Causes of Haze in the Gorge (CoHaGo) Draft Report

Mark Green Jin Xu Narendra Adhikari George Nikolich Desert Research Institute

March 7, 2006

1. Introduction	3
Summary of the Haze Gradient Study	3
Overview of field study design	8
2. Field measurement program	10
3. Statistical Description of Data	13
Summary of IMPROVE like aerosol data	13
Comparison of IMPROVE and IMPROVE like aerosol data	16
Comparison between DRUM and filter data	18
Comparisons between filter and high time resolved data	20
Optec nephelometers and Radiance nephelometers comparison	23
Comparison between Optec nephelometer measured and reconstructed aerosol light	
scattering coefficients	
Comparison between Radiance nephelometer measured and IMPROVE reconstructe	:d
dry aerosol light scattering coefficients	. 29
Relationship between high time resolution chemical measurements and aerosol light	
scattering coefficient	
Relationship between Aethalometer EC and Sunset Laboratory EC	35
4. Attribution	. 37
PMF analysis	37
Methodology	
PMF Results for Mt. Zion (COGO1)	38
PMF Results for Wishram (CORI1)	. 44
PMF attribution by chemical compound and to light extinction	49
PMF analysis results by wind pattern (cluster)	51
Episode analysis	
November 2004 Episode	
February 2004 episode	
August 2004 episode	
July 2004 episode	64
Summary of Episode Analyses	
5. Brief discussion of hypotheses tested	
References:	74

1. Introduction

The Causes of Haze in the Gorge (CoHaGo) study is a data analysis effort intended to add to the understanding of the source areas and source types contributing significantly to haze in the Columbia River Gorge in the States of Washington and Oregon. The study is a follow-up to the Columbia River Gorge Haze Gradient Study (Green et. al, 2006). While the Haze Gradient Study used primarily nephelometer and surface meteorological data to understand spatial and temporal patterns in haze in the Gorge, CoHaGo makes use of additional aerosol chemical composition to enhance understanding of haze in the Gorge.

Summary of the Haze Gradient Study

The field portion of the Columbia River Gorge Haze Gradient Study was conducted from July 2003 through February 2005. Measurements included particle light scattering bsp at nine locations from downriver from the Gorge (Sauvie Island) to upriver from the Gorge (Towal Road), including several sites in the Gorge. Monitoring site locations are shown in Figure 1-1. Meteorological measurements were taken at all sites except one (Memaloose).



Figure 1-1a. Map of western sites (Sauvie Island, Steigerwald, Mt. Zion, and Strunk Road).

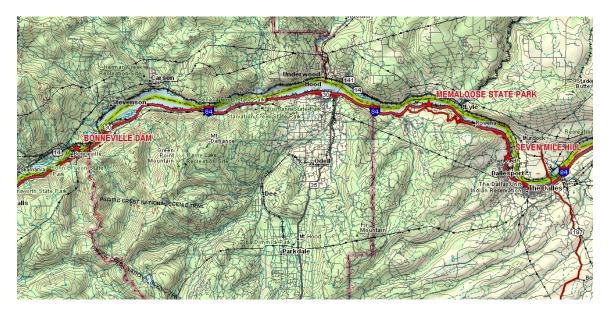


Figure 1-1b. Monitoring sites in the central Gorge (Bonneville, Memaloose State Park, and Sevenmile Hill).

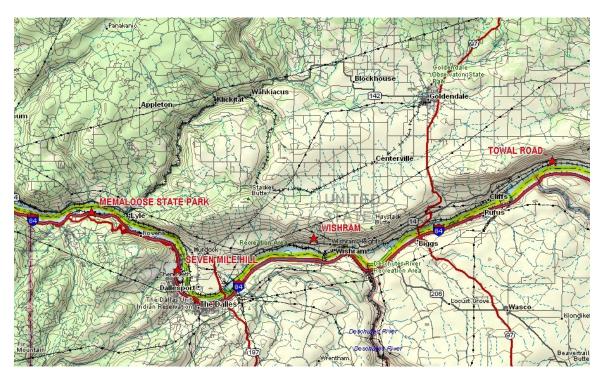


Figure 1-1c. Monitoring sites in the eastern Gorge (Memaloose, Seven Mile Hill, Wishram, and Towal Road).

Because of the large number of days (>600) monitored, a statistical method (cluster analysis) was used to group days with similar wind patterns. Summaries of wind, pressure, particle light scattering (bsp), and light absorption were computed for each group of similar days (each cluster). Wind direction data showed that winds were

channelled through the gorge with wind directions having a bi-modal distribution, upriver or downriver (Figure 1-2). Wind data were then classified as to their component upriver (basically west to east). Upriver was termed "upgorge", downriver termed "downgorge". Light scattering data were interpreted with respect to wind transport patterns to gain insight into likely source areas for each group of days.

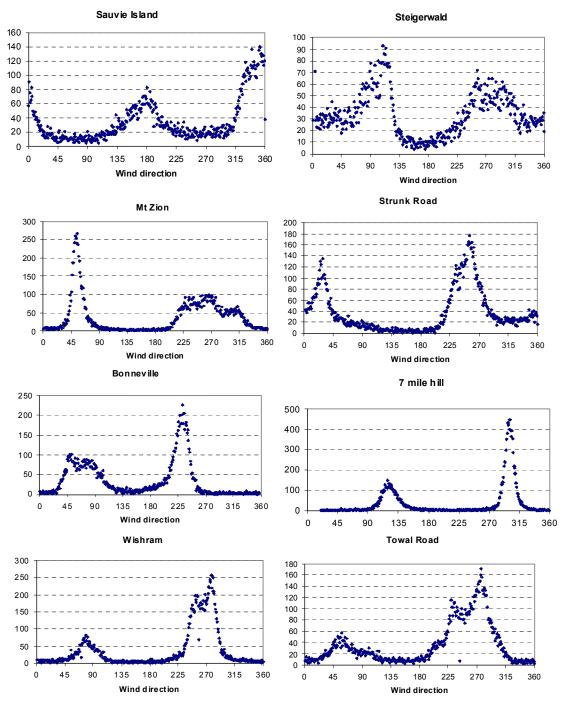


Figure 1-2. Frequency distribution of wind direction by site. X-axis is direction from which wind is blowing (meteorological convention); y-axis is number of hours with wind

from each one-degree increment in direction. Period of record is July 1, 2003 to February 28, 2005.

Five clusters of similar days were identified:

- 1) light upgorge flow
- 2) moderate upgorge flow
- 3) strong upgorge flow
- 4) light downgorge flow (diurnal reversal at eastern sites)
- 5) winter downgorge flow (light at east end, strong at west end)

Daily averaged upgorge wind component for each cluster is shown in Figure 1-3.

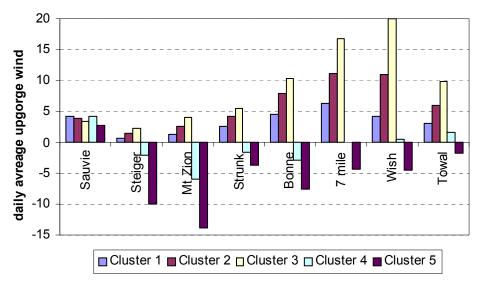


Figure 1-3. Daily average upgorge wind speed by cluster for each monitoring site.

The percentage frequency of occurrence of each cluster by month is shown tabularly in Table 1-1 and graphically in Figure 1-4.

Table 1-1. Percentage of days in each month assigned to each cluster type.

Cluster	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1	15	9	19	27	13	13	9	19	18	24	19	25
2	6	5	13	20	29	33	29	40	35	27	12	13
3	6	14	35	20	48	37	56	35	28	18	17	6
4	10	21	16	27	10	17	5	5	18	22	28	19
5	63	51	16	7	0	0	0	0	0	9	24	38

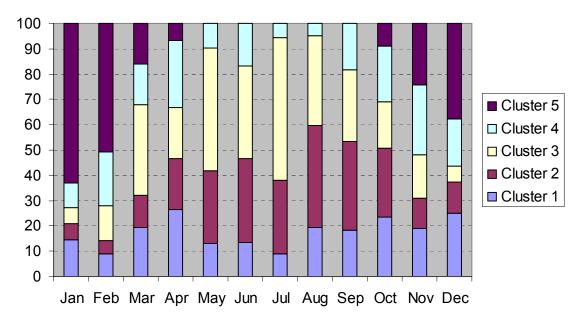


Figure 1-4. Frequency of occurrence of each cluster by month.

Strong upgorge (3) was the predominant pattern in mid-summer; Winter downgorge (5) was the most frequent winter pattern and never occurred from My through September. Light upgorge (1) and light downgorge (4) were most frequent in fall and spring transition months; moderate upgorge (2) was most frequent in late summer to early fall.

Winter downgorge (5) had the highest average bsp at all sites except Sauvie Island and Steigerwald (Figure 1-5). Highest bsp for winter downgorge was at the eastern sites, with a decrease with distance downgorge. Bsp increased again at Sauvie Island as the flow exited the Gorge and crossed the Portland/Vancouver area. This transport and bsp gradient pattern suggests that sources east of the Gorge cause much of the haze and that the Portland/Vancouver area contributes additional aerosol to the Sauvie Island site.

Light downgorge (4) had the highest bsp at Sauvie Island, suggesting impact from nearby sources such as the Portland/Vancouver area and/or downriver industry.

For days without precipitation, all the upgorge clusters (1-3) had highest bsp at Mt. Zion and a decreasing bsp with distance into the Gorge. Light upgorge (1) and moderate upgorge (2) showed diurnal patterns of increasing bsp progressing upgorge to the Bonneville site during the day. Bsp also increased across the Portland/Vancouver area for each cluster, suggesting the urban area as a significant contributor to aerosol in the Gorge for these clusters.

Light downgorge (4) and winter downgorge (5) showed an increase in bsp from Wishram to Sevenmile Hill and Memaloose, suggesting impact from The Dalles area. At Sevenmile Hill for light downgorge (4), the diurnal change in wind direction from upgorge to downgorge is accompanied by an increase in bsp (when the direction is from The Dalles).

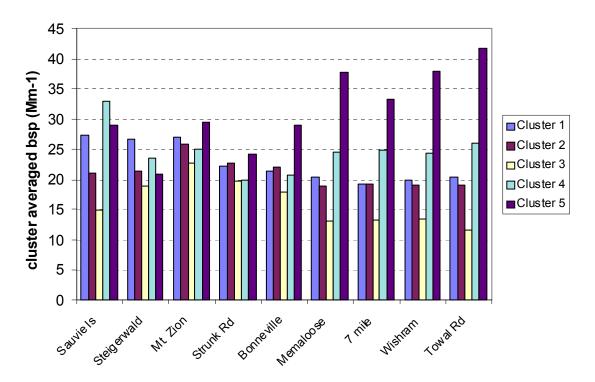


Figure 1-5. Average bsp (Mm⁻¹) at each nephelometer site for each cluster. Average is over all hours for all days within each cluster.

At Mt. Zion and Wishram, light absorption was a minor contributor to haze.

Overview of field study design

The field study encompassed July 2003 through February 2005. The period from July 2003 through November 2003 included only measurements in support of the Haze Gradient Study. Starting in December 2003, measurements using additional instrumentation were taken. This included two winter intensive periods focusing on the eastern Gorge: Dec 1, 2003 to Feb 28, 2004 and Dec 1 2004 to Feb 28, 2005 and one summer/fall intensive period focusing on the western Gorge (July 1, 2004 to Nov 30, 2004). During winter, focus was on the eastern Gorge because flows from east to west through the Gorge are most common in winter and are often associated with high levels of aerosols (causing haze). During summer, flow is nearly always from west to east (upriver), thus the western Gorge was the recipient of enhanced measurements. Autumn is a transitional period with flow more from the west than from the east and for the fall of 2004 it was decided to leave the additional instrumentation in the western Gorge through November.

Additional instruments provided continuous high-time resolved concentrations of sulfate, nitrate, organic carbon and elemental carbon. Used in conjunction with the light scattering (nephelometers) and surface meteorologic measurements this was anticipated

to provide considerable insight into source type and areas contributing to haze in the Gorge. A detailed description of the monitoring program is given in Section 2.

2. Field measurement program

Table 2-1 is a summary of the field study measurements.

Light scattering was measured using Radiance Research M903 nephelometers at eight sites. The Radiance nephelometers are set to maintain relative humidity (RH) of not more than 50%; this is accomplished by heating the inlet air stream. This was done to allow for comparisons of scattering along the Gorge uncomplicated by different amounts of particle growth due to varying RH among sites. Optec NGN-2 nephelometers (Molenar, undated) were operated at Wishram and Mt. Zion; they have been operating long-term at these IMPROVE protocol sites The Optec nephelometers are unheated and thus represent a more accurate estimate of light scattering, especially under higher RH conditions.

IMPROVE samplers have been operating long-term at Wishram and Mt. Zion. They provide for chemical speciation of $PM_{2.5}$ and mass of PM_{10} (Malm *et al.*, 1994). The IMPROVE samplers operate one day in three so two-thirds of the days in the study period had no data from these samplers. From January 2004 – February 2005 additional ion analysis was done for the Wishram and Mt Zion IMPROVE samples. This included analysis of cations (NH4⁺, K⁺, Na⁺, Mg⁺⁺, Ca⁺⁺) as well as anions (in the standard analysis).

For some days corresponding to IMPROVE sampling days, PM2.5 filter samples using the "IMPROVE like" International Aerosol Sampler (IAS) were collected at Sauvie Island (summer intensive), Bonneville (summer and winter intensives), and Towal Road (winter intensives) and chemically speciated. The IAS unit collects discrete (time-integrated) aerosol samples in the PM_{2.5} mode on three independent channels for analysis of mass, PESA and elemental, ion, and elemental/organic carbon fraction. The IAS collected samples 1 day in 3 to match IMPROVE sampling dates during the Columbia River Gorge Study. Unlike the IMPROVE "module" which contains 3 unique PM_{2.5} samplers, the IAS uses the IMPROVE cyclone to effect a PM_{2.5} cutpoint and traps the particles on 3 independent filters for analysis. Thus, the flow rate (23 liters/minute) and cyclone, cassette and filter media are identical to the IMPROVE units, but 1/3 the flow through each filter (and non-independent channels) is resulted.

A Sunset Laboratory carbon analyzer (Birch and Cary 1996) was operated at Mt Zion during summer-fall 2004, at Bonneville from summer 2004-winter 2005 and at Wishram during winter 2003-2004 and winter 2004-2005. This instrument gave continuous concentrations of organic and elemental carbon (OC/EC) for 2 hour periods (except for about 15 minutes analysis time each 2 hours).

Sulfate and nitrate were measured at the same locations and for approximately the same time periods as the OC/EC measurements. The instrumentation was Rupprecht & Patashnick series 8400S for sulfate and series 8400N for nitrate. Continuous data are available at 10 minute intervals.

As part of the haze gradient study, Aethalometers (Allen *et al.*, 1999; Moosmuller *et al.*, 1998) were operated at Wishram and Mt. Zion from July 2003- February 2005. Aethalometers give an estimate of elemental carbon by determining absorption due to particles deposited on a filter. Data is available for 5 minute average time periods, but is generally better when averaged over a longer time interval (e.g. one-hour).

