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Chemical and physical processes controlling the distribution of aerosols in the Lower Fraser Valley, Canada, during the Pacific 2001 field campaign

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Abstract

High-resolution size-resolved mass concentration of organic and inorganic species present in/on sub-micron particles measured during the PACIFIC 2001 field study in the Lower Fraser Valley (LFV) are presented. The measurements of major particulate species (organics, sulfate, nitrate and ammonium) were made in situ and in real time at three different sites representing urban (Slocan Park), semi-rural (Sumas) and rural (Langley) areas, using two Aerodyne aerosol mass spectrometers (AMSs). The total non-refractory $PM_{1.0}$ mass concentrations at the three sites were found to range from 0.12 to 24.50 $\mu g\,m^{-3}$, with an average concentration of 4.76 $\mu g\,m^{-3}$. A large variability in aerosol composition was observed in the LFV, depending on meteorological conditions. Generally, during southwesterly wind conditions, inorganic species accounted for 50% of total mass loadings in the LFV, while during stagnant conditions organic species made up the majority of the particle mass. The organic aerosol species exhibit a bimodal size distribution, while the inorganic species are in most cases confined to the accumulation mode centered around 400 nm. Background sulfate levels of $\sim 1\,\mu g\,m^{-3}$ were observed in the LFV during the entire campaign. Transport is found to be an important factor controlling the composition of sulfate in the LFV. Several photochemical events leading to the observation of substantial increases of sulfate in the LFV were also identified. Many of these events involve sulfate-dominated growth of small particles and appear to occur on a regional scale within the LFV.

Keywords: Aerodyne aerosol mass spectrometer; Primary aerosol; Secondary aerosol; Lower Fraser Valley; Organic aerosol; Inorganic aerosol; Back trajectories; Transport

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1. Introduction

In the summer of 2001, the PACIFIC 2001 field study was carried out in the Lower Fraser Valley (LFV), Vancouver, Canada to improve our understanding of fine particulates and ozone in that area, including the horizontal and vertical distribution and physical and chemical characteristics of fine particulate matter (PM), the major physical and chemical processes in the formation of secondary aerosols and ozone, and the roles of biogenic and transportation sector emissions. High ozone levels, as well as poor visibility and possible health effects due to elevated fine particles in the area, have triggered a concern by environmental health authorities to investigate and determine concrete effective control strategies for reducing photochemical smog in the LFV (Brauer and Brook, 1997). It is now well established that fine PM has a direct impact on visibility and can impact regional climate as a result of its light-scattering, light-absorbing, and cloud-modification properties (Baumgardner et al., 2002). Several other studies show a direct link between fine particles and human health effects (Donaldson et al., 1998). Atmospheric PM is either emitted directly from a primary source or produced as secondary condensable products by the oxidation of some volatile inorganic or organic species (Brown et al., 2002). In the summer of 1993, the PACIFIC '93 field experiment was carried out in the LFV to enhance our knowledge of the physical and chemical processes important in the formation of ground level ozone (Steyn et al., 1997). However, limited measurements of PM were made during this study to provide insight into the composition, size distribution and vertical profiles of PM (Hoff et al., 1997; Pryor et al., 1997; Pryor and Barthelmie, 2000).

In this paper, we present results from an aerosol mass spectrometer (AMS), which provides the chemically speciated mass loadings and size distributions for ambient aerosol measured in situ and in real time at three different sites representing urban, semi-rural and rural areas. The measurements were made as part of the PACIFIC 2001 field campaign from 11 August to 01 September 2001. This paper compares the physical and chemical properties of aerosols measured at three sites and uses this information together with meteorological back-trajectory analysis to determine the impact of various local sources (anthropogenic, agricultural and oceanic) and atmospheric transport on the aerosols observed in the LFV. In the companion paper (Alfarra et al., 2004), a detailed analysis of the physical and chemical properties of the aerosols is presented.

2. Experimental

2.1. Sampling locations

Three major sampling sites, Slocan Park (representing an urban setting and located about 15 km from downtown Vancouver), Langley (representing rural setting), and Sumas (representing semi-rural setting), as well as intensive airborne measurements (Li, 2004; Snyder and Strawbridge, 2004) were used in order to better characterize the vertical distribution of PM2.5 and other pollutants in the LFV. A more detailed description of all sites is given by Li (2004). At all sites, the PMs were sampled at 6 m above the ground through an insulated copper tube (1/2±″ o.d., 8 m long) and a standard PM2.5 cyclone (URG-200-30EN, URG, USA) at a flow rate of about $10\,\mathrm{l\,min^{-1}}$. The first AMS was installed at Slocan Park from 11 August to 24 August 2001, and then re-deployed to Sumas site from 25 August to 01 September 2001. A second AMS was deployed at the Langley site from 11 August to 01 September 2001.

2.2. Aerosol sampling and analysis

Chemically classified and size-resolved mass loadings of sub-micron aerosol were measured in situ and in real time using an AMS developed at Aerodyne Research, Inc. (Billerica, MA, USA). The AMS measures both the mass concentrations of chemical species and the vacuum aerodynamic size (D_{va}) of aerosol that are sampled into the AMS at a flow rate of $0.1\,\mathrm{l\,min^{-1}}$ and focused with an aerodynamic lens (Zhang et al., 2002). The focused particle beam exiting the lens is directed toward a heated tungsten surface (vaporizer) maintained at a temperature of about 550 °C. Chemical components of particles that impact the surface are flash vaporized and the resulting vapor plume ionized at standard 70 eV electron impact and analyzed using a quadrupole mass spectrometer (Balzers, QMA410, Liechtenstein). The vaporized species analyzed by the AMS are referred to as non-refractory (NR), and are defined as all chemical components that vaporize (within a second) at the vaporizer temperature of ~550 °C. This includes most atmospheric aerosol composition (for example, most organic carbon and inorganics such as NH_4NO_3 and $(NH_4)_nSO_4$), with the major exception of crustal oxides, and elemental carbon. At the 550 °C temperature, there is also limited sensitivity to many inorganics such as seasalt. The AMS measures the vacuum aerodynamic diameter (D_{va}) of the particles and is defined as

$$D_{\mathrm{va}} = \sqrt{\frac{\rho}{\chi\rho_0}}\,D_{\mathrm{a}},$$

where ρ is the particle material density, ρ_0 is unit density ($1\,\mathrm{g\,cm^{-3}}$), χ is the dynamic shape factor that accounts for particle asphericity and D_{a} is the classical aerodynamic diameter. The transmission of the AMS aerosol sampling system corresponds to a size cut of about $PM_{1.0}$, based on D_{va} sizing. Note that for spherical particles, $D_{\mathrm{va}} = \sqrt{\rho} \times D_{\mathrm{a}}$ (where D is the geometric diameter).

Quantitative mass calibration of the instrument was performed by using a pure monodisperse ammonium nitrate aerosol source. Particles were generated with an atomizer (TSI, Model 3076, USA) and then dried ($<20\%$ RH) by passing the airflow through a silica gel. The monodisperse aerosol was generated by passing the polydisperse flow exiting the dryer into a differential mobility analyzer (TSI, Model 3071, USA). A detailed discussion of the quantitative mass calibration procedure is presented in the companion paper (Alfarra et al., 2004). The long-term stability of the instrument was followed during the field campaign by multiple quantitative calibrations and electron multiplier calibrations. The velocity calibration of the AMS was performed by using a certified polystyrene nanosphere (Duke Scientific Corporation, CA, USA), with a hydrodynamic diameter in the range of 40–1300 nm. The transmission efficiency of particles in the $D_{\mathrm{va}} = 60-600\,\mathrm{nm}$ size range is nearly 100% (Zhang et al., 2002). A particle collection efficiency (CE) is used to correct for particles that do not reach the vaporizer (see companion paper, Alfarra et al., 2004). This CE accounts for $<100\%$ transmission of particles smaller and larger than 60 and 600 nm, respectively, and for reduced focusing of aspherical particles. A CE of 1 was used at Langley and a CE of 0.5 was used at Slocan and Sumas. A detailed discussion about the CE used during PACIFIC 2001 is present in the companion paper (Alfarra et al., 2004).

