nitrate fraction and growth factors was −0.09 at Langley. At Eagle Ridge, the coefficients were 0.20 and −0.05 for 110 and 75 nm particles, respectively. This poor correlation may be an artefact resulting from the fact that the small increase in nitrate occurred simultaneously with a large increase in organic fraction; thus, any influence of nitrate may have been masked.

4. Estimating growth factor from particle composition

The AMS compositional measurements provided good time resolution and the ability to select a size range that includes the size selected by the hTDMAs. The AMS measures the vacuum-aerodynamic size of particles, while the hTDMA uses mobility diameter to select size. The particle effective density relates the two diameters (Jimenez et al., 2003a). For spherical particles, with the dynamic shape factor of unity, the effective density is equal to the density of the particle material. Since particle composition and therefore density was found to vary only slowly, it is reasonable to assume a constant density over any sample period. AMS data corresponding to the mobility diameter range of 67–107 nm were used to determine the volume fractions contributed by sulphate, nitrate and organics. As discussed earlier particles at both sites were fully neutralised. As a result, ammonium sulphate and ammonium nitrate were chosen to represent the sulphate and nitrate fraction. Nitrate and sulphate mass concentrations were converted to dry volume concentrations using densities of 1.725 and 1.769 g cm⁻³, respectively, for ammonium nitrate and ammonium sulphate. A density of 1.4 g cm⁻³ (Dick et al., 2000) was used to convert organic mass to volume; this density is equivalent to the density of water-soluble organics such as glutaric and adipic acid. Due to the large organic mass contribution and the small contribution of the organics to the overall growth factor, the density of the organic fraction was not found to significantly affect the results. A 30% change in the density produced a 2% change in the estimated growth factors.

Using particle composition data, predicted growth factors were calculated and compared with measurements for both hTDMAs. A number of studies have used various forms of the ZSR empirical mixing rule (Stokes and Robinson, 1966) to estimate hygroscopic growth factors of internally mixed particles (Cruz and Pandis, 2000; Dick et al., 2000; Choi and Chan, 2002; Prenni et al., 2003; Wise et al., 2003). These studies have found the ZSR method to provide a good approximation. As illustrated in Eq. (1), this method assumes that at a specific relative humidity the total water content of a mixed particle is equal to the sum of the water contents of the individual components in their pure forms

\[ GF_{\text{est}} = (\varepsilon_s GF_s^3 + \varepsilon_o GF_o^3 + \varepsilon_b GF_b^3)^{1/3}. \]

(1)

\[ GF_{\text{est}} \] is the estimated growth factor, \( GF_s \), \( GF_o \), and \( GF_b \) are growth factors for ammonium sulphate, ammonium nitrate, organics and black carbon. \( \varepsilon_i \) is the volume fraction for species \( i \). To use Eq. (1), the growth factor of each component must first be determined. Eq. (2) was used to calculate growth factors of the inorganic components

\[ GF_{\text{inorg}} = \left( \frac{\rho_{\text{dry}}}{w_{\text{sol}}} \right)^{1/3}. \]

(2)

\( \rho_{\text{dry}} \) is the density of the dry particle, \( \rho_{\text{sol}} \) is the density of the solution and \( w \) is the solute weight percent. Solute weight percent and solution density at various water activities were calculated using the relationship determined by Tang and Munkelwitz (1994). At 80% relative humidity \( GF_s \) and \( GF_o \) were calculated to be 1.46 and 1.48, respectively. The organic fraction of atmospheric particles was likely composed of a number of different organic species, with different hygroscopic properties. For ambient particles, assigning hygroscopic behaviour to the organic fraction can be difficult, due to the lack of data on the individual organic species and their hygroscopic properties. As one approach to
this problem, the growth factor of the 'less' hygroscopic particles was used to estimate the average growth due to the organic fraction, since these particles appear to be almost entirely organic. Akilulu and Mozurkewich (2004) discuss the justification of this approach in more detail.

As noted above, bimodal distributions were observed at both Langley and Eagle Ridge when the near-monodisperse aerosol was humidified. During these times, sampled particles were externally mixed and were comprised of a 'less' hygroscopic fraction and a 'more' hygroscopic fraction. The 'less' hygroscopic particles had average growth factor at 80% relative humidity of 1.06 (±0.04) and 1.07 (±0.04) at Langley and Eagle Ridge. The values given in the brackets are 1 standard deviation. These growth factor are comparable to that previously observed for organic particles (Virkkula et al., 1999; Peng et al., 2001) and is typical of particles sampled at a forested site (Golden Ears Provincial Park, British Columbia) (Shantz et al., 2004) as well as for particles observed during a rainy period at Eagle Ridge (Akilulu and Mozurkewich, 2004). Using the values of 1.06 and 1.07 as GF₀ at 80% relative humidity, GFₑₑ was calculated using Eq. (1). This provided an initial comparison with the measured growth factors.

To test the impact of including black carbon when estimating growth factors; calculations were done both excluding (Kₑₑ = 0) and including black carbon. For the latter, black carbon fractions were estimated as described in Section 3.1. The estimated black carbon mass concentration was converted to dry volume using the density of 1.6 g cm⁻³. The black carbon fraction was assumed to be non-hygroscopic (GFₑₑ = 1)

The measured and calculated growth factors are compared in Fig. 5. The predicted values over-estimate particle hygroscopicity by up to 36% with Kₑₑ = 0 and up to 32% when black carbon was included. Including black carbon improved the results by only 1% on average. The most likely explanations for these over-predictions of growth factors are that GF₀ may be less than the estimated value and that the ZSR mixing rule may not always be valid. The correlation was better at Langley than at Eagle Ridge; this suggests that some of the deviations might be due to nitrate, which had smaller volume fractions at Langley.