Davis Rotating Drum Universal Monitors (DRUM) samplers (Raabe et al., 1988; Lundgren, 1967; Bench et al., 2002) were operated at Mt. Zion in the summer to fall 2004, at Bonneville from summer 2004 to winter 2004-2005 and at Wishram during winter 2003-2004 and winter 2004-2005. The 8-Stage Rotating DRUM Impactor Sampler (8-RDI) is a cascade impactor. The sampler used operated at 16.7 liters per minute allowing it to couple to a 10 μ m cutpoint ("PM₁₀") inlet (URG Corp.). The aerosol sample for each stage is deposited onto a rotating drum faced with a removable greased Mylar impaction surface. As the drum rotates a continuous aerosol sample is laid down along the direction of rotation with density varying along the length of the Mylar strip in proportion to the aerosol collected as the substrate rotates. Analysis using narrow beam techniques (s-XRF (Knochel, 1990) and PESA(Bench et al., 2002)) for elements and hydrogen, respectively, and Beta-ray attenuation for mass produces data with time resolution proportional to the ratio of drum surface speed divided by the beam width. Sampling allowed 42-day continuous record in 8 size bins (10-5, 5-2.5, 2.5-1.15, 1.15-0.75, 0.75-0.56, 0.56-0.34, 0.34-0.26, 0.26-0.09 micrometers aerodynamic diameter) analyzable in 3-hr time steps.

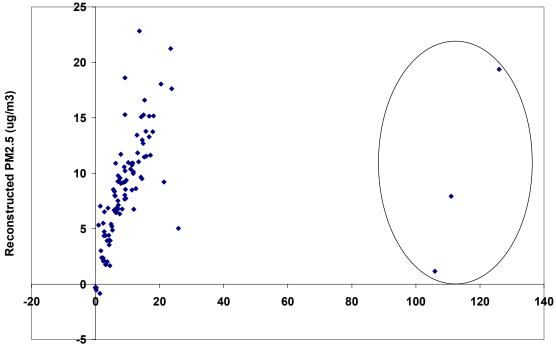
Table 2-1. Sur	mmary of n	neasurement pro-	ogram.						
Measurement	Sauvie Is	Steigerwald	Mt Zion	Strunk Rd	Bonneville	Memaloose	7 mile	Wishram	Towal Rd
Bsp Optec			7/1/03-2/28/05					7/1/03-2/28/05	
Bsp Radiance	8/5/03- 2//28/05	7/1/03-2/28/05	7/1/03-2/28/05	7/1/03- 2/28/05	8/7/03-2/28/05	8/7/03-2/28/05	8/14/03- 2/28/05	7/1/03-2/28/05	7/17/03- 2/28/05
Sfc Met	8/5/03- 2//28/05	7/1/03-2/28/05	7/1/03-2/28/05	7/1/03- 2/28/05	8/7/03-2/28/05	8/7/03-2/28/05	8/14/03- 2/28/05	7/1/03-2/28/05	7/17/03- 2/28/05
IMPROVE PM2.5 speciation, PM10 mass			Every third day 7/1/03-2/28/05					Every third day 7/1/03-2/28/05	
Cation analysis of IMPROVE			Every 3rd day 1/04-2/05					Every third day 1/04-2/05	
IMPROVE- like PM2.5 speciation	Some days 7/04- 11/04				Some days 12/03,2/04, 7/04- 1/05				Some days 12/03,2/4,12/0 4-2/05
Time resolved EC/OC			6/28/04-11/10/04		6/30/04-2/28/05			12/18/03-3/1/04, 12/1/04-2/28/05	
Time resolved SO4			7/19/04-11/29/04		1/10/04-3/8/04, 6/28/04-2/28/05			1/4/04-2/12/04, 11/29/04-2/28/05	
Time resolved NO3			6/30/04-11/29/04		1/30/04-2/20/04, 6/28/04-2/28/05			1/10/04-3/2/04, 11/29/04-2/28/05	
Aethalometer			7/103-2/27/05					7/2/03-2/28/05	
DRUM samplers			6/30/04-8/11/04, 8/19/04-11/2/04		12/4/03-2/24/04, 7/16/04-11/2/04, 12/2/04-2/23/05			12/3/03-1/12/04, 12/2/04-2/23/05	
SODAR									

3. Statistical Description of Data

In this section summaries of the monitoring data are presented. In addition to summarizing measurements from each instrument, we compare measurements of the same compounds measured by different instruments at the same site (e.g. IMPROVE OC versus time-resolved OC by Sunset Laboratory instrument); and measured versus derived parameters (such as measured and reconstructed light scattering). These summaries and comparisons are done in order to better understand the quality of the data and the appropriate uses for each measurement. For example some high-time resolved data may be less accurate than 24-hour averaged IMPROVE data but may be quite useful in indicating timing of increased haze causing components. While perhaps only semi-quantitative, the high time resolved measurements may provide for a better understanding of source-receptor relationships.

Summary of IMPROVE like aerosol data

A total of 99 sets of samples and 2 sets of field blanks were collected in Sauvie Island, Bonn2 (Cascade Island), BonnDam (Bonneville Dam at Robbins Island), and Towal Rd using the IAS samplers. The average concentrations of the two blanks were subtracted from the measured sample concentrations in this analysis. The concentrations of major chemical components were calculated using the IMPROVE methodology (based on equations listed in Table 3-1). Figure 3-1 shows the comparison between measured and reconstructed $PM_{2.5}$ mass (i.e. sum of the concentrations of the major chemical components listed in Table 1). As it indicates, measured $PM_{2.5}$ mass concentrations were over 100 µg/m³ for three data points, much higher than the reconstructed mass. This may be due to mistakes in filter weighting. These three data points are removed from the analysis later in this section. Also, no $PM_{2.5}$ mass was reported for samples collected on 10/27/2004 at Bonn2, and this set of data is removed as well. Figure 3-2 shows a correlation between the measured and reconstructed $PM_{2.5}$ of 0.62 after the three outliers and one missing data point are removed (i.e. a total of 95 sets of samples).



Measured PM2.5 (ug/m3)

Figure 3-1. Comparison between measured and reconstructed $PM_{2.5}$ mass.

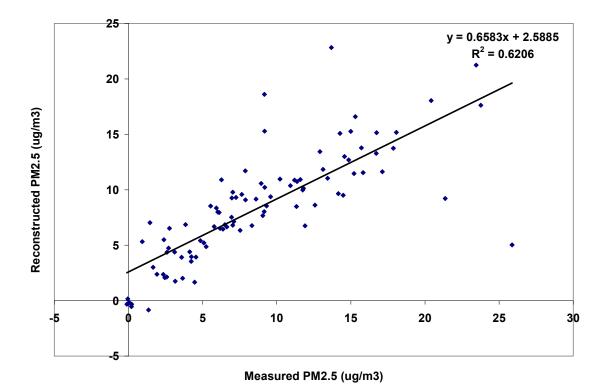


Figure 3-2. Comparison between measured and reconstructed $PM_{2.5}$ mass after removing the three outliers.

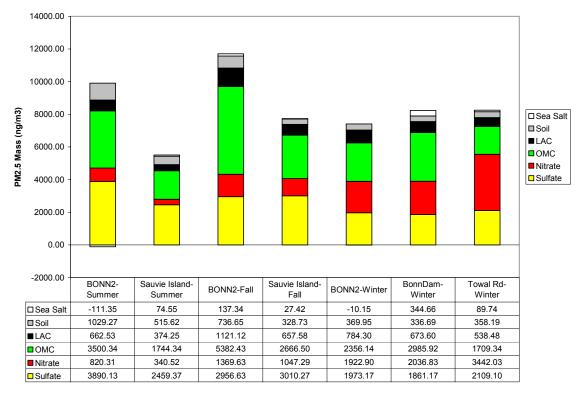


Figure 3-3. PM2.5 average chemical speciation (ng/m3) based on IAS samples.

Figure 3-3 summaries the aerosol chemical speciation data measured at Sauvie Island, Bonn2 (Cascade Island), BonnDam (Bonneville Dam at Robbins Island) and Towal Rd using the IAS samplers. Figure 3-3 suggests that sulfate and organics are the major aerosol components at Bonneville and Sauvie Island during the summer. Sulfate contributes about 40% and 45% to PM2.5 mass in Bonneville and Sauvie Island during the summer, and OMC contributes 36% and 32%, respectively. During the fall, 46% and 34% of PM_{2.5} is organics in Bonneville and Sauvie Island, and sulfate contributes 25% and 39%, respectively. In the winter, OMC contributes 32% and 36% to PM2.5 mass at Bonn2 and BonnDam, and sulfate and nitrate each contributes about 20-25% at both sites. Nitrate is the largest contributor to PM2.5 at Towal road in winter, with a contribution of 42%,

Bonneville had higher concentrations of sulfate, nitrate and OMC than Sauvie Island in summer and higher OMC in fall, although sulfate and nitrate levels were similar in fall. In winter, Wishram had higher nitrate than the Bonneville sites, while Bonneville had higher OMC and sulfate was about the same as at Wishram.

Species	Formula	Assumption				
Sulfate	4.125[S]	All elemental S is from sulfate. All sulfate is from ammonium sulfate.				
Nitrate	1.29[NO3]	Denuder efficiency is close to				

Table 3-1. Aerosol major chemical components

		100%. All nitrate is from ammonium nitrate.
Organic Mass by Carbon (OMC)	1.4 * OC	Average organic molecule is 70% carbon.
Light Absorbing Carbon (LAC)	EC1+EC2+EC3-OP	
Fine Soil (Soil)	2.2[A1]+2.49[Si]+1.63[Ca]+ 2.42[Fe]+1.94[Ti]	[Soil K]=0.6[Fe]. FeO and Fe ₂ O ₃ are equally abundant. A factor of 1.16 is used for MgO, Na ₂ O, H ₂ O, CO ₂ .
Sea Salt	1.8 * [Cl ⁻]	

Comparison of IMPROVE and IAS aerosol data

Figure 3-4 summarizes the seasonal average chemical speciation of $PM_{2.5}$ based on IMPROVE aerosol data at Mt. Zion and Wishram. OMC is the largest contributor to $PM_{2.5}$ at both sites except in the summer at Mt. Zion and in the winter at Wishram. The figure also indicates that, in average, the aerosol loading and chemical speciation at Mt. Zion and Wishram are pretty similar, though sulfate concentration is a little bit higher at Mt. Zion during the summer and nitrate is higher at Wishram during the winter.

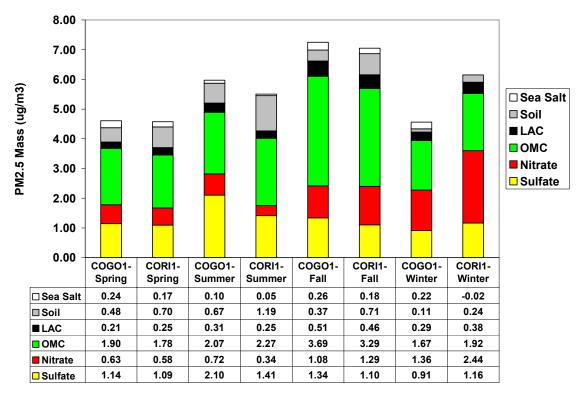
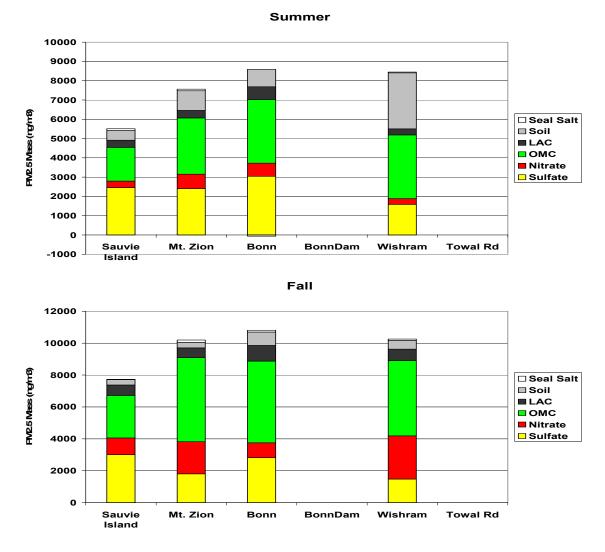


Figure 3-4. PM2.5 chemical speciation (μ g/m3)based on IMPROVE data (7/2003 – 12/2004) collected at COGO1 (Mt. Zion) and CORI1 (Wishram).

Figure 3-5 shows the comparison of seasonal average of IMPROVE and IAS filter data during the time periods when IAS samples were collected. The sites are listed from west to east in the figures. The aerosol loading at Sauvie Island is generally lower than other sites in summer and fall. In general, there is relatively more organics on the west side of gorge during the summer and fall, and more nitrate on the east side of the gorge during the winter.



17

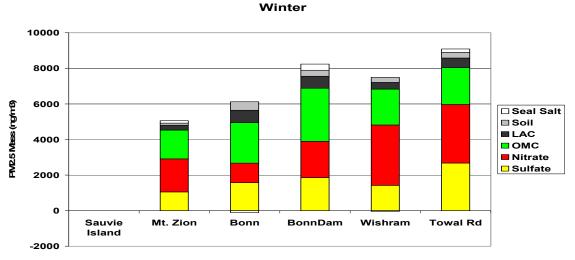


Figure 3-5. Comparison of seasonal average IMPROVE and IAS data during summer, fall, and winter.

Comparison between DRUM and filter data

As shown in the Figures 3-6 and 3-7, $PM_{2.5}$ filter measured S is about twice the DRUM (0.09 – 2.5 µm) measured S at both sites. At Bonneville, filter measured Si and Ca agree with the DRUM data fairly well. But at Mt. Zion, filter measured Si and Ca are much lower than the DRUM values. As for Na measurements, no correlation has been found between filter and DRUM data.

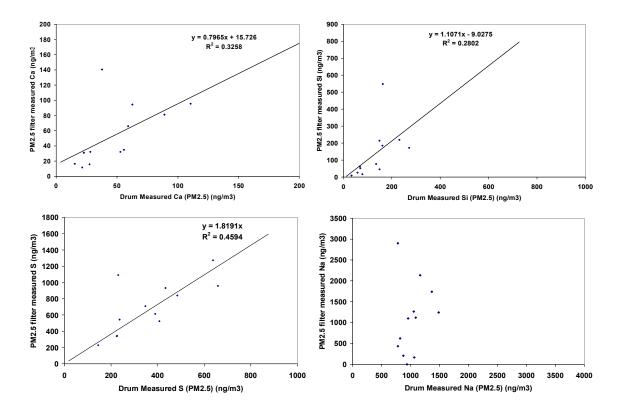


Figure 3-6. Comparison between DRUM and filter measured S, Na, Si and Ca concentrations for $PM_{2.5}$ at Bonneville.

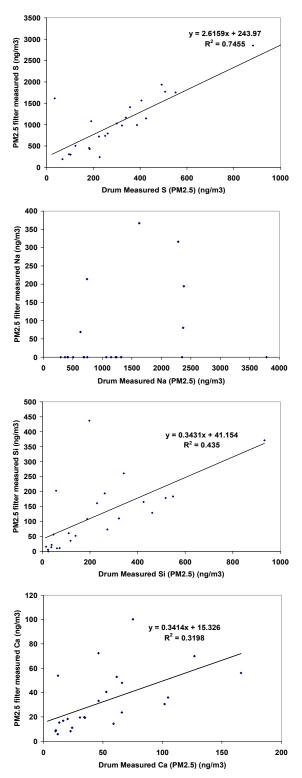


Figure 3-7. Comparison between DRUM and filter measured S, Na, Si and Ca concentrations for $PM_{2.5}$ at Mt. Zion.

Comparisons between filter and high time resolved data

High time resolved measurements of SO4, NO3, OC, and EC are compared to the 24hour averaged IMPROVE measurements at Wishram and Mt. Zion and to the 24-hour averaged IAS measurements at Bonneville (Figures 3-8 to 3-10).

The time-resolved sulfate tended to be higher than the 24-hour filter sulfate at all sites. There was poor correlation at Wishram and Bonneville, but better correlation ($r^2=0.61$) at Mt Zion. At Mt. Zion the time-resolved sulfate was about 50% higher than the IMPROVE sulfate.