In the AMS, the uncertainty in the measurement is due to the counting statistics of the individual ions, the uncertainty in the response of the electron multiplier to individual ions, the uncertainty in the ionization efficiency, and the uncertainty in the CE. The overall analytical uncertainty for mass loading measurement was estimated by propagating the various uncertainties through the calculation of the concentration, and was found typically in the range of 30%. The detection limit of the system is calculated automatically for all data via AMS data analysis software (Allan et al., 2003a) and is estimated at three times the standard deviation of the blank (no particle sampling). During PACIFIC 2001 experiment, the sensitivity is estimated to be $0.02\,\mu\mathrm{g\,m^{-3}}$ for sulfate, nitrate and ammonium, and $0.05\,\mu\mathrm{g\,m^{-3}}$ for organics during 15 min sampling time.

In this paper, we report the measured size distributions and mass loadings in $\mu\mathrm{g\,m^{-3}}$ for $\mathrm{PM_{1.0}}$ for four major species: NR organics, sulfate, nitrate and ammonium.

2.3. Air mass trajectory analysis

In order to better characterize the origin of air masses that reach the LFV, we have used air mass back-trajectory analysis to identify the various types of air transport situations and potential source regions impacting the Slocan Park, Langley, and Sumas sites. Three-dimensional 5-day back trajectories reaching the sites at different heights (250, 500 and 1000 m) at each hour were calculated to identify the origin of the air masses, except at Sumas site, where the initial arrival height was set to 350 m. The back trajectories were calculated by using the HYSPLIT4 (Hybrid Single Particle Lagrangian Integrated Trajectories) model together with the Eta Data Assimilation System (EDAS) data for input of the wind field. More information about this model is available at the National Oceanic and Atmospheric Administration, USA (NOAA) website (www.arl.noaa.gov).

3. Results and discussion

3.1. Aerosol composition and size distribution in the LFV

As previously mentioned, the chemical and size-resolved distributions of NR, fine particulate ($\sim\mathrm{PM_{1.0}}$) organics, sulfate, nitrate and ammonium components are reported and discussed in this paper. Fig. 1 shows the time series profile of mass loadings of organics, sulfate, nitrate and ammonium measured at the Slocan Park, Langley and Sumas sites during the PACIFIC 2001 campaign. The sampling frequency was set at 15 min integration time at both Langley and Slocan Park and 5 min integration time at the Sumas site. The average mass loading observed at each site is summarized in Tables 1 and 2. The relative mass contribution of each aerosol species with respect to the summed mass of all four species is also shown in the table. The size distribution time trends ($\mathrm{d}M/\mathrm{d}\log(D_{\mathrm{va}})$), measured by the AMS for NR organic-, nitrate-, ammonium- and sulfate-containing aerosols are presented in Figs. 2a–d. In the sections that follow, the variability in the measured aerosol chemical and physical properties is used together with back-trajectory analysis in order to characterize the aerosol sources, secondary formation, and transport processes that impact each site and the overall LFV.

3.1.1. Slocan Park site

Fig. 3 shows the time series profiles of the total NR mass loadings, ambient temperature, dew point, wind speed and wind direction measured at the Slocan site during the PACIFIC 2001 campaign. It can be seen from Fig. 3 that the site was mostly influenced by moderate southerly wind during the daytime and by low easterly wind during the night and early morning. Also, ambient temperature exhibits a clear diurnal pattern before 21 August, with a maximum during the day averaging 23 °C, and a minimum during the night averaging 15 °C. The dew point also shows a diurnal pattern, varying between 11 °C and 15 °C, with the maximum observed

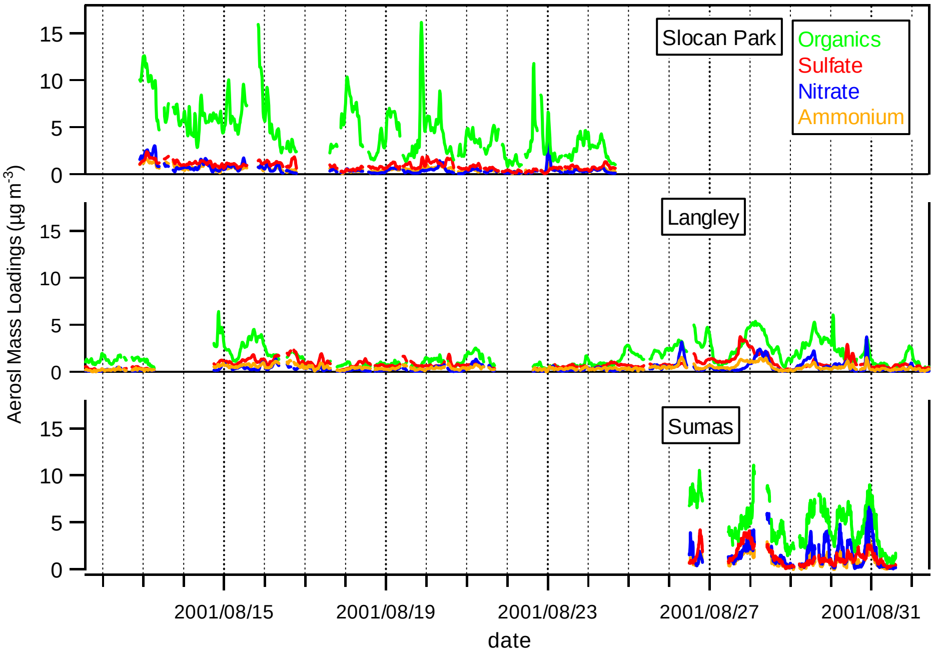

Fig. 1. Particle mass loadings of organics, sulfate, nitrate and ammonium measured at Slocan Park, Sumas and Langley sites during PACIFIC 2002 field campaign.

Table 1
Average mass loadings and standard deviations of organics, sulfate, ammonium and nitrate measured during PACIFIC 2001, in Vancouver, Canada at Langley and Slocan Park from 11 to 24 August 2001

Particulate species	Langley		Slocan Park	
	Data range min–max	Average ($\pm 1\sigma$) $\mu g\,m^{-3}$	Data range min–max	Average ($\pm 1\sigma$) $\mu g\,m^{-3}$
Organics	d.l.–9.26	1.27 (0.97)	0.79–16.13	4.62 (2.69)
Sulfate	d.l.–2.81	0.74 (0.45)	0.05–2.38	0.88 (0.41)
Ammonium	d.l.–1.69	0.41 (0.28)	0.01–1.63	0.53 (0.28)
Nitrate	d.l.–1.51	0.29 (0.25)	0.05–3.65	0.56 (0.52)

Table 2
Average mass loadings and standard deviations of organics, sulfate, ammonium and nitrate measured during PACIFIC 2001, in Vancouver, Canada at Langley and Sumas from 26 to 31 August 2001

Particulate species	Langley		Sumas	
	Data range min–max	Average ($\pm 1\sigma$) $\mu g\,m^{-3}$	Data range min–max	Average ($\pm 1\sigma$) $\mu g\,m^{-3}$
Organics	0.01.–10.71	2.26 (1.43)	d.l.–15.31	4.74 (2.29)
Sulfate	0.12–3.92	0.98 (0.72)	d.l.–4.53	1.29 (0.94)
Ammonium	d.l.–1.93	0.51 (0.37)	d.l.–4.43	0.92 (0.75)
Nitrate	0.01–5.05	0.59 (0.67)	d.l.–9.06	1.62 (1.55)

during the day and minimum during the night. Rain showers and cloudy skies were frequent between 21 and 24 August 2001.