To explore the possibility that GF₀ might be lower than assumed, we used the measured growth factors and Eq. (1) to solve for GF₀. At Eagle Ridge, this gave very low values of GF₀ (<0.8), between 19:50 and 23:50 on 29th August. At this time increasing nitrate volume fraction was observed at Eagle Ridge, reaching 0.47 by 21:00. Values of GF₀ less than unity indicate that water uptake by the particles was less than expected for the inorganic fraction. We believe that low values of GF₀ may have been due to interaction between the different components of the particles. Such an interaction could result in reduction of inorganic growth factors so that the ZSR equation may not be valid. Saxena et al. (1995) found lower than expected water uptake for urban influenced particles containing significant nitrate and chloride contributions. Chan and Chan (2003), using laboratory-generated particles found interaction between the organic fraction and sodium chloride that resulted in lower than predicted water uptake. However, such interaction was largely not found between organics and ammonium sulphate. Thus, it appears that during this period, the organics may have reduced water uptake by NH₄NO₃. Another possibility is that some of the nitrate may have been in the form of organic nitrates, but there is no other evidence in support of this.

Outside of this period, variation in GF₀ was not apparent for the 75 nm particles at Eagle Ridge. For the particles at Langley and the 110 nm particles at Eagle Ridge, higher organic growth factors were observed prior to 12:00 28th August (see Table 1). A few data points that gave GF₀ less than 0.95 were removed; most of these data points occurred in the latter part of the study (period 2 in Table 1) when GF₀ were generally lower. Between these two sample periods, there appears to have been a change in the water uptake by organic compounds in the particles. Higher GF₀ were observed during the segment of the study when the measured growth factors were higher (Fig. 3) and the air mass was primarily impacted by SO₂ sources (Boudries et al., 2004). Thus, it is likely that the aerosol composition at these times was dominated by secondary particulate matter. During periods of lower GF₀, the air mass was impacted by urban emissions from the city of Vancouver (Boudries et al., 2004) and likely contained particles that had undergone less processing.

5. Conclusions

Particles in the mobility diameter range 67–107 nm were predominantly organic at both
Fig. 5. Estimated and measured growth factor for 80% relative humidity at Langley and Eagle Ridge. Panel (a) shows results for 100 nm particles at Langley. Panel (b) and (c) show results for 110 and 75 nm at Eagle Ridge, respectively. The correlation coefficient $R$ was 0.83 ($n = 68$) at Langley. At Eagle Ridge the coefficient were 0.74 ($n = 62$) for 110 nm and 0.66 ($n = 101$) for 76 nm.

### Table 1

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Langley and Eagle Ridge. Average sulphate mass concentrations at the two sites were comparable, while nitrate and organic mass were higher at Eagle Ridge. Linear correlation between MOUDI and AMS measurement showed the total sulphate fraction to be inorganic. However, nitrate mass measured by the MOUDI was lower than that measured by the AMS; this was especially true at Eagle Ridge. The discrepancy between the two types of measurements in the lower particle size range may be due to volatilisation of ammonium nitrate from the MOUDI filters.
Despite the differences in particle composition, hygroscopic growth factors at the two sites were found to be similar. This is in agreement with other studies that found air processing in the Lower Fraser Valley to be dominated by regional rather than local events. Measured growth factors at the two sites correlated well with particle sulphate, indicating that this fraction played the dominant role in particle hygroscopicity. The correlation of the growth factor with the nitrate fraction was not significant.

Growth factors were calculated using AMS composition data and the ZSR mixing rule. In these calculations the average growth due to the organic fraction was estimated from the less hygroscopic particles. Generally good agreement between measured and calculated growth factors was obtained when the aerosol consisted almost entirely of sulphate and organics. These calculations assumed that the sulphate was ammonium sulphate and that the organic density was 1.4 g cm\(^{-3}\); the results were not sensitive to these assumptions. Agreement was somewhat better when the fraction of black carbon at the sampled size was assumed to be the same for fine particles as a whole; however, the effect of including black carbon was very small, changing the growth factor on average by about 1%.

Some of the scatter in the data may be attributed to temporal variation of the growth factor of the organic fraction. To test this, the growth factor of the organic fraction was allowed to vary with time in order to force the calculated and measured growth factors to agree. The resulting variations in the growth factor of the organic fraction were small but significant. Trajectory analysis showed that when higher organic growth factors were observed, the air mass was impacted mainly by SO\(_2\) sources; the particle organic matter at these times was likely to be secondary particulate matter. Lower organic growth factors were observed when the air mass was impacted by urban emissions form the city of Vancouver; at these times a larger fraction of the particulate organic matter was probably primary emissions. Greater hygroscopicity for secondary organics is consistent with the results of several recent AMS studies that have shown that secondary organics have a higher degree of oxidation than primary organics (Alfarra et al., 2004; Takami et al., 2005; Zhang et al., 2005; Maheswar et al., 2005).

When the nitrate fraction was high, agreement between calculated and measured growth factors was poor unless it was assumed that the nitrate takes up much less water than ammonium nitrate. The cause may be the failure of the ZSR approximation in this case. Although the ZSR approximation has been shown to be good for sulphate/organic mixtures, it is known to fail for some salt/organic mixtures. To our knowledge there are no data for mixtures of ammonium nitrate and organic compounds.

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