Nitrate from the time-resolved and filter measurements tended to be of similar overall magnitude; the squared correlation coefficients ranged from $r^2=0.38$ at Wishram to $r^2=0.85$ at Bonneville.

OC concentrations measured by the time-resolved and filter methods were comparable. R^2 ranged from 0.62 at Bonneville to 0.72 at Wishram.

For EC, the time resolved measurements gave about $\frac{1}{2}$ the concentration of the filter based measurements. This is expected to result from the different temperature programs applied to the Sunset Carbon analyzer compared to the IMPROVE method of determining the split between OC and EC. The factor of $\frac{1}{2}$ is consistent with other studies (Chow *et al.*, 2001; Green *et al.*, 2003). The correlations ranged from r²=0.46 at Bonneville to r²=0.62 at Wishram.

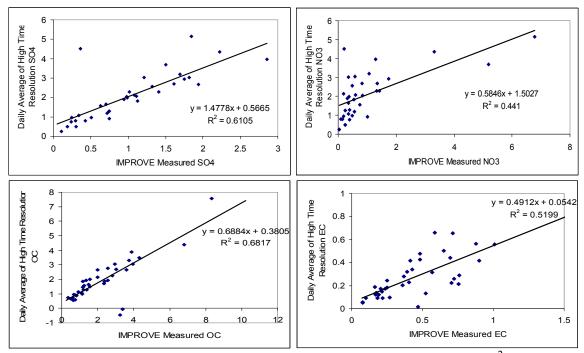


Figure 3-8. Comparison between 24 hour average of high time resolved SO_4^{2-} , NO_3^{-} , OC and EC measurements and IMPROVE daily filter measurements at Mt. Zion.

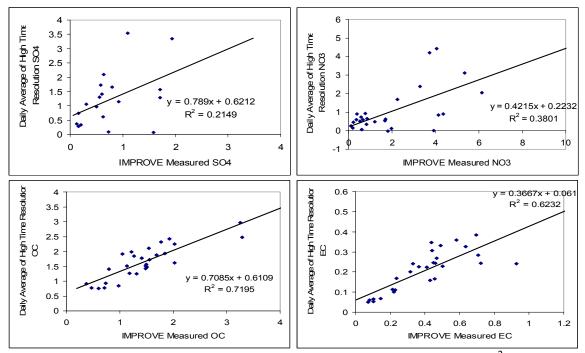


Figure 3-9. Comparison between 24 hour average of high time resolved SO_4^{2-} , NO_3^{-} , OC and EC measurements and IMPROVE daily filter measurements at Wishram.

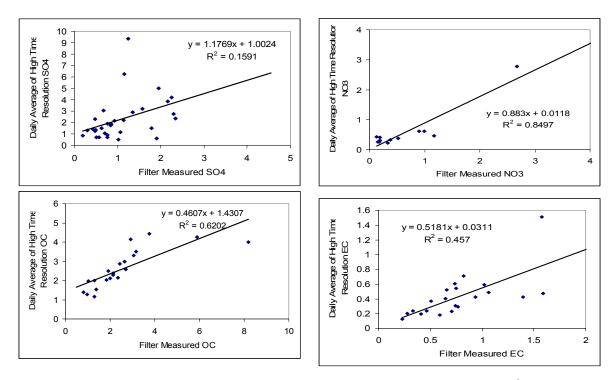


Figure 3-10. Comparison between 24 hour average of high time resolved $SO_4^{2-}NO_3^{-}$, OC and EC measurements and daily filter measurements at Bonneville.

Optec nephelometers and Radiance nephelometers comparison

At Wishram and Mt. Zion both Optec and Radiance Research nephelometers were operated. The Optec nephelometers are ambient, while the Radiance Research nephelometers sample after heating to control RH to 50% or less. Due to the water growth of hygroscopic aerosol (especially that containing sulfate and nitrate) at higher humidities, it is expected to have higher particle light scattering (bsp) at high humidities from an unheated nephelometer. The Optec and Radiaince Research nephelometers also have different effective wavelengths for measuring scattering (about 550 nm for the Optec, 525 nm for the Radiance Research). Because scattering is inversely proportional to wavelength, the wavelength difference alone would cause the Radiance Research scattering to be about 5% higher than the Optec scattering. Figure 3-11 is an example time series plot of hourly averaged bsp at Mt Zion from the Optec and Radiance nephelometers from January 14-April 23, 2004. It can be noted that they track closely, but that the Optec values tend to be higher. Figure 3-12 shows the ratio of average Optec bsp/ average Radiance bsp at each site by each integer ambient RH value (as measured with the Optec RH sensor). At RH below about 55%, the Radiance nephelometer tends to have higher bsp than the Optec nephelometer both at Wishram and Mt. Zion. At RH >60%, the Optec nephelometer has higher average bsp than does the Radiance nephelometer at each site; the ratio increases with RH. Values for RH above 90% were not computed – the Optec nephelometer data is flagged when RH>90%. The higher bsp from the ambient Optec nephelometer is expected at high RH (due to water growth); the

lower bsp for the Optec neph at low RH is probably due to the shorter effective wavelength for the Radiance Research nephelometer compared to the Optec nephelometer.

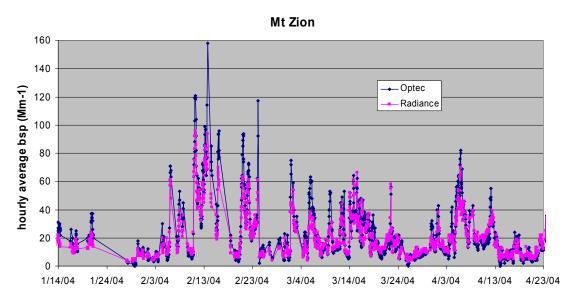


Figure 3-11. Example time series comparison of Optec and Radiance Research light scattering at Mt. Zion.

Figures 3-13 and 3-14 show scatterplots of Optec bsp versus an adjusted Radiance bsp at each site. The radiance bsp for each hour was adjusted by multiplying its value by the average ratio of Optec/Radiance bsp at that hours relative humidity (as plotted in Figure 3-12). When adjusting for the average difference between instruments at each integer RH value, they correlate with an r^2 of 0.96 at Mt. Zion and 0.90 at Wishram. Thus the difference between the two is highly predictable based on RH.

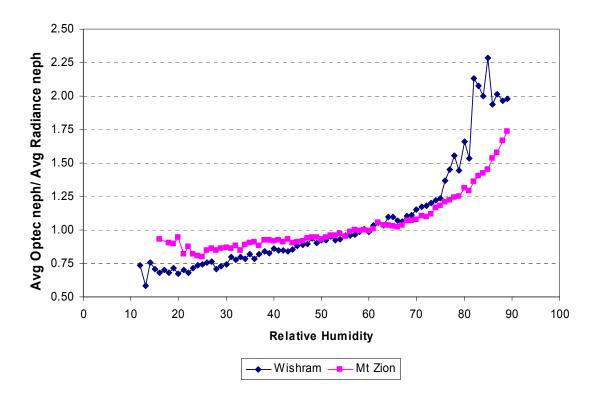


Figure 3-12. Average ratio of Optec nephelometer light scattering to Radiance Research nephelometer light scattering by integer relative humidity value.

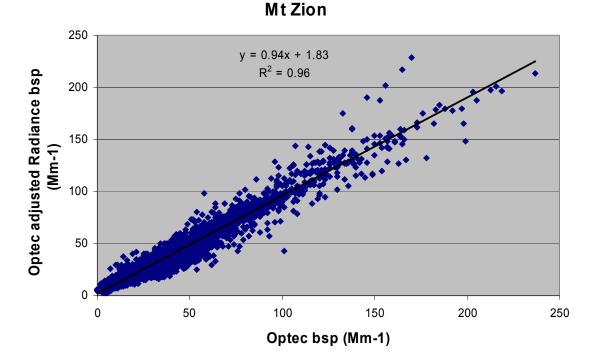


Figure 3-13. Scatterplot of Optec light scattering versus Radiance Research light scattering adjusted by RH, Mt. Zion.

25

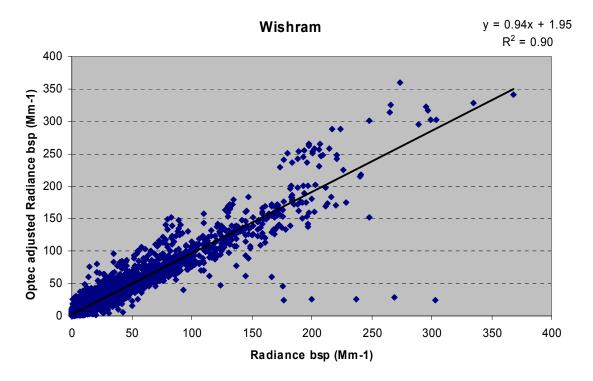


Figure 3-14. Scatterplot of Optec light scattering versus Radiance Research light scattering adjusted by RH, Wishram.

Comparison between Optec nephelometer measured and reconstructed aerosol light scattering coefficients

Comparison of measured light scattering to light scattering estimated using aerosol data gives us an idea of how reasonable our assumptions about the effects of aerosol components on scattering are. If the measured and aerosol reconstructed scattering are highly correlated and have similar magnitude, we can be confident that both the aerosol and light scattering measurements and our choices of scattering efficiencies are reasonable. Attribution of haze to chemical components can then be done with confidence. It should be noted that when under high RH conditions, the heated Radiance Research nephelometers underestimate true light scattering.

Figure 3-15 and 3-17 show the comparison between daily averages of Optec nephelometer measured aerosol light scattering coefficients at Wishram and Mt. Zion, and calculated light scattering coefficients. The calculated scattering uses IMPROVE aerosol data from Wishram and Mt. Zion and the IMPROVE reconstructed scattering equation shown below (with relative humidity (RH) adjustment factors based on daily average of measured RH at the site). The Optec data have been screened to remove data points with data flags associated with them. Days with less than 12 valid (i.e. no data flag) hourly Optec data were also excluded from the comparison. In general, the measured and calculated aerosol light scattering coefficients agree well. As shown in Figure 3-16 and 3-18, OMC is the largest aerosol contributor to light extinction at both sites. However, the fraction of extinction of the hygroscopic components (sulfate and nitrate) increases compared to the dry case considered later, while the fractional amount of non-hygroscopic components (OMC, EC, fine soil, coarse mass) decreases compared to the dry extinction estimate (see Table 3-2).

Bsp = 3 [Sulfate] + 3[Nitrate] + 4[OMC] + 1[Soil] + 0.6[CM](1)

where the concentrations of the major chemical components are calculated using the equations listed in Table 1 [Watson, 2002; IMPROVE, 2004; VIEWS, 2004]. The units of B_{sp} and the concentrations of major light scattering aerosol components are Mm⁻¹ and $\mu g m^{-3}$, respectively.

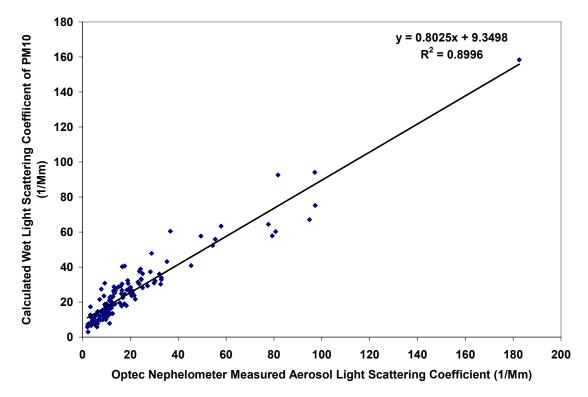


Figure 3-15. Calculated wet light scattering coefficient of PM_{10} using IMPROVE aerosol data from Wishram vs. daily average Optec nephelometer measured aerosol light extinction coefficient at Wishram.

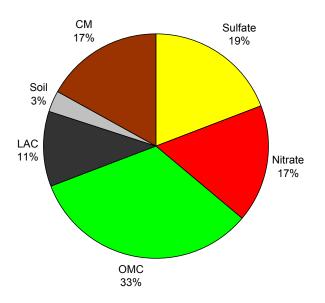


Figure 3-16. Contribution of major chemical components to aerosol light extinction (light scattering + light absorption by LAC) coefficient at Wishram.

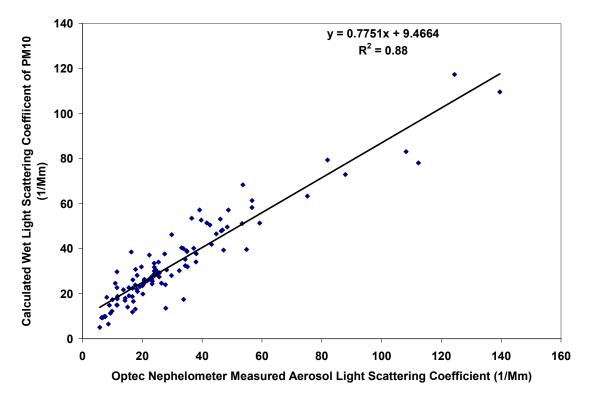


Figure 3-17. Calculated wet light scattering coefficient of PM_{10} using IMPROVE aerosol data from MT. ZION vs. daily average Optec nephelometer measured aerosol light extinction coefficient at Mt. Zion.

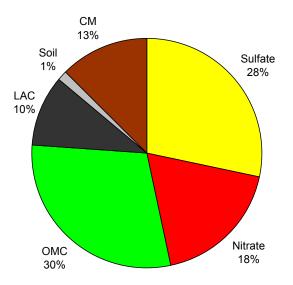


Figure 3-18. Contribution of major chemical components to aerosol light extinction (light scattering + light absorption by LAC) coefficient at Mt. Zion.

Table 3-2. Percentage of reconstructed light extinction by compound for Wishram and Mt. Zion- dry scattering and wet scattering cases.

Wishram	Sulfate	Nitrate	OMC	LAC	Soil	СМ
Dry	14	13	39	14	3	17
Wet	16	17	33	11	3	17
Mt Zion						
Dry	17	12	40	14	2	15
Wet	28	18	30	10	1	13

Comparison between Radiance nephelometer measured and IMPROVE reconstructed dry aerosol light scattering coefficients

Figures 3-19 and 3-21 show the comparison between daily averages of Radiance Research nephelometer measured dry aerosol light scattering coefficients (relatively humidity (RH) less than 50%) at Wishram and Mt. Zion, and calculated dry light scattering coefficients (without relative humidity adjustment factors). In general, the measured and reconstructed light scattering coefficients agree with each very well ($R^2 \sim 0.8$). On average, more than 85% of the dry aerosol light scattering is due to major

chemical components of particles with aerodynamic diameters less than 10 micrometers (PM_{10}) .

Figure 3-20 and 3-22 illustrates the average percentage contribution of each major chemical component to dry aerosol light extinction based on the IMPROVE data from July 2003 to December 2004. At both Wishram and Mt. Zion, OMC is the largest contributor to dry aerosol light extinction, with a contribution of ~40% at both sites. Sulfate, nitrate, coarse mass, and light absorbing carbon are similar contributors to dry light extinction at both sites, ranging from 12% to 17% each.

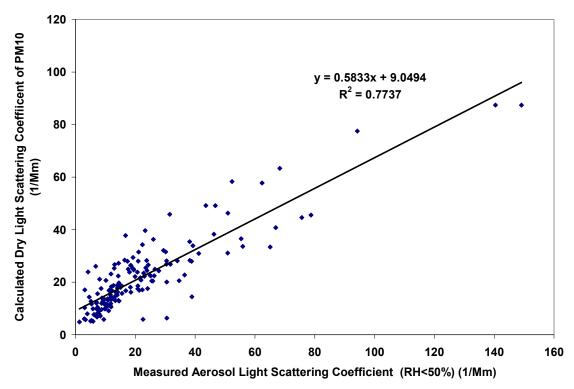


Figure 3-19. Calculated dry light scattering coefficient of PM_{10} using IMPROVE aerosol data from Wishram vs. daily average measured aerosol light extinction coefficient at Wishram.