Although events with increased total aerosol concentration were observed throughout the measurement time period at Slocan, there was a significant difference in the background aerosol loading measured between the time periods marked as A and B in Fig. 3. Time period A was characterized by higher aerosol loadings of approximately 8.05 $\mu g\,m^{-3}$, while B was characterized by lower loadings of 4.61 $\mu g\,m^{-3}$. The temperature and dewpoint traces also show that higher temperatures were experienced at Slocan during period A and significantly lower temperatures approaching the dewpoint were observed during period B. While the local wind speed and direction do not provide a clear indication of a change in meteorological conditions between these two time periods, 5-day back trajectories arriving at Slocan Park every hour show a drastic change in air flow pattern between the first and the second periods.

Typical air flow trajectories presented in Fig. 4 show that high aerosol loadings of Period A were characterized by relatively stagnant northern air masses, which crossed straight through downtown Vancouver before

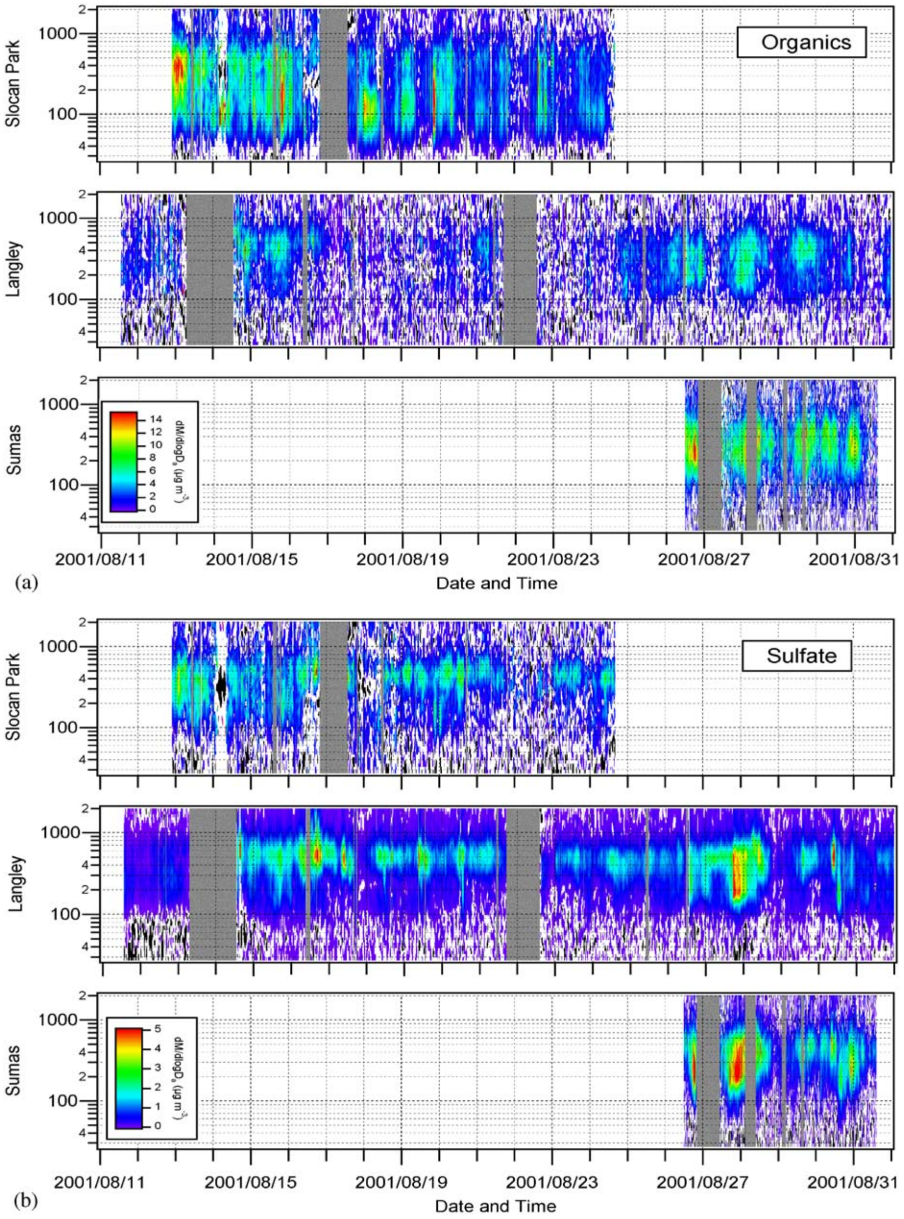

Fig. 2. Time-series size distribution at Slocan Park, Langley and Sumas during PACIFIC 2001. (a) Organics (top panel), (b) sulfate (bottom panel). Time-series size distribution at Slocan Park, Langley and Sumas during PACIFIC 2001. (c) Nitrate (top panel), (d) ammonium (bottom panel). The y scale represents D_{va} in nm.

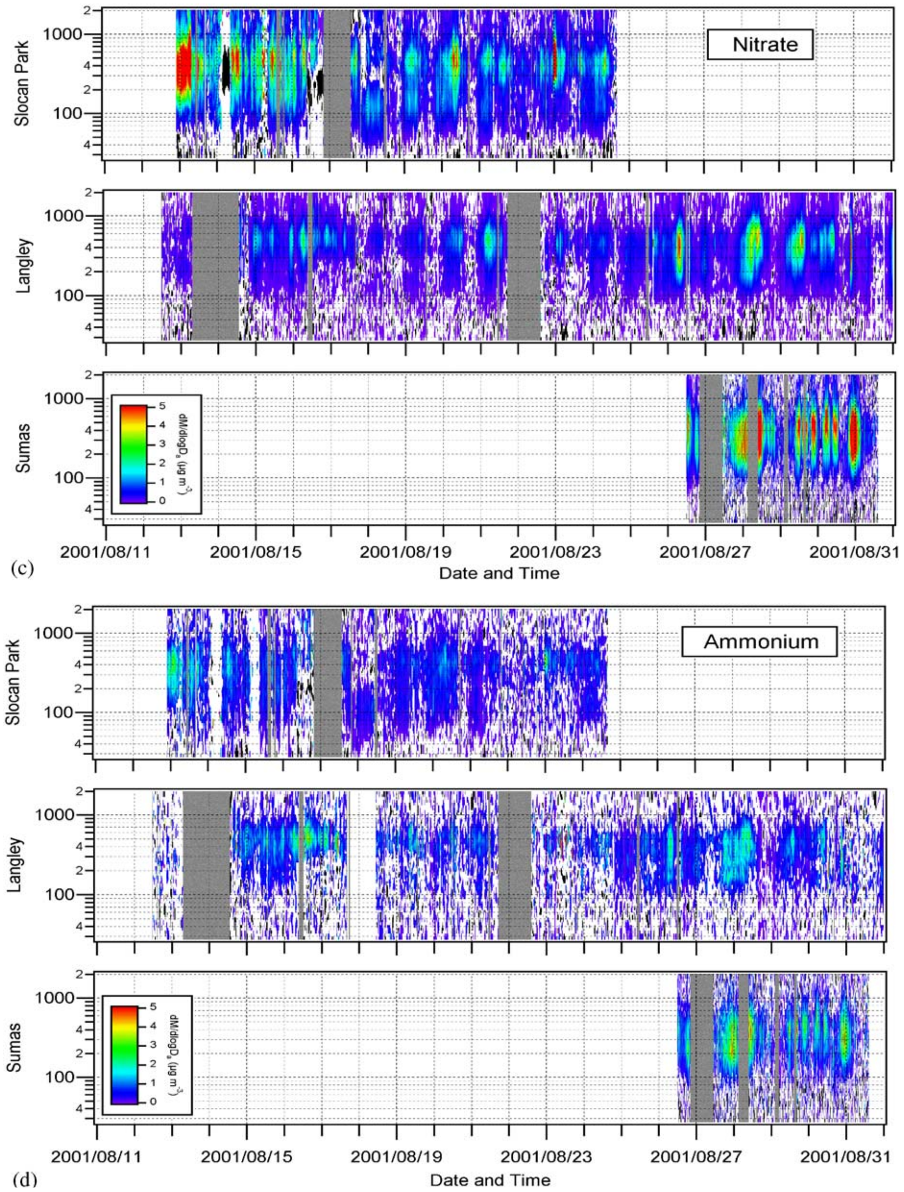

Fig. 2. (*Continued*)

reaching the sampling site. In contrast, an inflow bringing cleaner southeast air originating in the Pacific Ocean with less impact from Vancouver city prevailed during the period of low aerosol loading. These trajectories are in agreement with the air flow analysis presented by Snyder and Strawbridge (2004). The shift of air masses, together with the cooler temperatures and cloudy, rainy weather that accompanied it, could explain the low mass concentrations measured during the second period.