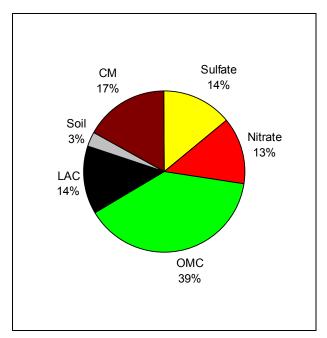


Figure 3-20. Average contribution of major aerosol components to dry aerosol light extinction coefficient (light scattering + light absorption by LAC) at Wishram based on IMPROVE data from Wishram.

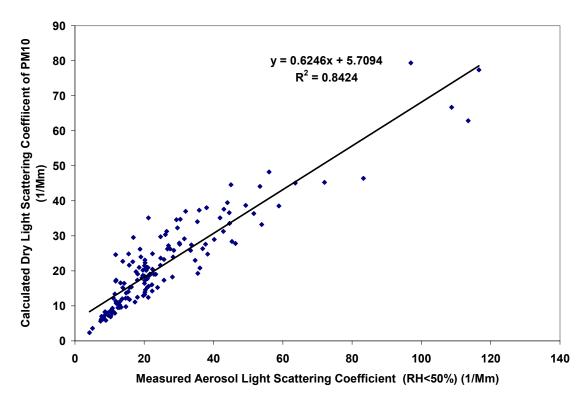


Figure 3-21. Calculated dry light scattering coefficient of PM_{10} using IMPROVE aerosol data from Mt. Zion vs. daily average measured aerosol light extinction coefficient at Mt. Zion.

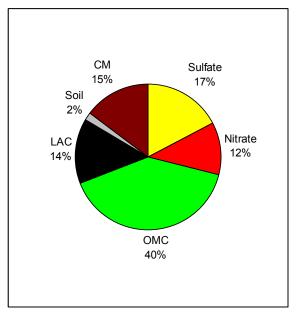


Figure 3-22. Average contribution of major aerosol components to dry aerosol light extinction coefficient (light scattering + light absorption by LAC) at Mt. Zion based on IMPROVE data from Mt. Zion.

Relationship between high time resolution chemical measurements and aerosol light scattering coefficient

High time resolution chemical measurements including sulfate, nitrate, OC/EC were measured in Bonneville, Wishram and Mt. Zion. Sulfate and nitrate were measured every 10 minutes, while OC/EC were measured every 2 hours. In order to compare the data, sulfate and nitrate values are averaged every 2 hours, so were the aerosol light scattering coefficients measured by Radiance Research nephelometers at the three sites. Then dry light scattering coefficients of OMC, sulfate and nitrate were calculated using a mass scattering efficiency of 4, 3 and 3 m²g⁻¹, respectively.

Figure 3-23 illustrates that a good correlation has been found between measured aerosol light scattering coefficient and the sum of calculated light scattering coefficients of OMC, sulfate and nitrate in Bonneville based on 1209 data points during June to November 2004. Figure 3-24 shows that, in average, OMC, sulfate and nitrate contributes 54%, 34% and 7% to light scattering, respectively. 5% of light scattering is due to other components including fine dust and bigger particles (i.e. > 2.5 μ m).

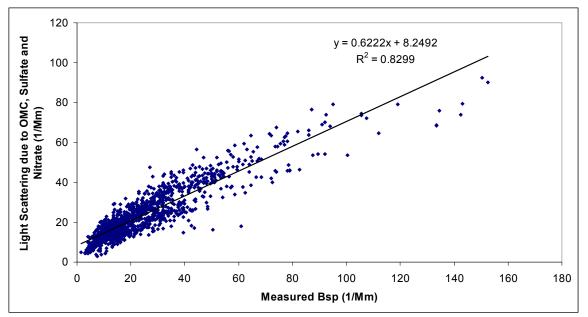


Figure 3-23. Relationship between measured aerosol light scattering coefficient (B_{sp} , 1/Mm) and sum of light scattering due to OC, sulfate and nitrate in Bonneville.

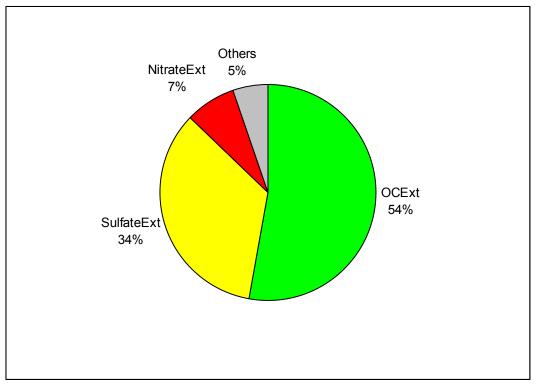


Figure 3-24. Average contribution to aerosol light scattering at Bonneville.

As shown in Figure 3-25, a relatively good correlation has been found between measured aerosol light scattering coefficient and the sum of calculated light scattering coefficients of OMC, sulfate and nitrate in Mt. Zion based on 949 data points during July to

November 2004, but the sum of the calculated OMC, sulfate and nitrate light scattering is only about 30% of aerosol light scattering measured directly.

Measured aerosol light scattering coefficient and the sum of calculated light scattering coefficients of OMC, sulfate and nitrate are not correlated at all in Wishram based on 607 data points during the winter of 2004 and 2005 as shown in Figure 3-26. It is not clear what are the reasons for this lack of correlation.

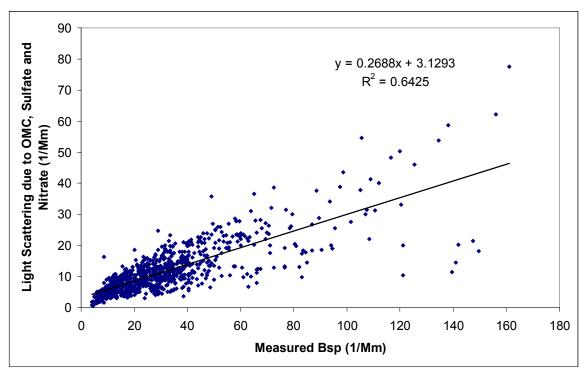


Figure 3-25. Relationship between measured aerosol light scattering coefficient (B_{sp} , 1/Mm) and sum of light scattering due to OC, sulfate and nitrate in Mt. Zion.

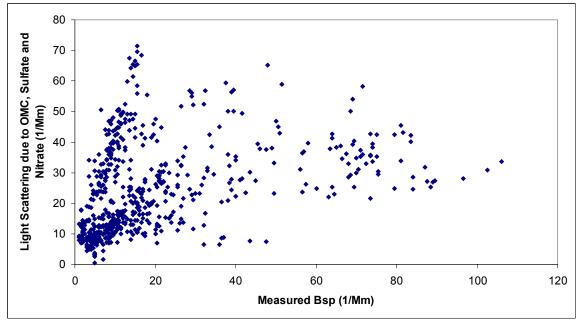
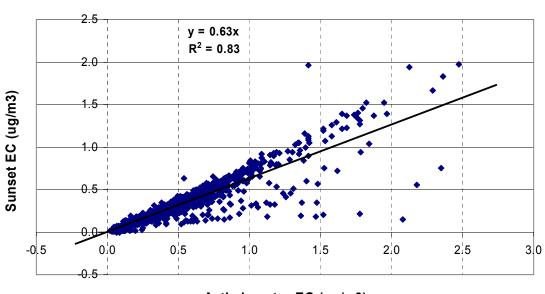


Figure 3-26. Relationship between measured aerosol light scattering coefficient (B_{sp} , 1/Mm) and sum of light scattering due to OC, sulfate and nitrate in Wishram.

Relationship between Aethalometer EC and Sunset Laboratory EC

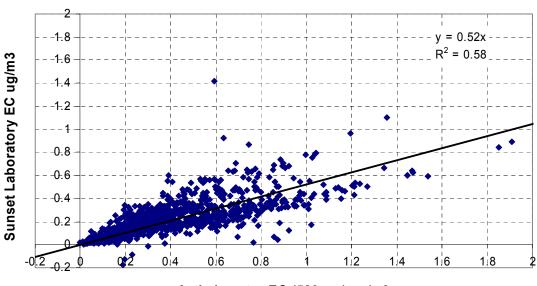
Figures 3-27 and 3-28 compare elemental carbon from the aethalometer (at 520 nm) and the Sunset Laboratory analyzer. Similarly to comparisons of the Sunset laboratory EC to IMPROVE EC, the Sunset Laboratory EC is nearly always lower than the aethalometer EC. Regression of Sunset laboratory EC against aethalometer EC showed a slope of 0.63 at Mt. Zion and 0.52 at Wishram. R^2 was 0.83 at Mt. Zion and 0.63 at Wishram.



Mt. Zion Sunset Laboratory EC and Aethalometer EC comparison

Aethalometer EC (ug/m3)

Figure 3-27. Sunset Laboratory EC concentration (μ g/m3) versus Aethalometer derived EC (μ g/m3) at Mt. Zion.



Wishram Sunset EC and Athalometer EC comparison

Aethalometer EC (520 nm) ug/m3

Figure 3-28. Sunset Laboratory EC concentration (μ g/m3) versus Aethalometer derived EC (μ g/m3) at Wishram.

4. Attribution

PMF analysis

In order to identify the sources of aerosols in the Columbia River Gorge, the Positive Matrix Factorization (PMF) receptor model was applied to the 24-hr integrated aerosol chemical composition data obtained at the Columbia River Gorge through the Interagency Monitoring of Protected Visual Environments (IMPROVE) program (sites Mt. Zion and Wishram) during the years 2003-2004. PMF was applied to each site to generate profiles of source factors. Normalized source profiles and the quantitative source contributions for each resolved factor were calculated. The major sources that contribute to the aerosol loadings and light extinction in the Columbia River Gorge were identified. The PMF results were also helped to identify pollution episodes.

Methodology

PMF is a statistical method that identifies a user specified number of source profiles (i.e. relative composition particle species for each source) and source strengths for each sample period that reduces the difference between measured and PMF fitted mass concentration [Kim et al., 2003; Liu et al., 2003; Kim and Hopke, 2004]. Equations 1 - 3 show the major steps of the model calculation.

$$X = GF + E \tag{1}$$

where: $\mathbf{X} (n * Sp) = a$ matrix of observed fine particulate species concentrations with the dimensions of number of observations by the number of species

G (n * f) = a matrix of source contributions by observation day with the dimensions of number of observations by the number of factors

F (f * Sp) = a matrix of source profiles with the dimensions of number of factors by the number of species

E(n * Sp) = a matrix of random errors with the dimensions of number of observations by number of species

The F and G matrices of the final solution are then normalized according to the following equations to determine the quantitative source contributions (C_i , $\mu g/m^3$)) and profiles for each source (S_i , $\mu g/\mu g$).

$$S_i = \frac{F_{ij}}{FM_i}$$
(2)

where:

 S_i = the row of the source profile matrix for source i

 F_{ij} = the source profile value for specie j of source i

 FM_i = the calculated average total fine mass contribution for source i

$$C_i = G_{ki} * FM_i \tag{3}$$

where:

 C_i = the column of the source contribution matrix for source i

 G_{ki} = the source contribution on day k for source i

 FM_i = the calculated average total fine mass contribution for source i

In this work, PM_{2.5} mass concentration was included in the PMF modeling (in X matrix), and the average total fine mass contribution of source i (FM_i) was calculated as part of the PMF modeling (in F matrix).

 $PM_{2.5}$ mass and chemical speciation data including analytical uncertainty and minimum detection limit were downloaded from the VIEWS web site [VIEWS, 2004]. Data are screened to remove the days when $PM_{2.5}$ mass concentration is missing. Data value and associated uncertainty are the measure data and analytical uncertainty + 1/3 * detection limit, respectively. If data is missing, then data value = geometric mean of the measured values, and uncertainty = 4 * geometric mean of the measured values. If data is below the detection limit, then the data value = 1/2 * detection limit, and the uncertainty = 5/6 * detection limit. The IMPROVE reported EC1 includes the OP concentration. In this work, OP was subtracted from EC1 and utilized as an independent variable (i.e. EC1 shown in this PMF work does not include OP). The model was run in robust mode - the value of outlier threshold distance is 4.0 (i.e. if the residue exceeds 4 times the standard deviation, a measured value is considered an outlier). F_{peak} value, which controls the rotational state of the solution, was set to be -1.0 and -1.5 for Mt. Zion and Wishram, respectively.

PMF Results for Mt. Zion (COGO1)

It was found that the K concentration on 7/5/2004 was more than 1 µg/m³, much higher than the average of 0.04 μ g/m³ in the rest of sampling periods. The data set for this sampling day was removed from the PMF modeling. Thus, a total of 220 samples collected in 2003 and 2004, and 33 species were used in the PMF modeling for Mt. Zion. Figure 4-1 illustrates the major source factors resolved by PMF based on PM_{2.5} chemical speciation data from the IMPROVE site . Seven source factors are identified. A factor with significant amount of Na, Cl and K is identified as from paper mill emissions. Vanadium (V) and Nickel, which is usually from oil combustion, is used as the signatures of the oil combustion source factor. The biomass smoke factor is dominated by OC/EC (with the presence of K), while secondary sulfate and nitrate factors are dominated by sulfate and nitrate, respectively. A mobile emission factor is identified with large fraction of EC1/EC2, and Zn. Major dust components such as silicon, calcium, iron, and potassium are present in the dust factor. Figure 4-2 shows the average contribution of each source factor to PM_{2.5} mass at the site based on the IMPROVE data available during the years 2003-2004. Smoke from biomass burning is the largest contributor to PM_{2.5} at Mt. Zion, with a contribution of 31%.

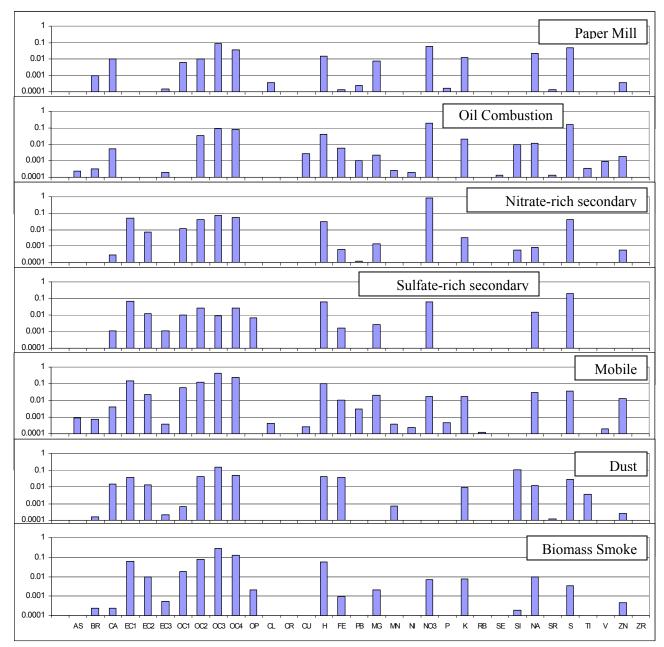


Figure 4-1. Factor profiles ($\mu g/\mu g$) resolved from PM_{2.5} samples at Mt. Zion.

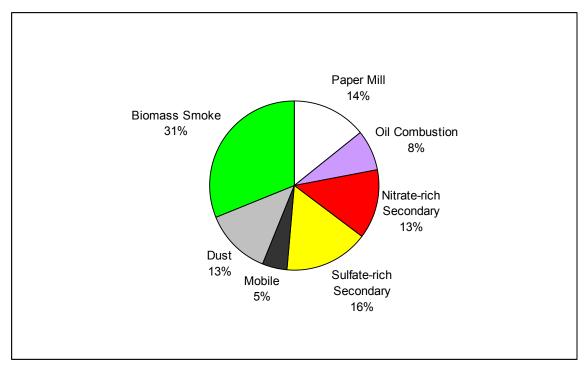
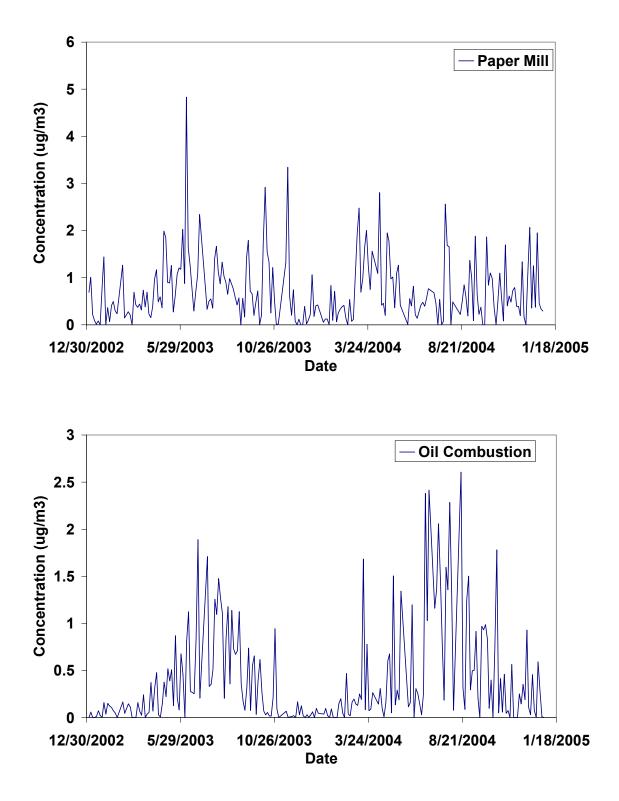
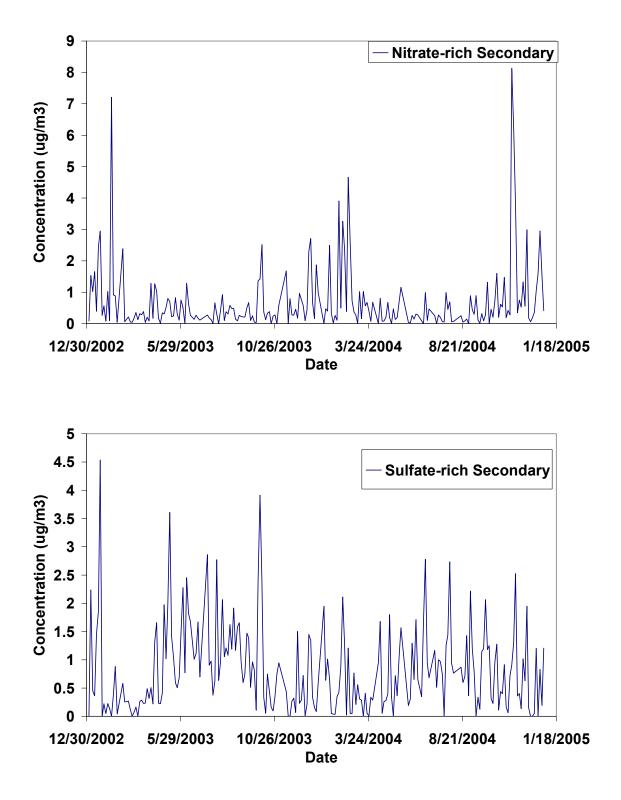
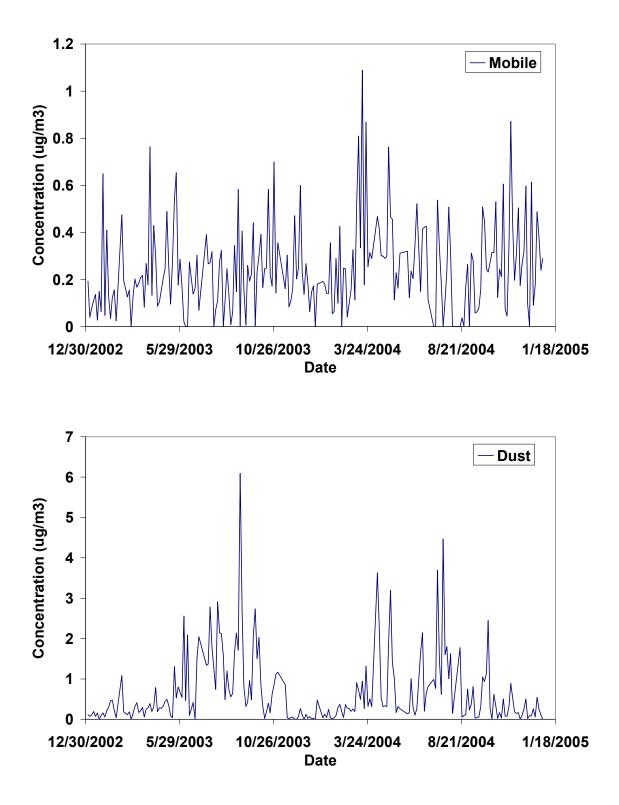


Figure 4-2. Average contribution of each factor to PM_{2.5} mass at Mt. Zion

Figure 4-3 shows the time series of contributions of each source to $PM_{2.5}$ mass during the years 2003-2004. They indicate that oil and sulfate factors contribute most during the summer season, while nitrate has the highest contribution in the winter. Smoke and dust are episodic sources – big peaks during dust and fire events, while the contributions of mobile and paper mill emissions are relatively constant throughout the year.







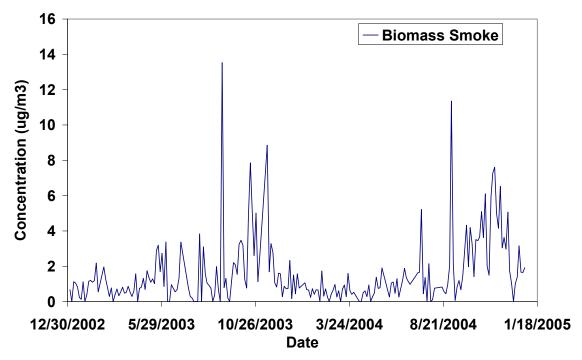


Figure 4-3. Time series of source contributions at Mt. Zion.

PMF Results for Wishram (CORI1)

A total of 237 samples collected in 2003 and 2004, and 33 species were used in the PMF modeling for Wishram. Figure 4-4 illustrates the major source factors resolved by PMF based on PM_{2.5} chemical speciation data. Five source factors are identified for Wishram. As with Mt. Zion, a biomass smoke factor is identified as dominated by OC/EC (with the presence of K), and secondary sulfate and nitrate factors are dominated by sulfate and nitrate, respectively. A mobile emission factor is identified with large fraction of EC1/EC2 and organics, as well as Zn and Pb. A dust factor dominated by mineral components silicon, calcium, iron, and potassium is identified. Figure 4-5 shows the average contribution of each source factor to $PM_{2,5}$ mass at Wishram based on the IMPROVE data available during the years 2003-2004. Smoke from biomass burning is the largest contributor to $PM_{2.5}$ at Wishram, with a contribution of 29%, followed by secondary sulfate and nitrate. Figure 4-6 shows the time series of contributions of each source to PM_{2.5} mass during the years 2003-2004. They indicate that sulfate factor contributes most during the summer season, while nitrate contributes most in the winter. Smoke and dust are episodic sources – big peaks during dust and fire pollution events, while the contributions of mobile and is relatively constant throughout the year.

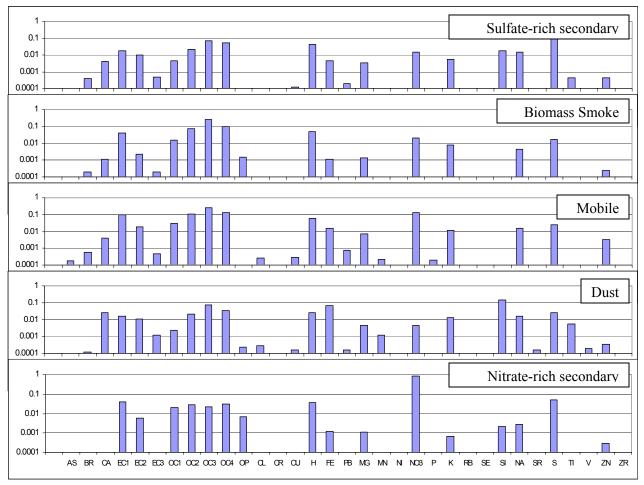


Figure 4-4. Factor profiles ($\mu g/\mu g$) resolved from PM_{2.5} samples at Wishram.

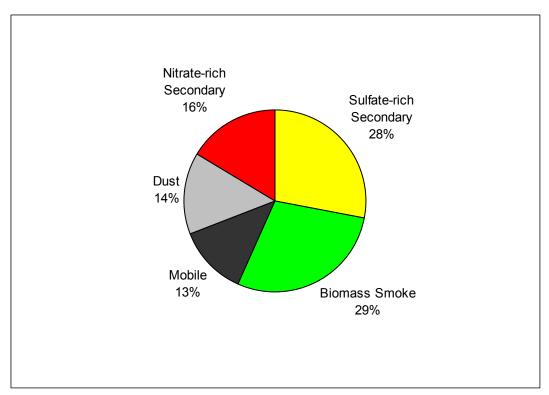
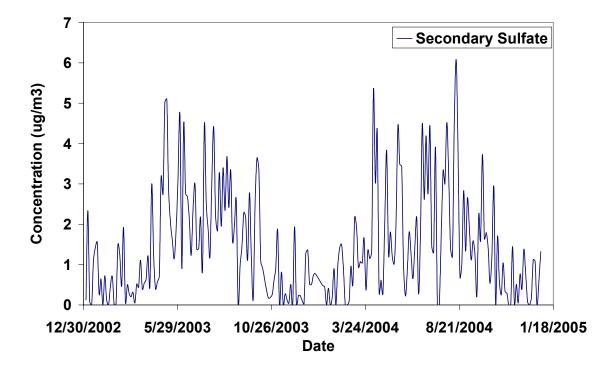
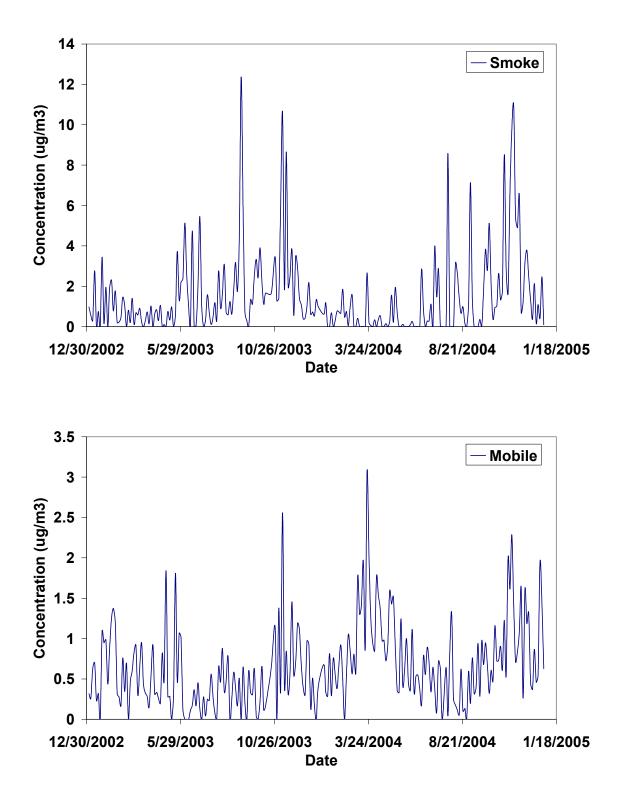


Figure 4-5. Average contribution of each factor to $PM_{2.5}$ mass at Wishram.





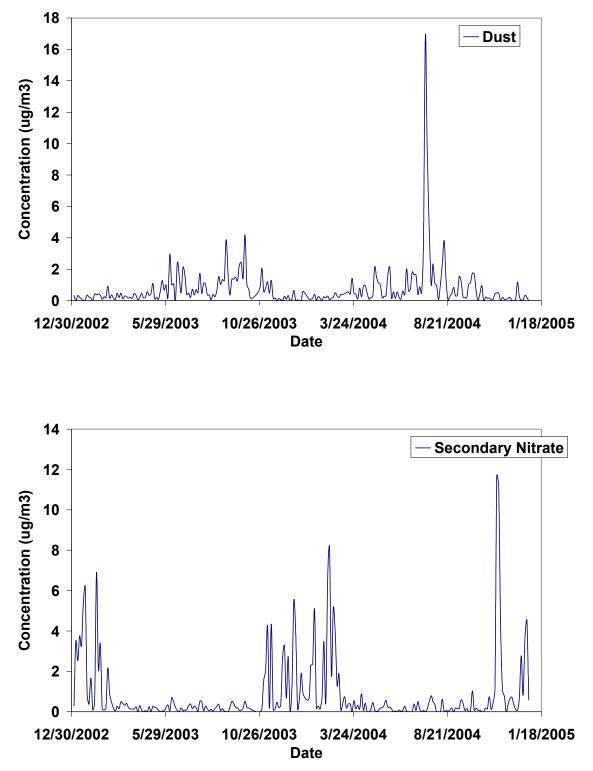


Figure 4-6. Time series of source contributions at Wishram.

PMF attribution by chemical compound and to light extinction

In the previous section we presented attribution of fine mass concentration by PMF source factor. Here we present the PMF attribution to the main chemical components of haze in the gorge- organic compounds, sulfate, and nitrate. We also use the results to generate the contribution of each factor to reconstructed light extinction (haze) at Mt Zion (Figure 4-7a and Wishram (Figure 4-7b).

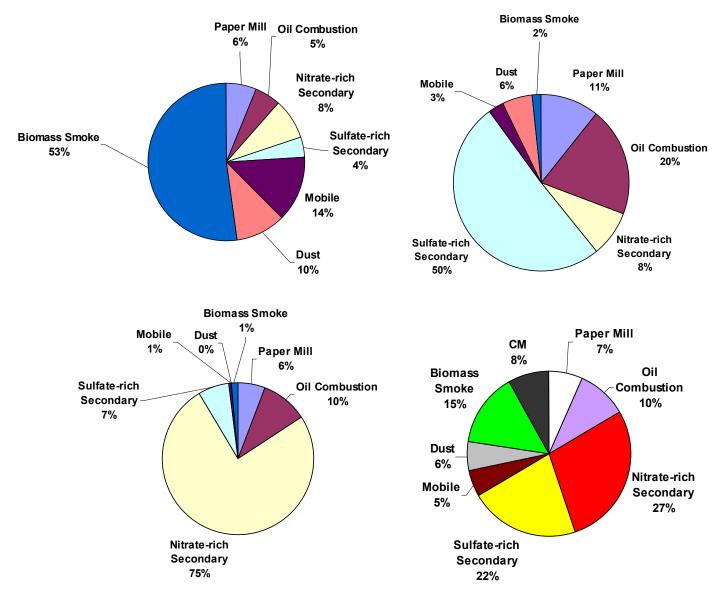


Figure 4-7a. Contribution of each source factor to Organic mass, sulfate, nitrate and reconstructed light extinction at Mt. Zion.