As shown in Fig. 1, the highest aerosol NR organic mass loadings observed during this campaign occurred during period A in Slocan Park. The organic loadings ranged from 1.36 to 15.92 $\mu g\, m^{-3}$, with an average concentration of 5.71 $\mu g\, m^{-3}$ and a standard deviation of 2.64 $\mu g\, m^{-3}$. During period B, the organic loadings ranged from 0.79 to 11.77 $\mu g\, m^{-3}$, with an average concentration of 3.11 $\mu g\, m^{-3}$ and a standard deviation of 1.65 $\mu g\, m^{-3}$. These concentrations compare well with observed values for urban areas (Fraser et al., 2002), but remain significantly lower than maximum $PM_{2.5}$ organic concentrations of 33.7 $\mu g\, m^{-3}$ measured during severe photochemical smog episodes in downtown Los Angeles (Schauer et al., 2002). Despite the distinct differences in

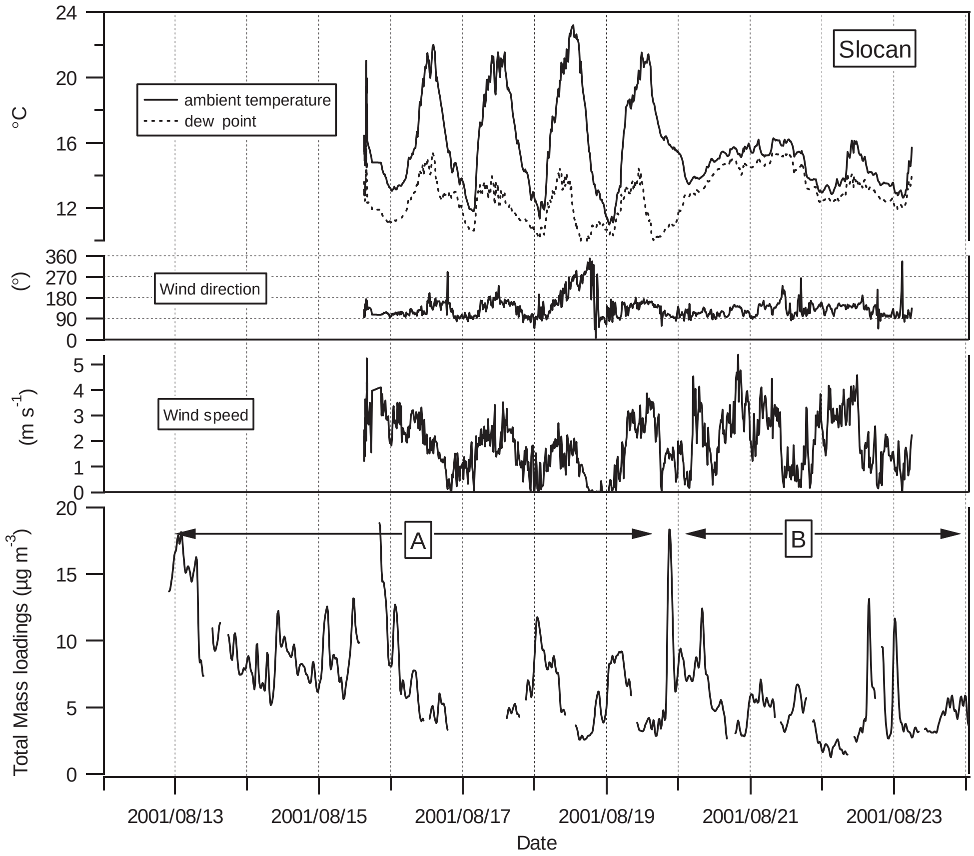

Fig. 3. Total particle NR mass loadings together with local meteorological data measured at Slocan Park site.

observed total aerosol loading and meteorology, the relative composition of the sampled aerosol did not differ greatly between periods A and B. During period A, when the air masses reaching Slocan had a larger impact from the city of Vancouver, the average aerosol composition was dominated by organic species (71% of average aerosol NR mass) with sulfate and ammonium, accounting for approximately 20% of the mass. During period B, organics, sulfate and ammonium accounted for 67%, 15%, and 9% of the NR mass, respectively. Nitrate accounted for about 9% of the mass during both time periods.

Fig. 5 shows the average size distribution of organics, sulfate and nitrate during periods A and B at Slocan. Although the absolute concentration of all species is higher in period A, the relative shapes of the size distribution are very similar during both periods. The variations of these average size distributions with time can also be seen in Figs. 2a–d. A clear bimodal distribution of organics peaking at 110 and 400 nm was observed during both periods at Slocan Park. Such a bimodal distribution is typical for organics in urban areas (Allan et al., 2003b; Jimenez et al., 2003; Drewnick et al., 2004). Previous AMS field studies from laboratory flame sources, motor vehicle sources, and ambient aerosol field experiments point to the difference between fresh primary organic particles and aged primary and secondary organic particles (Allan et al., 2003b; Canagaratna et al., 2004). These studies show that in many urban environments the small organic mode is dominated by almost purely organic aerosol, mostly from local mobile vehicle sources, while the larger mode is partially composed of regional, photochemically processed (oxidized) organic aerosol. A detailed analysis of the mass spectra and size distributions obtained at Langley is consistent with this picture and suggests that the organic aerosol species measured at Langley during both periods have two main sources: local emissions in the urban area, and transport of photochemically aged regional aerosol (see Alfarra et al. (2004) for more details about this analysis).

Previous studies have also shown that the aged 400 nm oxidized organic mode is usually internally mixed with sulfate (Allan et al., 2003b; Jimenez et al., 2003; Drewnick et al., 2003). The sulfate distributions shown in both part A and part B of Fig. 5 are consistent with

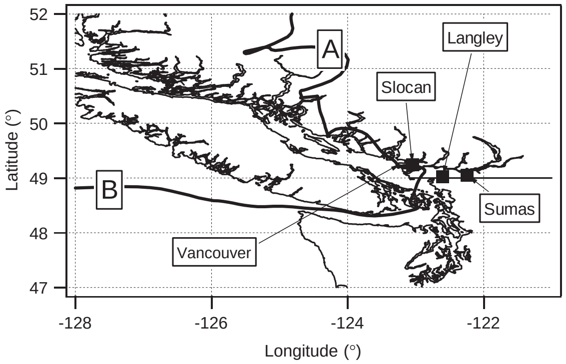

Fig. 4. Typical 5-day back trajectories arriving at Slocan site during high (period A) and low (period B) mass loadings.