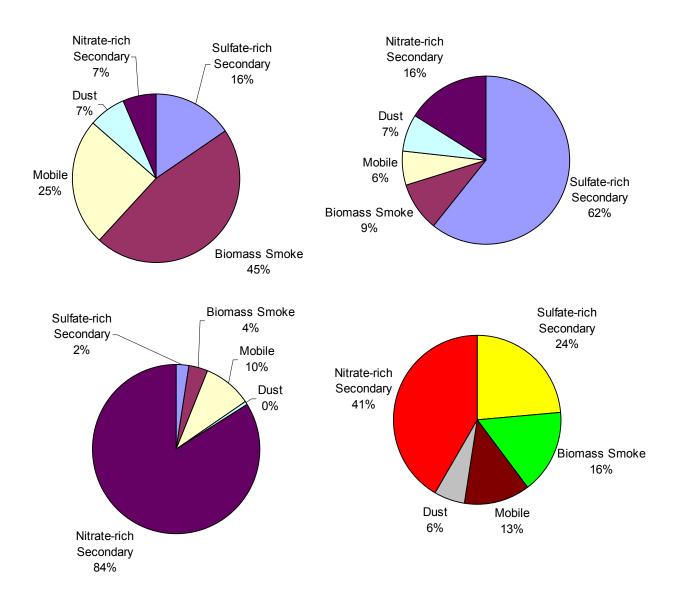


Figure 4-7b. Contribution of each source factor to Organic mass, sulfate, nitrate and reconstructed light extinction at Wishram.

Organic mass was attributed about ½ to biomass smoke at both sites, with mobile being the next largest contributor. Sulfate rich secondary contributed half the sulfate at Mt. Zion and 62% at Wishram. The oil combustion and paper mill factors were the next largest contributors to sulfate at Mt. Zion. Nitrate-rich secondary contributed about 16% of the sulfate at Wishram, suggesting a linkage between sulfate and nitrate sources at Wishram (discussed more later). The nitrate-rich secondary factor accounted for 75% of the nitrate and Mt. Zion and 84% at Wishram. The only other factors contributing significantly to nitrate were oil combustion (10%) at Mt. Zion and mobile (10%) at Wishram.

For reconstructed extinction, chemical component mass contributions for each factor were multiplied by the IMPROVE default extinction efficiencies and relative humidity growth factors. Coarse mass was not used in the PMF analysis so the coarse mass concentrations for each sample period were multiplied by the IMPROVE default value of $0.6 \text{ m}^2\text{g}^{-1}$. The nitrate-rich secondary factor was the greatest contributor to reconstructed light extinction at both sites. Sulfate-rich secondary was the second highest at both sites and biomass smoke third highest. Coarse mass plus dust was 14% of reconstructed extinction at Mt. Zion and 15% at Wishram. Oil combustion was 10% at Mt. Zion, paper mill 7% and mobile 5%. Mobile was 12% at Wishram.

PMF analysis results by wind pattern (cluster)

Percentage of PM2.5 mass attributed to each source factor by wind pattern type (cluster) at Wishram and Mt. Zion is shown in Tables 4-1 and 4-2. At Wishram, sulfate-rich secondary is the most important factor for the 3 upgorge patterns and is minor for the winter downgorge. Biomass smoke is the largest contributor to the light downgorge pattern, and is about 30% of PM2.5 mass for the light and moderate upgorge and winter downgorge. The dust factor is highest for the usually summertime moderate and strong upgorge patterns. Nitrate rich secondary is the largest factor for the winter downgorge patterns.

This summary implies most sulfate at Wishram is from the west, most nitrate is from the east, and biomass smoke comes from both east and west.

type (eruster) at wisinam.								
	Light	Moderate	Strong	Light	Winter			
	upgorge	upgorge	upgorge	downgorge	downgorge			
Percentage of PM2.5	(1)	(2)	(3)	(4)	(5)			
Sulfate-rich secondary	33	33	44	16	9			
Biomass smoke	31	28	19	37	33			
Mobile	17	12	10	16	9			
Dust	15	22	22	12	6			
Nitrate-rich secondary	5	5	5	19	44			

Table 4-1. Percentage of PM2.5 mass attributed to each source factor by wind pattern type (cluster) at Wishram.

Table 4-2. Percentage of PM2.5 mass attributed to each source factor by wind pattern type (cluster) at Mt. Zion.

	Light	Moderate	Strong	Light	Winter
Percentage of	upgorge	upgorge	upgorge	downgorge	downgorge
PM2.5	(1)	(2)	(3)	(4)	(5)
Paper Mill	14	15	19	10	6
Oil					
Combustion	8	14	14	3	1
Nitrate-rich					
secondary	10	7	9	12	34
Sulfate-rich					
secondary	17	13	16	10	19

Mobile	5	4	5	5	3
Dust	14	18	12	16	5
Biomass	20	20	25	12	20
smoke	32	29	20	43	32

At Mt. Zion, the biomass smoke factor has the largest contribution to PM2.5 mass for all wind patterns except winter downgorge, where nitrate-rich secondary is slightly higher. The paper mill factor is highest for the upgorge types, which is reasonable because the main paper mill is west of Mt. Zion. Sulfate-rich secondary ranges from 10-19 percent, is associated with both upgorge and downgorge flow and is marginally highest for winter downgorge. This result appears to conflict with the result for Wishram for which winter downgorge has the lowest sulfate factor contribution. However it could be that sources between Wishram and Mt. Zion are contributing to higher sulfate there for wind type 5 or that emissions of SO2 upwind of the gorge have not converted a large fraction of the SO2 to sulfate by the time the emissions reach Wishram (but convert more during transport to Mt. Zion). Also as we shall soon see, the nitrate-rich secondary factor at Wishram contains significant amounts of sulfate as well.

The oil combustion factor is highest for moderate and strong upgorge and near zero for the downgorge wind patterns. The dust factor is significant for all but the winter downgorge (winter only) factor. The mobile factor is small for all wind patterns. The nitrate factor is associated mainly with downgorge flow.

Sulfate attribution by wind field type

Here we give results of the PMF analysis specific to attribution of particulate sulfur to PMF factors (Tables 4-3 and 4-4). At Wishram for upgorge winds about 70-80% of the sulfate is attributed to the secondary sulfate factor. Smaller percentages are associated with Biomass smoke, mobile, and dust factors, with smoke factor associated sulfate higher with downgorge flow. An interesting finding is that for wind type 5, winter downgorge, over one-half of the sulfate is attributed to the secondary-nitrate factor. This suggests that the source or sources contributing to secondary nitrate also have substantial sulfate associated with them. (The mass contribution to nitrate from this factor is much higher than to sulfate). The Boardman power plant is a large source of SO2 and NOx in the region- precursor compounds to particulate sulfate and nitrate. Because the nitrate factor has substantial sulfate attributed to it is reasonable to suggest that the "secondary nitrate" factor may be largely a "Boardman power plant" factor. This is supported by the fact that the contribution from this factor is highest when winds are from the east (toward Wishram from the Boardman power plant).

The sulfate attribution at Mt. Zion (Table 4-4) also shows a nitrate-rich secondary factor also containing some sulfate that is most important for downgorge flows. The mass contribution to sulfate for this factor is about ½ at Mt. Zion as it is at Wishram, but the profile (ratio of nitrate to sulfate) is about the same at both locations. The sulfate-rich secondary source at Mt. Zion is higher than at Wishram (over twice in terms of mass concentration), implying additional sources of sulfate or more complete conversion as

discussed earlier. Other significant contributors to sulfate at Mt. Zion are the paper mill and oil combustion factors, both most important with upgorge flow (from the west).

	light	moderate	Strong	light	winter	
	upgorge	upgorge	upgorge	downgorge	downgorge	
Wishram	(1)	(2)	(3)	(4)	(5)	All types
% Sulfate-rich						
secondary	70	70	78	44	24	61
% Biomass						
smoke	10	9	5	15	14	10
% Mobile	8	6	4	10	5	6
% Dust	8	11	9	8	4	8
% Nitrate-rich						
secondary	5	4	4	23	53	14

Table 4-3. Percentage of sulfate attribution at Wishram by PMF factor and wind type.

Table 4-4. Percentage of sulfate attribution at Mt. Zion by PMF factor and wind type.

	light			light	winter	
	upgorge	moderate	Strong	downgorge	downgorge	
Mt Zion	(1)	upgorge (2)	upgorge (3)	(4)	(5)	All types
% Paper Mill	10	11	13	11	5	11
% Oil						
Combustion	20	33	30	13	2	23
% Nitrate-rich						
secondary	6	4	5	12	23	8
%Sulfate-rich						
secondary	53	40	44	46	64	48
% Mobile	3	2	3	5	2	3
% Dust	6	7	4	11	2	6
% Biomass						
smoke	2	1	1	4	2	2

Episode analysis

November 2004 Episode

An extended episode of high bsp at all sites occurred during early-mid November 2004. Daily averaged bsp for all nephelometer sites is shown in Figure 4-8. Also shown is the cluster number. National Weather Service sites in eastern Washington and eastern Oregon (Walla Walla, Pasco, and Pendleton) reported light winds, high RH and smoke/haze and fog leading up to and during the episode. The episode started as light upgorge flow on November 6 turned to light downgorge flow on November 7-8. Bsp levels dipped slightly with light downgorge flow on November 9 then rose with downgorge flow on November 10, which continued for a few days with a gradual reduction in daily average bsp. All sites except Sauvie Island and Steigerwald had daily average bsp peaking on November 10. Towal Road and Wishram had daily average bsp of over 200 Mm⁻¹ on November 10, and bsp on that date generally decreased from east to west. Time resolved sulfate (SO4), nitrate (NO3), and OC/EC were available for

Bonneville and Mt. Zion for this period (although Mt Zion OC/EC was only available for the early part of the episode). Hourly averaged bsp, SO4, NO3, and OC at Bonneville and Mt. Zion for November 7- November 15 are shown in Figures 4-9a and 4-9b.

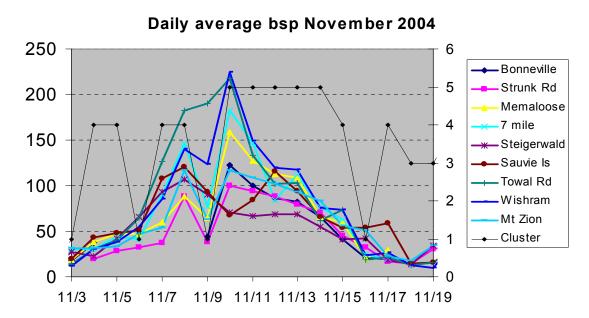


Figure 4-8. Daily average particle light scattering for the November 2004 episode.

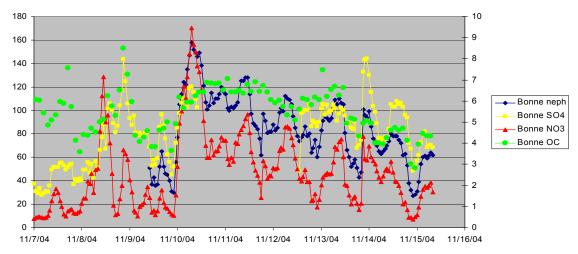


Figure 4-9a. Particle light scattering and high time resolved sulfate, nitrate, and organic carbon at Bonneville for the November 2004 episode.

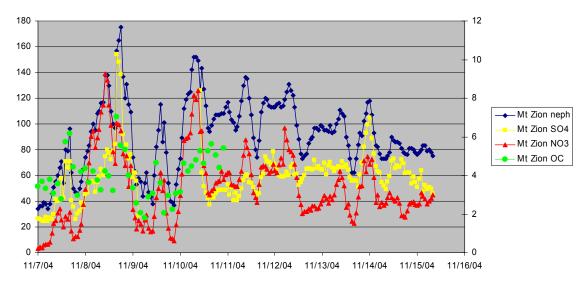


Figure 4-9b. Particle light scattering and high time resolved sulfate, nitrate, and organic carbon at Mt. Zion for the November 2004 episode.

This episode had elevated concentrations of sulfate, nitrate, and organic carbon. Sulfate concentrations were as high as 10 μ g/m3 at Mt Zion and 8 μ g/m3 at Bonneville. Nitrate reached hourly average concentrations of over 9 μ g/m3 at both locations. Peak OC concentrations were about 8 μ g/m3 at Bonneville and 7 μ g/m3 at Mt. Zion and concentrations were generally higher at Bonneville than at Mt. Zion.

Figure 4-10 compares Mt Zion and Bonneville NO3 during the episode. Mt. Zion experienced peak nitrate on November 8, Bonneville on November 10.

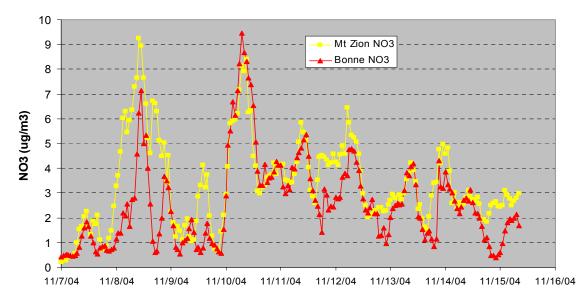


Figure 4-10. Time series of high-time resolved nitrate at Mt. Zion and Bonneville for the November 2004 episode.

Next we will compare upgorge wind component (essentially wind from the west) with bsp at the sites.

Figure 4-11 uses the Sevenmile Hill site as an example for trends in bsp and winds over the episode. Light upgorge (west to east winds) during November 5-6 transitioned to light downgorge winds during November 7-8. A steady rise is bsp was associated with this wind shift. Late in the day on November 8, winds briefly became upgorge (from the west) at about 10 mph. Concurrent with this wind shift was a large drop in bsp from over 180 Mm-1 to less than 40 Mm-1. After about 12 hours of upgorge flow, winds became downgorge near midday on November 11. Concurrent with the shift was a rapid rise in bsp to over 200 Mm-1. Bsp remained high but gradually decreased under continued light dowgorge flow over the next few days, then dropped rapidly to under 20 Mm-1 on November 15 as winds became upgorge at 10-15 mph.

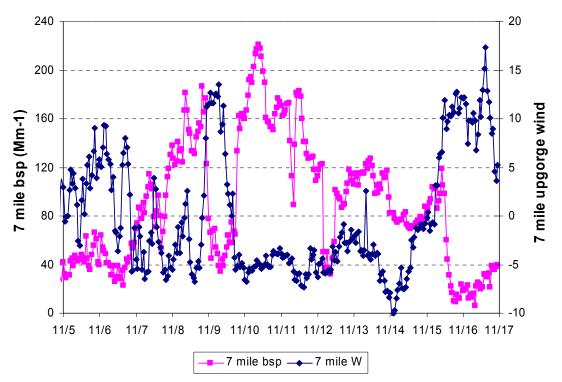


Figure 4-11. Time series of bsp and upgorge wind component at Sevenmile Hill during the November 2004 episode.

This wind/bsp pattern was common at other sites and indicates sources to the east of the Gorge as being sources of the high bsp. As levels of bsp decreased from east to west, this suggests that most impact was due to sources east of the Gorge rather than within the Gorge.

PMF results for episode

PMF results are available for Wishram and Mt. Zion. Table 4-5 gives the percentage of fine mass apportioned to each source averaged over the peak episode days with IMPROVE samples (November 8, November 11, and November 14).

Table 4-5. Percentage of fine mass apportioned by PMF to each source factor at Wishram and Mt. Zion (for the samples of 11/8,11,11, and 11/14 2004).

	Sulfate	Biomass	Mobile	Dust	Nitrate	Oil	Paper
	rich	burning			rich	combustion	mill
Mt. Zion	9.8	41.1	3.1	3.3	37.4	1.2	4.1
Wishram	2.4	43.3	7.4	1.6	45.3	NA	NA

The bulk of the fine mass was attributed to biomass burning and nitrate-rich secondary aerosol.

February 2004 episode

This episode was characterized by strong synoptic scale high pressure systems to the east of the study area. This resulted in an east to west pressure gradient and downgorge flow (cluster 5) every day from February 10-17, 2004. The downgorge flow varied in strength with variations in the pressure gradients. Figure 4-12 shows the time series of hourly averaged light scattering at the nephelometer sites.

Bsp rose rapidly (from <20 Mm⁻¹ to 80-100 Mm⁻¹) at all sites during from evening of February 10 to early morning on February 11 and were similar in magnitude at all sites early February 11. This rise coincided with an increase in downgorge at the sites, suggested transport down gorge from the east (Figure 4-13). Bsp at all but the easternmost sites decreased substantially from the morning of February 11 to midday February 12. This decrease in bsp occurred while downgorge winds were strong (Figure 4-13), suggesting a dilution of aerosol. A rise in bsp then followed, peaking in early evening on February 13 at the western sites and gradually declining the rest of the episode. The rise to a peak at the western sites occurred as downgorge winds eased, possibly reducing the dilution effect. At the eastern sites of Towal Road, Wishram, and Memaloose, bsp continued to rise until the late hours of February 14 to the early hours of February 15. During portions of the episode there were small gradients of bsp throughout the gorge and while later in the episode, large gradients existed.

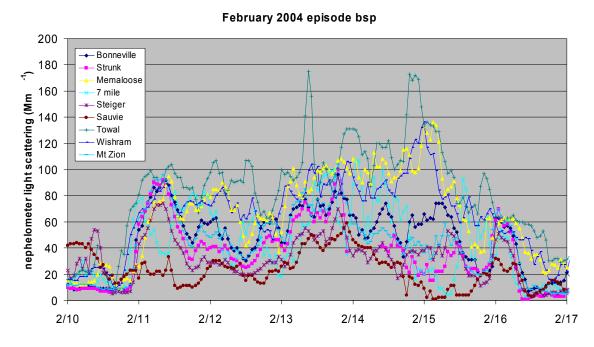
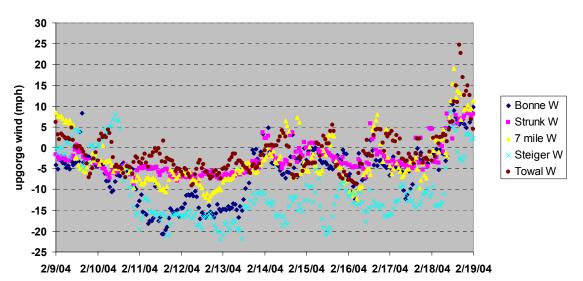


Figure 4-12. Time series of light scattering (Mm⁻¹) for February 2004 episode.

Hourly light scattering, NO3 and SO4 at Bonneville for the episode are shown in Figure 4-14. Time series of hourly light scattering, NO3, SO4, and OC at Wishram are shown in Figure 4-15. Bonneville was missing OC data for the entire period and Wishram was missing SO4 data for much of the episode. At Bonneville NO3 peaked on February 11 and was higher than at Wishram where NO3 peaked on February 12. The nearly equal light scattering peaks for Bonneville on February 11 and February 13 coincided with peaks in NO3 and SO4, respectively. The nephelometer peak at Wishram was midnight to 1 am February 15 and did not have especially high NO3 for the episode; however SO4 was missing and may have been high- Wishram had an increase in IMPROVE SO4 from 1.7 μ g/m3 on February 12 to 3.5 μ g/m3 on February 15.



February 2004 episode upgorge wind at selected sites

Figure 4-13. Upgorge wind component for February 2004 episode at selected sites.

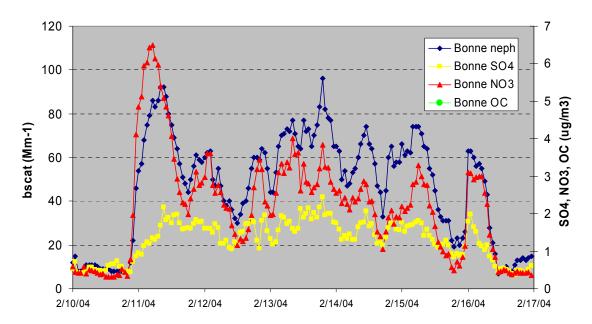


Figure 4-14. Time series of light scattering, NO3 and SO4 at Bonneville - February 2004 episode.

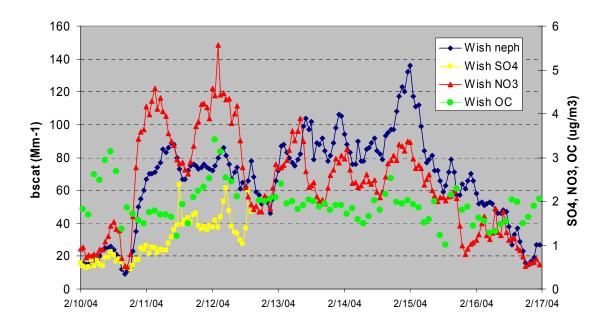


Figure 4-15. Time series of light scattering, NO3, SO4, and OC at Wishram - February 2004 episode.

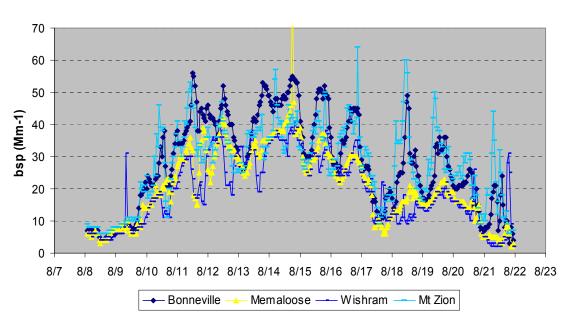
Table 4-6 shows the apportionment to source factors by PMF for the February 12 and February 15, 2004 samples. The bulk of the apportionment is to the nitrate rich factor at both sites, with sulfate-rich also important. The biomass burning factor accounted for about 10% of the fine mass at each site.

Table 4-6. Percentage of fine mass apportioned by PMF to each source factor at Wishram and Mt. Zion (for the samples of 2/12 and 2/15 2004).

	Sulfate	Biomass	Mobile	Dust	Nitrate	Oil	Paper
	rich	burning			rich	combustion	mill
Mt. Zion	29.8	9.0	2.2	2.1	49.5	0.4	7
Wishram	14.0	11.2	2.4	1.6	70.9	NA	NA

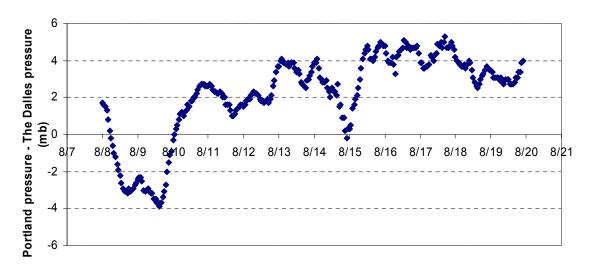
August 2004 episode

The August 2004 episode had several days of continuously elevated bsp at the nephelometer sites. Figure 4-16 shows time series of bsp at representative sites. Bsp tended higher at the western sites and Bonneville than at the eastern sites. August 8 and 9 had light downgorge flow (cluster 4) and low bsp. From August 10-14, the height of the episode, light upgorge flow prevailed (cluster 1). The pressure gradient between The Dalles and Portland Intl. Airport is shown in Figure 4-17.



August 2004 episode hourly bsp at selected sites

Figure 4-16. Time series of bsp at selected sites for the August 2004 episode.

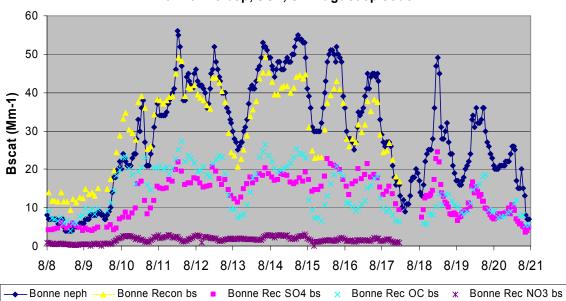


PDX-DLS pressure for August 2004 episode

Figure 4-17. Pressure at The Dalles – pressure at Portland International Airport (mb) for August 2004 episode. (Values greater than zero suggest flow from west to east (upgorge).

The pressure gradient was downgorge at the beginning of the episode, explaining the light downgorge flow observed. During August 10, the pressure gradient and flow became light upgorge and the bsp increased.

Figure 4-18 shows a time series of bsp, reconstructed bsp, and estimated bsp due to sulfate, nitrate, and organic carbon at Bonneville for the episode. Measured and reconstructed scattering compare well both in magnitude and trend. Reconstructed bsp was due about equally to sulfate and organic carbon, with a very minor contribution from nitrate.



Bonneville bsp, SO4, OC August episode

Figure 4-18. Bsp, reconstructed bsp, and estimated bsp due to sulfate, nitrate, and organic carbon for the August 2004 episode.

Figure 4-19 shows organic carbon concentration at IMPROVE sites in Washington, Idaho, and Oregon for August 13, 2004. The Wishram and Mt. Zion IMPROVE samples are not available for this date. OC concentrations were generally between 2 and 4 μ g/m3, with over 8 μ g/m3 at Sawtooth Wilderness Area. This suggests impacts from fires in the region. Figure 4-20 shows sulfate levels at IMPROVE sites in the Pacific Northwest for August 16, 2004 (Wishram and Mt. Zion again missing). Increased levels of sulfate are seen at sites in Washington and Oregon in the central and northern Cascades, Puget Sound and Olympic National Park. The high-time resolution sulfate monitor at Mt. Zion (data not shown) gave much lower values than the one at Bonneville, possibly due to a problem with the monitor at Mt. Zion.

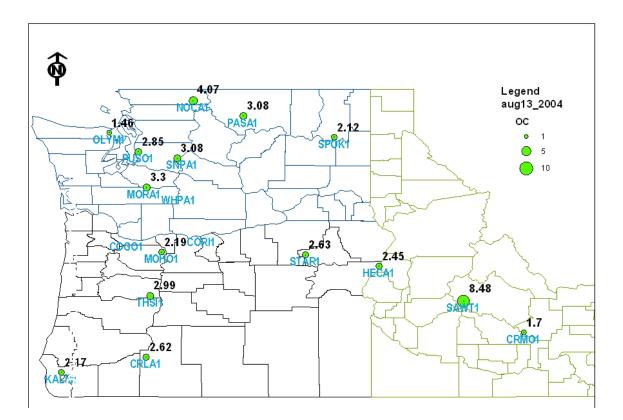


Figure 4-19. Organic carbon concentrations at IMPROVE sites in the Pacific Northwest August 13, 2004.

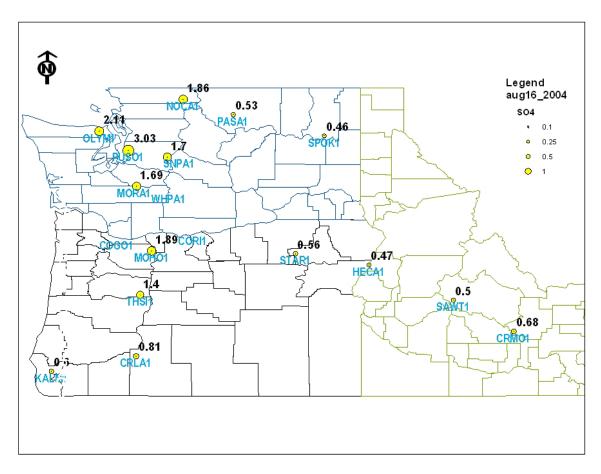
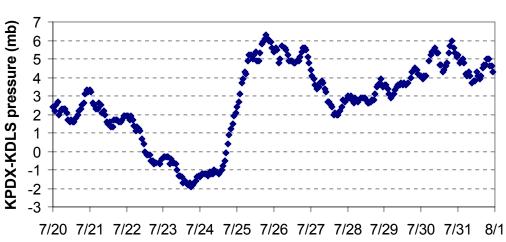


Figure 4-20. Sulfate concentrations at IMPROVE sites in the Pacific Northwest for August 16, 2004.

July 2004 episode

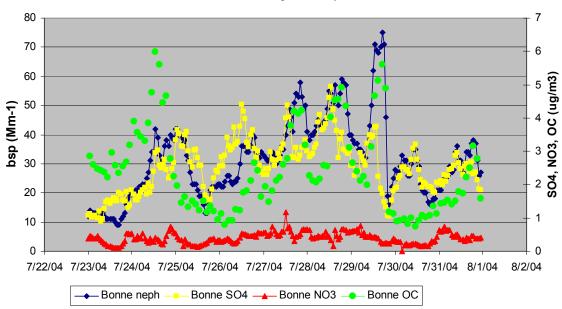
The episode began with a light downgorge flow as the pressure was higher at The Dalles than Portland (Figure 4-21). The pressure gradient changed direction late on July 24 and intensified on July 25 leading to upgorge flow the remainder of the episode. Time series of bsp, sulfate, organic carbon, and nitrate at Bonneville and Mt. Zion are shown in Figures 4-22 and 4-23.

Organic carbon and sulfate are significant at both Bonneville and Mt. Zion. As is typical in summer nitrate is low. Time series plots separately comparing bsp, sulfate, and organic carbon at Bonneville and Mt. Zion are shown in Figures 4-24 to 4-26. Bsp, sulfate, and OC track well and are quite similar magnitude for the two sites except for July 31 when sulfate and bsp are much higher at Mt. Zion. The DRUM data at Mt. Zion (Figure 4-27) and Bonneville show increases in fine sodium and potassium concurrent with increase in fine sulfur. From the PMF analysis, this suggests significant paper mill impact to particulate sulfur (sulfate) at Mt. Zion and Bonneville during this time period.



Portland to Dalles Pressure Gradient July 04 episode

Figure 4-21. Pressure at Portland minus pressure at The Dalles July 2004 episode.



Bonneville July 2004 episode

Figure 4-22. Time series of bsp (Mm⁻¹) and sulfate, nitrate, and organic carbon concentrations (µg/m3) at Bonneville for the July 2004 episode.



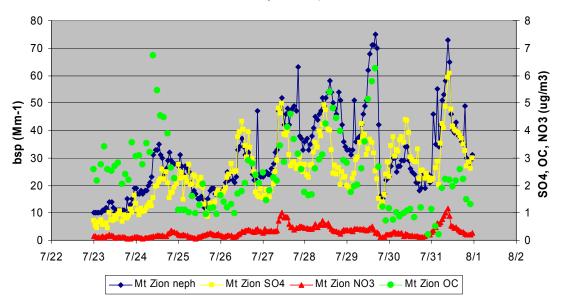
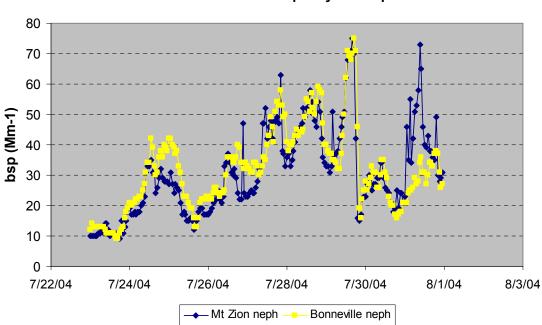
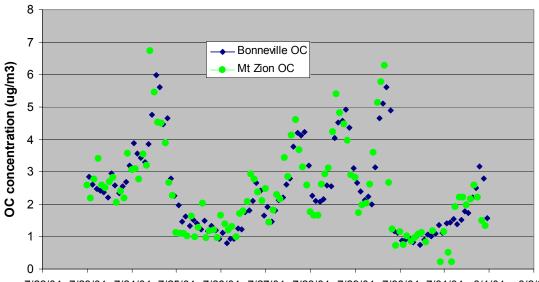


Figure 4-23. Time series of bsp (Mm-1) and sulfate, nitrate, and organic carbon concentrations at Mt. Zion, July 2004 episode.