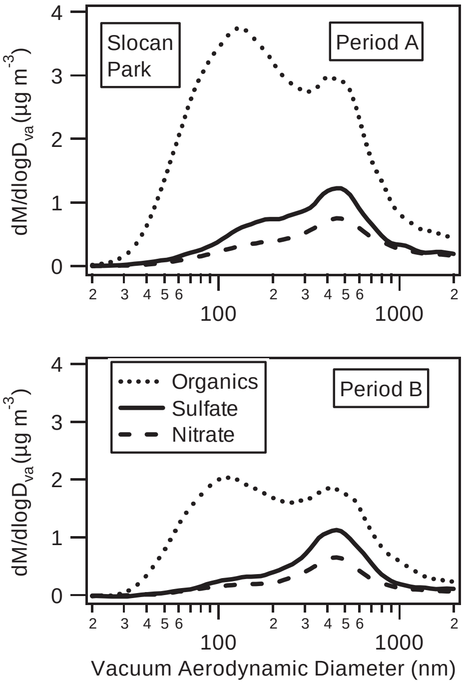

Fig. 5. Average mass distribution of organics, sulfate and nitrate measured at Slocan Park site during periods A and B.

this and indicate that most of the sulfate seen at Slocan Park is in this larger mode, likely due to aerosol aging processes. Local production of sulfate, as characterized by strong diurnal sulfate events peaking in the afternoon, does not appear to have a strong impact at Slocan Park. However, we note that the sulfate distribution does contain a small mode centered around 200 nm during period A. Small (<250 nm) sulfate particles are generally associated with local photochemical production of sulfate (Zhang et al., 2004). The fact that the small sulfate mode is more intense in period A rather than period B indicates that the relatively stagnant, urban-influenced air masses during period A were more photochemically active and more conducive towards local production of sulfate. This is also true of ammonium and nitrate, as shown in Figs. 2c and d, where small particles containing both of these species were observed.

3.1.2. Langley site

Time series profiles of total NR mass loadings, ambient temperature, dew point, wind speed and wind direction measured at Langley are presented in Fig. 6. The entire period of the experiment was characterized by a moderate southerly wind not exceeding 3 m s^{-1}, and interrupted by light winds of variable directions mostly from the north. At night, wind speed dropped to almost zero and increased during the day to reach its maximum between 1 and 3 m s^{-1}. The air was very humid at Langley; the relative humidity was close to 100% during the night and early morning and decreased after sunrise to an average value of 60%. Between 21 and 24 August, there were frequent rain showers and clouds.

Langley differs from the Slocan site in that its inorganic composition accounted for about 50% of total mass loadings. The main components were organics (50%) and sulfate (25%), followed by ammonium (13%) and nitrate (12%). Sulfate concentrations measured at the Langley site were found in the range 0.09−3.91 μg m^{-3}, with an average of 0.82 μg m^{-3} and a standard deviation of 0.56 μg m^{-3}. As shown in Fig. 1, a diurnal variation of sulfate was observed at Langley site between 15 and 21 August, with a maximum during the day (10 a.m.–2 p.m.) and a minimum during the night (12–5 a.m.). The top panel of Fig. 7 shows that high levels of particulate sulfate were correlated with high levels of gas phase SO_2. This correlation may suggest that sulfate is being photochemically produced from SO_2 in the air mass that was advected to the site during the day. Very recently, Brock et al. (2002) show potential formation of new particulate sulfate through oxidation of SO_2 by OH within 2 h of emission from power plants. As shown in the bottom panel of Fig. 7, varying degrees of sulfate production are observed during these events. Back-trajectory analysis can be used to identify possible SO_2 sources for these and other sulfate events observed at the Langley site (this analysis is discussed in more detail in Section 3.2). Based on this analysis, the sulfate events observed at Langley appear to be related to SO_2 sources southwest of the site, e.g. the refineries at Bellingham in the state of Washington (USA). Fig. 7 also shows a background sulfate level at Langley of about 1 μg m^{-3}. This level compares very well with the background sulfate levels measured at Slocan Park and Sumas during the entire campaign.

Nitrate mass loadings present in/on $PM_{1.0}$ at Langley were in the range 0.03–5.05 μg m^{-3}, with an average

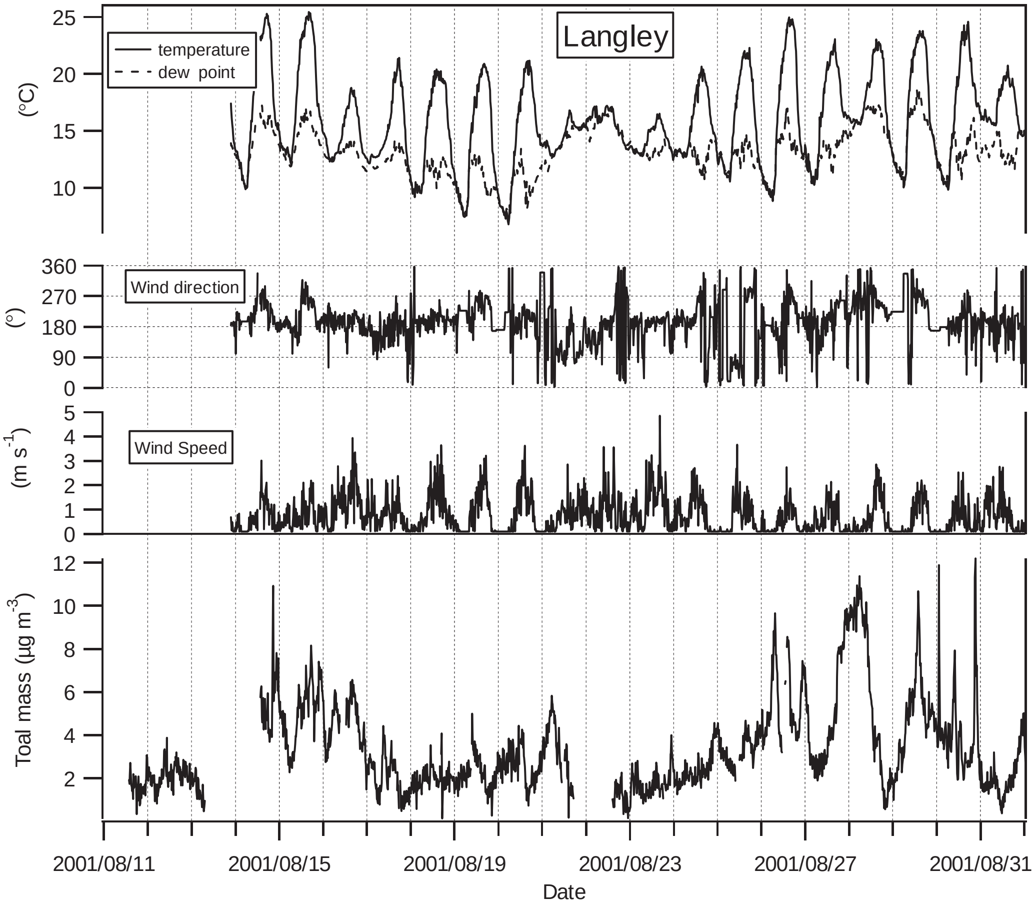

Fig. 6. Total particle NR mass loadings together with meteorological data measured at Langley site.

value of 0.39 $\mu g\,m^{-3}$, and a standard deviation of 0.46 $\mu g\,m^{-3}$. Nitrate also exhibits a clear diurnal pattern with a maximum early in the morning (8–10 a.m.) and minimum late in the afternoon (5–8 p.m.). Nitrate concentrations at Langley appear to be strongly influenced by ambient temperature and humidity. This effect on the formation of ammonium nitrate in atmospheric particles has been well studied (Seinfeld and Pandis, 1998). The higher aerosol nitrate levels at Langley, when compared with Slocan Park, are likely due to the fact that there is a correspondingly higher gas-phase ammonia concentration at Langley (Pryor et al., 2004), which is available to neutralize the sulfate and nitrate in the aerosol.

The total organic loadings at Langley did not show a good correlation in time with any of the aerosol inorganic species (sulfate ($R^2 = 0.27$), nitrate ($R^2 = 0.37$), ammonium ($R^2 = 0.40$)). The organic concentration varied between 0.05 and 10.71 $\mu g\,m^{-3}$, with an average of 1.65 $\mu g\,m^{-3}$ and a standard deviation of 1.22 $\mu g\,m^{-3}$. In addition to relatively low organic aerosol concentrations, the Langley site differed from Slocan because, rather than the bimodal organic size distributions observed at Slocan, the organic aerosols at Langley were clearly dominated by contributions from accumulation mode particles above 250 nm. This difference in size distributions between the two sites is clearly seen in Fig. 2. This indicates that the organic aerosol observed at Langley was mostly photochemically processed, regional aerosol, although primary organic aerosols may also have entered this mode due to coagulation. It is important to note, however, that back-trajectory analysis shows that the small mode organic aerosol contribution does increase at Langley during time periods (i.e. midnight, 28 August) when it is exposed to air masses that have been more directly influenced by the Vancouver urban center. This is likely the effect of relatively recent traffic emissions from the urban core being directly advected to the site.

Another feature of the Langley site is the variability of its aerosol composition. Fig. 8 shows three distinct periods (referred as C, D and E) with different aerosol

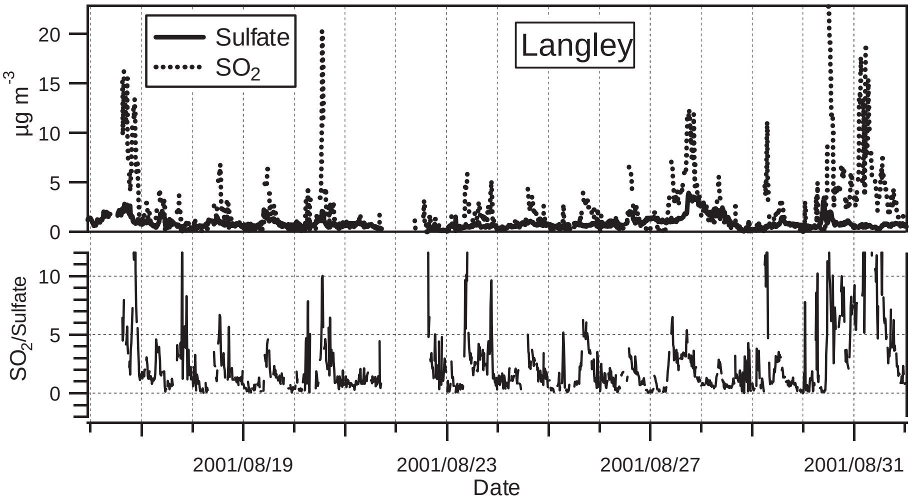

Fig. 7. Time series of pariculate sulfate and SO_2 measured at Langley site.

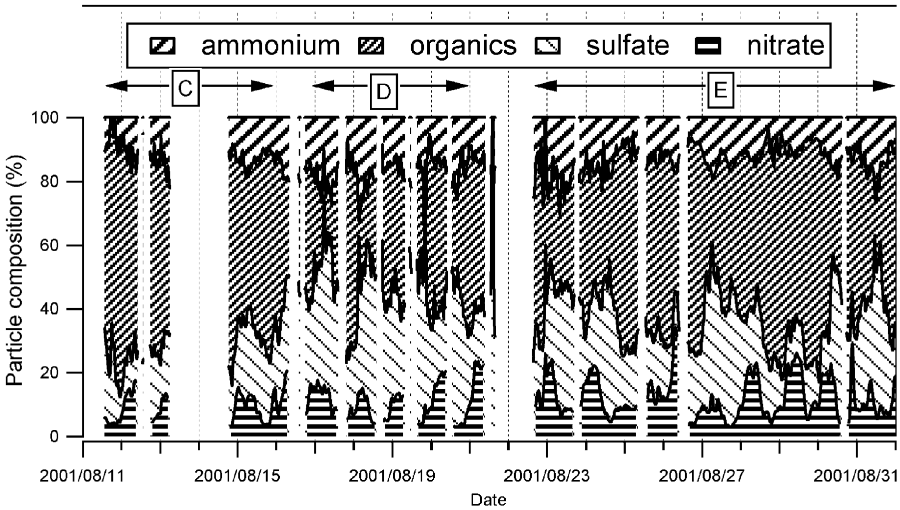

Fig. 8. Variation in particle composition of organics, sulfate, nitrate and ammonium measured at Langley site.

composition. Nitrate shows a clear diurnal cycle throughout all the periods, as discussed above. Period "C", from 11 to 16 August, shows a large contribution from organics, reaching over 75% of total NR $PM_{1.0}$ mass concentration. During period "D", from 16 to 20 August, sulfate became the primary component of aerosol, reaching 50% of total mass concentration. Finally, period "E" from 23 to 31 August, shows daily variation in the dominant aerosol species, alternating between organics, sulfate and nitrate dominance. Five-day back-trajectories arriving at Langley every hour also show three distinct patterns during these time periods. Fig. 9 shows typical Lagrangian 5-day back trajectories for each of these periods. During period C, back trajectories originating 5 days earlier north of Vancouver travel slowly along the northwest coastline and through the urban area in Vancouver before arriving to the LFV, creating a condition of stagnant air masses within the valley. A clear shift in air mass origin from the northwest to southwest is observed during period D, when oceanic air masses reach the Langley site directly from the southwest. The last period (E) has been referred to as an "unsettled" period during which there was stagnation and an alternation between air masses that pass through the Vancouver urban area (high organic aerosol content) and those that bypassed the urban area and arrived from the southwest direction of Langley (high sulfate aerosol content). This observation

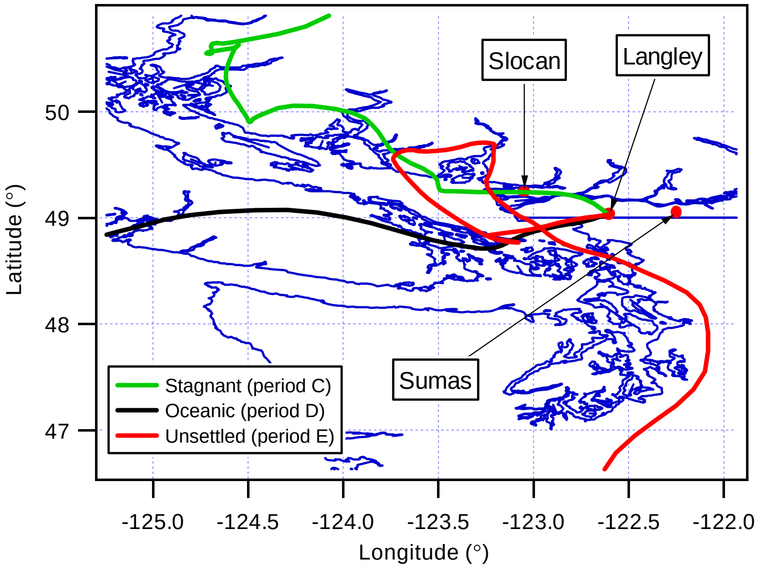

Fig. 9. Typical Langrangian 5-day back trajectories of air parcels arriving at Langley site every hour.

is consistent with the meteorological conditions outlined by Snyder and Strawbridge (2004), where three major weather patterns have been identified. This analysis demonstrates that air mass transport, determined by the meteorological conditions, played a major role affecting particulate mass loadings and composition in the LFV, in good agreement with Brook et al. (2004) analysis using Rapid Acquisition Scanning Aerosol Lidar (RASCAL) and AERosol Imaging Airborne Lidar (AERIAL) instruments for vertical and special characterization of airborne aerosols.

3.1.3. Sumas site

At the Sumas site, measurements were conducted for only 6 days (from 25 to 31 August 2001). The average composition at Sumas was quite similar to that measured at Slocan Park. The organic fraction represents about 56% of total mass loading, followed by nitrate (19), sulfate (15%), and ammonium (10%). The organic mass loadings were found in the range 0.05–15.31 $\mu g\,m^{-3}$, with an average value of 4.74 $\mu g\,m^{-3}$ and a standard deviation of 2.29 $\mu g\,m^{-3}$. The highest $PM_{1.0}$ nitrate concentration was measured at Sumas and was found in a range d.l.–9.06 $\mu g\,m^{-3}$, with an average concentration of 1.62 $\mu g\,m^{-3}$ and a standard deviation of 1.55 $\mu g\,m^{-3}$, exceeding the organic fraction in some cases, and representing about 40% of total fine PM loading. As shown in Fig. 1, all measured particulate species exhibit significant temporal variability.