Mt Zion and Bonneville bsp July 2004 episode

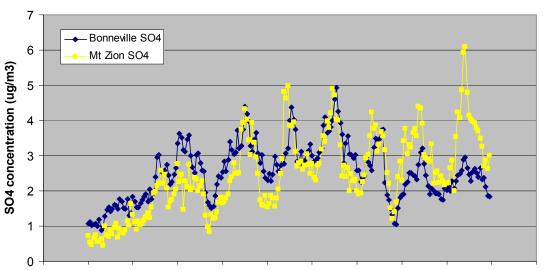
Figure 4-24. Time series of light scattering (Mm⁻¹) at Bonneville and Mt. Zion, July 2004 episode.



Bonneville and Mt Zion OC July 2004 episode

7/22/04 7/23/04 7/24/04 7/25/04 7/26/04 7/27/04 7/28/04 7/29/04 7/30/04 7/31/04 8/1/04 8/2/04

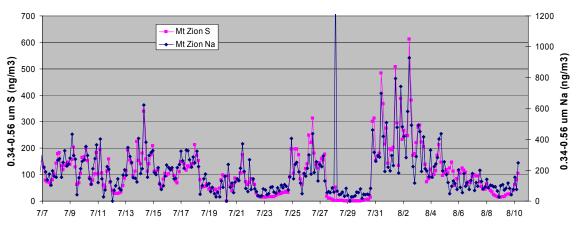
Figure 4-25. Time series of organic carbon at Bonneville and Mt. Zion July 2004 episode.



Bonneville and Mt Zion SO4 July 2004 episode

7/22/04 7/23/04 7/24/04 7/25/04 7/26/04 7/27/04 7/28/04 7/29/04 7/30/04 7/31/04 8/1/04 8/2/04

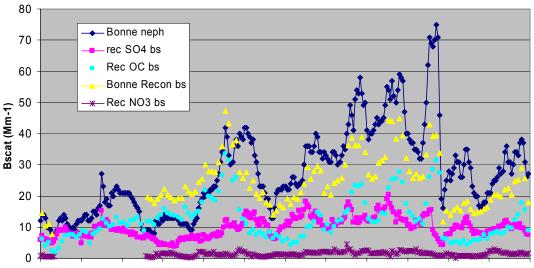
Figure 4-26. Time series of sulfate at Bonneville and Mt. Zion July 2004 episode.



Mt Zion 0.34-0.56 um S vs Na July-Aug 2004

Figure 4-27. Time series of DRUM 0.34-0.56 um particulate sulfur and sodium concentrations for the July-August DRUM samples.

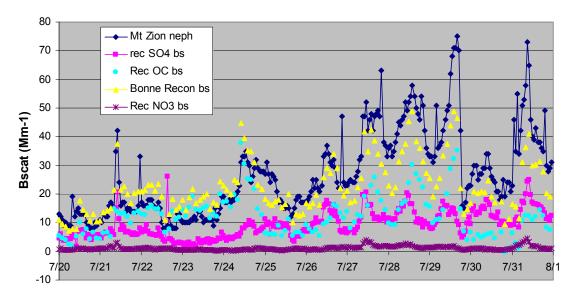
Light scattering at Bonneville and Mt. Zion was dominated by sulfate and organic carbon (Figures 4-28 and 4-29. Using sulfate, organic carbon, and nitrate, the reconstructed scattering was 90% of measured scattering at Bonneville and 85% of measured scattering at Mt. Zion. At Bonneville organic compounds contributed an estimated 45% of scattering, sulfate 36%, and nitrate 5%. At Mt. Zion results were quite similar, with organic compounds contributing an estimated 46% of scattering, sulfate 35%, and nitrate 4%.



Bonneville measured and reconstructed bsp July episode

7/20/04 7/21/04 7/22/04 7/23/04 7/24/04 7/25/04 7/26/04 7/27/04 7/28/04 7/29/04 7/30/04 7/31/04 8/1/04

Figure 4-28. Time series of measured and reconstructed scattering and scattering by major components at Bonneville - July 2004 episode. Reconstructed light scattering is computed for sulfate, nitrate, and organic carbon compounds only.



Mt Zion measured and reconstructed bsp July 2004 episode

Figure 4-29. Time series of measured and reconstructed scattering and scattering by major components at Mt. Zion - July 2004 episode. Reconstructed light scattering is computed for sulfate, nitrate, and organic carbon compounds only.

Concentrations of organic carbon and sulfate on July 29, 2004 at IMPROVE sites in Washington, Oregon, and Idaho are shown in Figures 4-30 and 4-31. OC concentrations were high throughout the region ranging from about 4-7 μ g/m3, except less than 3 μ g/m3 at Mt. Zion. This widespread distribution of high OC suggest impacts form forest fires. Sulfate concentrations were less regionally consistent, highest near the Gorge and the Puget Sound area and low east of the Cascades.

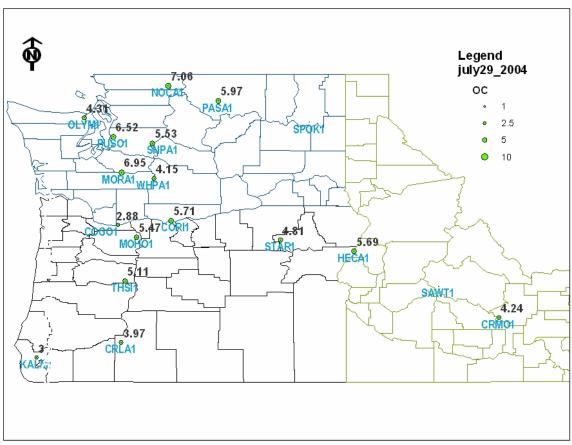


Figure 4-30. Organic carbon concentrations at IMPROVE sites in the Pacific northwest, July 29, 2004.

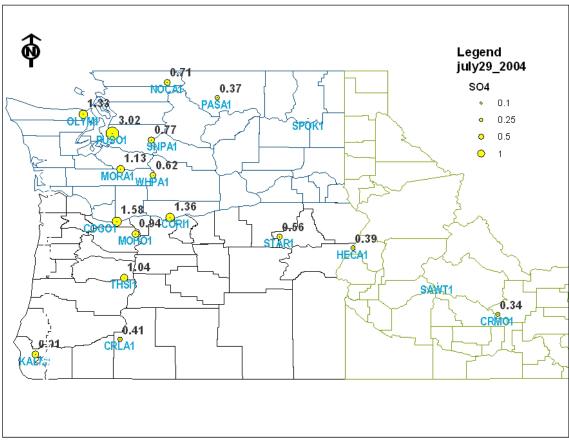


Figure 4-31. Sulfate concentrations at IMPROVE sites in the Pacific northwest, July 29, 2004.

Summary of Episode Analyses

The November 2004 episode was the most severe in terms of an extended period of high light scattering. Biomass burning and nitrate-rich secondary factors were the major factors. Substantial sulfate was measured as well. The nitrate and sulfate may have been in large part due to the Boardman power plant. The biomass burning may be from residential wood combustion in the Columbia River Basin.

The February 2004 episode was mainly nitrate-rich and sulfate-rich secondary. This may be mainly from Boardman power plant and urban emissions in the Columbia River Basin.

The August 2004 episode was mainly SO4 and OC dominated. Fires likely caused much of the OC. Sulfate was from unspecified sources to the west of the Gorge.

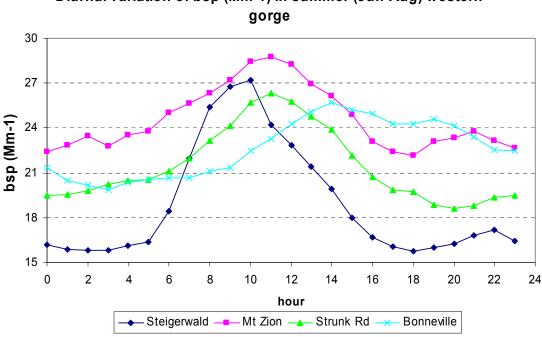
The July 2004 episode was due mainly to OC and sulfate. Again fires were the main cause of the OC. Presence of sodium and potassium noted in the DRUM data suggest paper mill contribution to the sulfate.

5. Brief discussion of hypotheses tested

The planning documents for the study (e.g. Green, 2001) laid out a series of hypotheses that many components of the field study were designed to test. The measurements needed to test these hypotheses were not all funded. We may address some of the hypotheses to a limited extent but conclusions are more speculative because of the limitations of the measurement program.

HYPOTHESIS 1: In the summer and early fall, visibility in the gorge, in particular the west end is significantly impacted by the Portland, Oregon/Vancouver, Washington metropolitan area and to a lesser extent other regional sources (Kelso/Longview, Centralia powerplant, Seattle/Tacoma, Vancouver B.C.).

The haze gradient study showed an increase in light scattering that propagated eastward through the gorge on days with winds from the Portland/Vancouver metropolitan area (Figure 5-1). This increase of light scattering coincided with an increase in wind speed to the east and was followed by a decrease in scattering later in the days as stronger winds and increased vertical mixing diluted the aerosol. The major components of light scattering in summer are organics and sulfate. Paper mills were responsible for about 6% of the light extinction in the western Gorge (Mt. Zion).



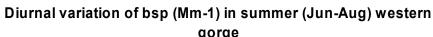


Figure 5-1. Diurnal pattern of particle light scattering in summer in the western Gorge.

HYPOTHESIS 2: Visibility in the gorge, in particular, the east end is significantly impacted by urban and industrial sources in or near the gorge plus regional sources north and east of the gorge in the Columbia River basin in winter

The haze gradient study showed that the highest light scattering throughout the gorge occurs during easterly (downgorge) wind conditions. These conditions occur mainly in winter. The highest scattering is east of the Gorge at Towal Road and generally decreases through the Gorge to the west. This pattern suggests major impacts to visibility in the Gorge from sources to the east of the Gorge. The occurrence of nitrate and sulfate together in the nitrate-rich secondary PMF factor suggests a large source (e.g. Boardman power plant) being largely responsible for this factor. This factor is greatest at Wishram and Mt. Zion with flow from the east. The biomass smoke factor is the second highest contributor to PM2.5 during the easterly flow days – this could be due to wood combustion in the Columbia River Basin cities and towns in winter. It was also noted that for downgorge flow an increase in light scattering occurs at monitors on either side of The Dalles. Also, when the wind shifts from westerly to easterly the scattering at Sevenmile Hill increases. These findings suggest impacts of local sources in or near The Dalles. It should be noted that this increase is a small fraction of the total light scattering.

HYPOTHESIS 3: SO_2 and NO_X emissions from the Boardman coal-fired power plant just east and south of the gorge interact with ammonia from adjacent feed lots, in the presence of frequent low clouds and fog in winter to produce significant quantities of ammonium sulfate and ammonium nitrate that then moves into the gorge under drainage and larger scale pressure gradient flows.

As noted above, the PMF and wind pattern analysis suggest that the Boardman power plant is contributing significantly to sulfate and nitrate in the Gorge during winter.

HYPOTHESIS 4: Sources within the gorge are only minor contributors to aerosol and haze in the gorge.

As noted above, the haze gradient study indicated that sources within the Gorge did contribute to scattering in the Gorge. This was noted for easterly flow or periods with diurnally varying flow direction. The increase due to sources within the Gorge appeared to be a small fraction of overall light scattering.

HYPOTHESIS 5: Smoke from wildfires, prescribed fires, agricultural burning, and home heating occasionally causes significant visibility degradation in the gorge and surrounding areas.

The PMF analysis attributed 15% of the light extinction at both Wishram and Mt. Zion to smoke. The smoke factor was important both in winter and summer- fall, suggesting contributions from all the sources listed in the hypothesis.

References:

Allen, G.A.; Lawrence, J.; and Koutrakis, P. (1999). "Field validation of a semicontinuous method for aerosol black carbon (aethalometer) and temporal patterns of summertime hourly black carbon measurements in southwestern Pennsylvania", Atmospheric Environment **33**, 817~823.

Bench, G., Grant, P., Ueda, D., Cliff, S., Perry, K., Cahill, T. (2002). The Use of STIM and PESA to Measure Profiles of Aerosol Mass and Hydrogen Content, Respectively, across Mylar Rotating Drum Impactor Samples, Aerosol Sci. and Tech. 36: 642–651.

Birch, M.E.; and Cary, R.A. (1996). "Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust." *Aerosol Science and Technology* **25**, 221-241.

Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., and Merrifield, T. (2001). Comparison of IMPROVE and NIOSH Carbon Measurements, Aerosol, Sci. Technol, **34**, 23-34.

Draxler, R. R. and G. D. Hess, Description of the Hysplit_4 modeling system. Report No. NOAA Tech Memo ERL ARL-224, December 1997. Prepared by Air Resources Laboratory, NOAA, Silver Spring, MD, 1997.

Green, M.; Arnott, P.; Walker, J.; and Etyemezian, V., 2003. Comparison of IMPROVE and NIOSH methods for elemental carbon aerosol measurements with a photoacoustic method in a wintertime urban desert environment. Abstracts of the 2003 European Aerosol Conference, *J. Aer. Sci.*, **34**, s1149-s1150.

Green, M., (2001). COLUMBIA RIVER GORGE VISIBILITY AND AIR QUALITY STUDY, Working Draft: Existing Knowledge and Additional Recommended Scientific Assessment to Consider. Prepared for Robert Bachman, US Forest Service, Portland, Oregon.

Interagency Monitoring of Protected Visual Environments (IMPROVE) – Data resources. National Park Service, Ft. Collins, CO. <u>http://vista.cira.colostate.edu/improve</u>, 2004.

Kim, E., P. K. Hopke, and E. S. Edgerton, Source identification of Atlanta aerosol by positive matrix factorization, *J. Air & Waste Manage. Assoc.*, 53:731-739, 2003.

Knochel, Basic Principles of XRF with Synchrotron Radiation, 2nd International Workshop on XRF and PIXE Applications in Life Science, Capri, Italy, 29-30 June, 1989, World Scientific Publishing Co., Singapore, 1990.

Liu, W, P. K. Hopke, and R. A. VanCuren, Origins of fine aerosol mass in the western United States using positive matrix factorization, *J. Geophys. Res.*, 108, D23, 4716, doi:10.1029/2003JD003678, 2003.

Lundgren, D. A., An Aerosol Sampler for Determination of Particle Concentration as a Function of Size and Time, J. Air Poll. Cont. Assoc. 17, 225-229 (1967).

Malm, W.C., J.F. Sisler, D. Huffman, R.A. Eldred, and T.A. Cahill. Spatial and seasonal trends in particle concentration and optical extinction in the United States. *Journal of Geophysical Research*, VOL. 99, No. D1, 1347-1370, 1994.

Malm, W. C., B. A. Schichtel, M. L. Pitchford, L. L. Ashbaugh, and R. A. Eldred, Spatial and monthly trends in speciated fine particle concentration in the United States, *J. Geophys. Res.*, 109, D03306, doi:10.1029/2003JD003739, 2004.

Molenar, J. "Theorectical and Experimental Analysis of the Optec NGN nephelometer". http://vista.cira.colostate.edu/improve/Publications/GrayLit/gray_literature.htm accessed February 2006.

Moosmuller, H. (1998). "Photoacoustic and filter measurements related to aerosol light absorption during the Northern Front Range Air Quality Study (Colorado 1996/1997)", *JGR*, **103**, issue D21, 28149-28157.

Raabe,O.G., Braaten, D.A., Axelbaum, R.L., Teague,S.V., Cahill, T.A. "Calibration studies of the DRUM impactor", J. Aerosol Sci., **1988**,19,183.

Visibility Information Exchange Web System (VIEWS) Database. Cooperative Institute for Research in the Atmosphere (CIRA), Colorado State University, Ft. Collins, CO. <u>http://vista.cira.colostate.edu/views/</u>, 2004.

Watson, J.G., Visibility: Science and regulation. J. Air & Waste Management Assoc., 52(6):628-713, 2002.