The Sumas site is located on the top edge of a small mountain at 300 m above sea level and is surrounded by medium size towns (100k, inhabitants) with significant traffic activity. Variation of the height of the inversion layer could play an important role in the composition of aerosol at Sumas. This may explain the low mass loadings measured during the nights of 27, 29 and 30 August. During the day, strong convective air flow occurs after the break-up of the nocturnal boundary layer in the valley and local emissions mostly from vehicles were advected to the site through up-slope flow from the south (Snyder and Strawbridge, 2004). Thus, early morning and late afternoon increases in aerosol loadings, that were dominated by organic species, could be attributed to the rush hour traffic in nearby towns. Hayden et al. (2004) present clear evidence that this site was impacted by fresh vehicle emissions on a daily basis from early morning until noontime, when nocturnal inversion in the valley broke up.

As presented in Fig. 10, all measured inorganic species at Sumas show a similar size distribution peaking at 440 nm, suggesting most likely that the nitrate, sulfate and ammonium are internally mixed in the aged aerosol. The organic size distribution peak at the same diameter indicates that the organic aerosol at Sumas also consists mostly of aged transported aerosol. The presence of small-size particulate organics in a range of 50–150 nm, when taken together with a detailed analysis of the aerosol mass spectra, indicates that fresh particulate emissions, most likely from local sources located in urban areas surrounding Sumas, also impact this site.

3.2. Sources of PM in the LFV

Several particulate pollution events, with substantial increases in NR $PM_{1.0}$ mass loadings, were measured during this campaign, and in this discussion we focus on the correlation between events observed at the various sites. Fig. 11 shows the time trends of sulfate, organics, and nitrate aerosol species at both Langley and Sumas. It is clear from this figure that there is a high degree of correlation between the observations at both sites. This suggests that many of the aerosol events in the LFV occur on a regional scale.

Of particular interest within this context are the events observed on 26–31 August at the Langley and Sumas sites. On 27 August at about 6 p.m., the time series profile (Fig. 1) at Langley shows a substantial increase of sulfate from an average concentration of 2 to about 5 μg m^{-3} in less than 3 h. Approximately 3 h later, Sumas experiences a similar increase in sulfate concentration. Fig. 2b shows that the increase in sulfate concentration on 27 August is also accompanied by an increased appearance of small sulfate-containing particles at both sites. The growth of these small particles started around 3 p.m. on 27 August and lasted for about 9 h. These observations are in good agreement with the particle growth observed by Mozurkewich et al. (2004) at Sumas during the same period of time using a scanning mobility particle sizer (SMPS).

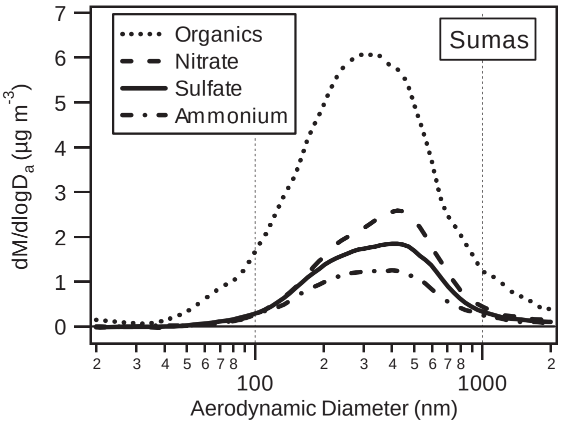

Fig. 10. Average mass distribution of organics, sulfate, nitrate and ammonium measured at Sumas site during the entire period of experiment.

Analysis of the variation in chemically speciated size distributions at Langley for three periods, representing before (period 1), during (period 2) and after (period 3) the initial growth phase of the 27 August event, is presented in Fig. 12. In period 1, the size distribution shows a mostly sulfate-dominated aerosol observed at both small and large diameters. During the initial growth (period 2), a significant increase in sulfate concentration was observed, with a large contribution from small particles below 250 nm representing about 43% of total sulfate. An increase in small organic particle mass is also observed during this time period, indicating that this particle growth event is dominated primarily by sulfate, with significant impact from organic species. The different size distributions observed during period 3 are due to changes in meteorological conditions, which are described in more detail below.

The similar observations at both Langley and Sumas during the 27 August event suggest that this particle

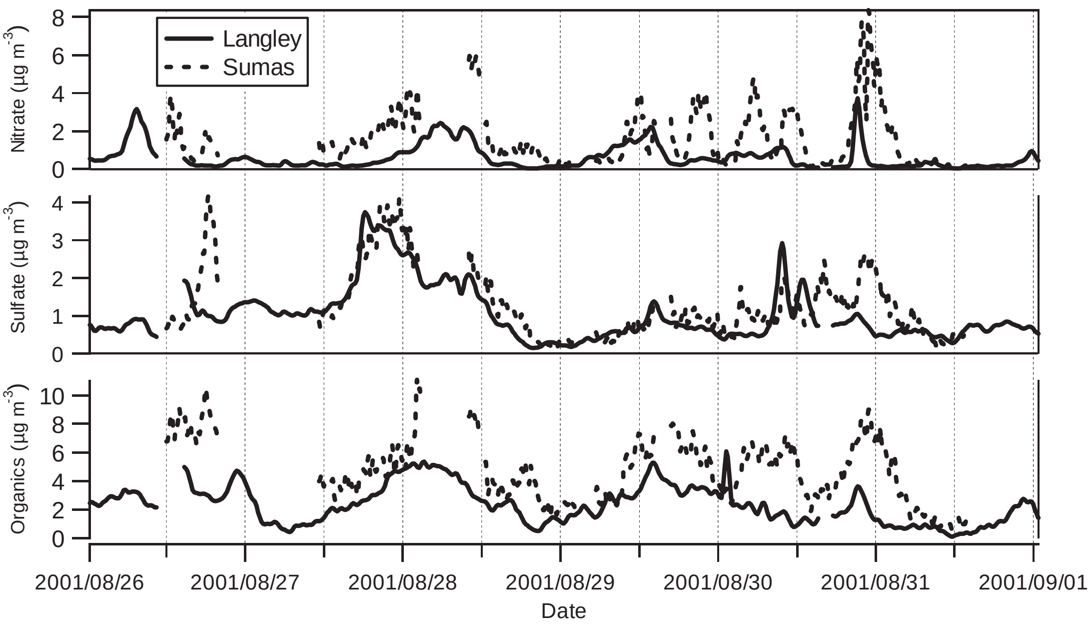

Fig. 11. Time series of organics, sulfate and nitrate at both Langely and Sumas.

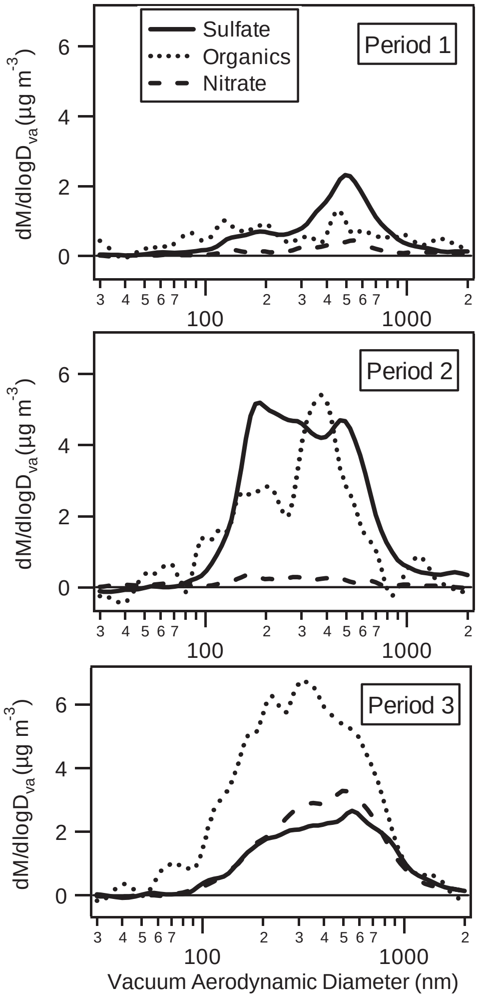

Fig. 12. Average mass distribution of organics, sulfate, nitrate and ammonium measured at Langley site during periods 1 (before sulfate event), (during sulfate event) and 3 (after sulfate event).

growth event occurs throughout the valley. Back trajectories arriving at Sumas and Langley every hour on 27 August indicate that both sites were influenced by the same air mass arriving first at Langley and then a few hours later at Sumas (Fig. 13). Hoff et al. (1997) pointed out during the PACIFIC ‘93 field campaign that seven major point sources impacted the PM in the LFV significantly. These point sources are shown in Fig. 13 as black triangles in order to evaluate their potential impact on PM sulfate or organics measured in the valley. It is clear from Fig. 13, that on 27 August, the most likely sources of SO_2 for photochemical production of sulfate are refineries and power plants indicated as S1 and S2. For example, the air masses that reached Langley at 6 p.m. and Sumas at 9 p.m. appear to have been impacted by S2 source around 4 p.m. and 2 p.m. Active photochemistry via oxidation of SO_2, leading to the formation of new particulate sulfate, is expected to occur during the transport of air masses between the sources S1 and S2 and the LFV. On 27 August, after the air masses shifted further north of the point source S1 and S2 and were no longer affecting the Langley site, a drop in sulfate concentrations was observed at both Langley and Sumas.

Another example of aerosol sulfate events occurred during the 16–20 August 2001 time period. During this period, a systematic increase of sulfate was observed at Langley almost every day between 11 a.m. and 3 p.m. The size distributions at Langley during these events also show the appearance of small sulfate particles. As on 27 August, this period was mostly influenced by air masses originating in the Pacific Ocean and arriving at Langley from the southwest near the S1 and S2 sources. Interestingly, although the AMS was not at the Sumas site during these period, DMA measurements by Mozurkewich et al. (2004) show significant aerosol nucleation and growth events between 10:30 and 12:00 p.m. during the same time periods as the Langley events. While the AMS inlet cutoff below 40 nm prevents us from measuring the actual nucleation event itself, the appearance of small particles at Langley during these time periods could also be a result of growth of recently formed particles from nucleation events at Langley. This phenomenon was also observed in a similar air quality study performed in Pittsburgh, PA (USA) in the summer of 2002 (Zhang et al., 2004). It is noteworthy that contrary to previous periods (sulfate events observed on 27 and 28 August), where organics show an increase in concentration during the growth event, these aerosol events were primarily dominated by sulfate. The organic mass loadings remained more or less steady during the entire 16–20 August time period. The average organic levels of $0.5\,\mu g\,m^{-3}$ measured during this period represent the lowest concentrations measured during the entire campaign and probably represent the background level of particulate organics in the LFV. The calculated back trajectories for this time period indicate that the low organic concentrations likely resulted from a lack of urban influence on the air masses that reach the LFV during 17–20 August at Langley, as well as a lack of organic particles or organic aerosol precursor emissions from the sources that produced the SO_2 reaching the sites.

Unlike Slocan, which is dominated by local vehicle emissions of organic aerosol and thus has distinct organic aerosol time trends and size distributions, the similar organic time trends at Langley and Sumas (see Fig. 11) indicate that both sites are impacted by regional organic aerosol contained in air masses that reach both sites. For example, the most significant organic event observed at both places occurred on 28 August. The dramatic change in aerosol composition from

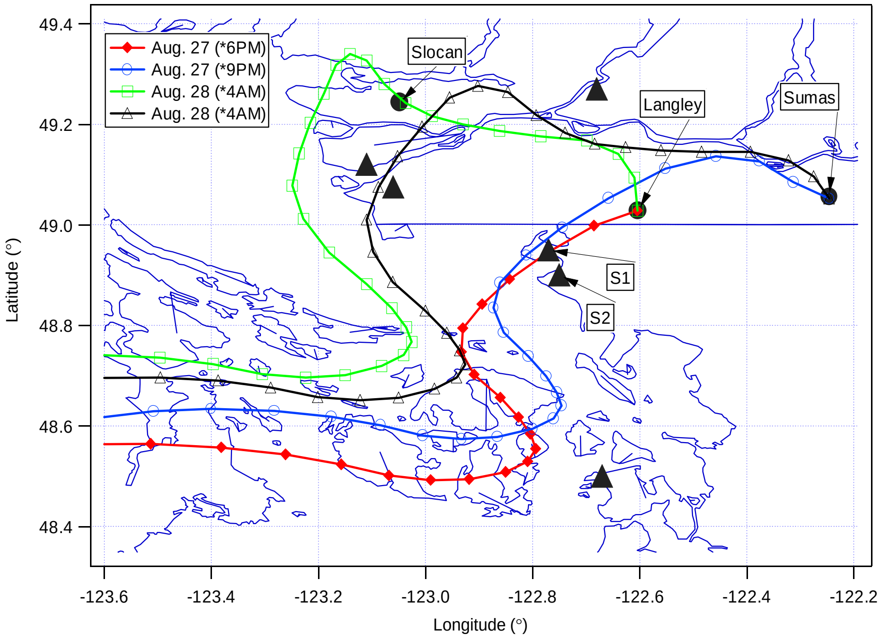

Fig. 13. Typical 5-day back trajectories arriving at Langley and Sumas during sulfate event (27 August 2001) and organic event (28 August after 1 a.m.). *: arrival time.

sulfate-dominated to organic-dominated aerosol corresponds in fact to a complete change in air mass origin especially 12–18 h before reaching the sampling sites at Langley and Sumas. In Fig. 13, typical 5-day back trajectories arriving at Langley and Sumas on 28 August at 4 a.m. show that during this event both sites were influenced by air masses that had been exposed to urban emissions from the city of Vancouver. This is consistent with the increase in organic aerosol content and the greater intensity of the small organic mode (see Fig. 2a) at both sites during this event.

The nitrate time trends for Sumas and Langley do have a general correlation with each other, but this correlation is not as strong as in the case of sulfate and organics. This is most likely due to the fact that the formation of nitrate aerosol is not only sensitive to the history and chemical composition of the air masses reaching each site, but also to the local temperature and humidity conditions at each site. Agricultural activity in the LFV could provide a source for the gas phase NH_3 needed to form the nitrate aerosol levels observed at the Langley and Sumas sites.

4. Conclusion

Real-time measurement of chemically speciated and size-resolved particles was performed by two Aerodyne AMSs from 11 August to 01 September 2001 in the LFV, Vancouver, Canada. Measurement at three major sites, Slocan, Langley and Sumas, representing, urban, rural and semi-rural environments, respectively, show high variability in aerosol mass concentrations and composition. At the urban site (Slocan Park), the aerosol composition was found to be dominated by organic species; a large fraction of this organic aerosol is attributed to fresh local emissions from mobile vehicles in the urban area that surrounds Slocan. In contrast, at the Langley site, the inorganic fraction accounted for at least 50% of total mass loadings. Most of the inorganic aerosol at Langley and Sumas appears to be photochemically processed, regional aerosol.

A background sulfate level of about $1\,\mu g\,m^{-3}$ was measured at all sites. Several sulfate events with increasing sulfate concentrations were measured in the LFV and were found to be correlated with gas phase SO_2. Back-trajectory analysis shows that most of these events were observed during southwesterly air flow. During these events, small sulfate-dominated particles were observed at both Sumas and Langley, indicating intense photochemistry and growth of secondary aerosol. Several important organic events that were not correlated with sulfate events were also observed during stagnant conditions at Langley and Sumas. These events occurred when the LFV was influenced by air masses from the west, which had been exposed to urban emissions from the Vancouver area. The near-simultaneous observation of sulfate, organic, and nitrate aerosol events at both the Langley and Sumas sites suggests that aerosol processes within the LFV occur on a regional scale. No correlation was observed between sulfate and organics at any of three sites, suggesting that the processes controlling their composition are either occurring separately or have different source regions.

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