Causes of Haze in the Gorge (CoHaGo)

Final Report

Submitted to:
Southwest Clean Air Agency
11815 NE 99th St.
Suite 1294
Vancouver, WA 89683

Prepared for:
Paul Mairose

By:
Mark Green
Jin Xu
Narendra Adhikari
George Nikolich

Desert Research Institute
Nevada System of Higher Education
2215 Raggio Parkway
Reno, NV 89512

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Table of Contents

Table of Contents................................................................................................................ 2
List of Tables ....................................................................................................................... 4
List of Figures .................................................................................................................... 5
1. Introduction ..................................................................................................................... 9
   1.1 Summary of the Haze Gradient Study ................................................................. 9
   1.2 Overview of field study design ....................................................................... 15
2. Field measurement program ......................................................................................... 17
3. Statistical Description of Data ...................................................................................... 20
   3.1 Summary of the International Aerosol Sampler (IAS) data ................................ 20
   3.2 Comparison of IMPROVE and IAS aerosol data .............................................. 23
   3.3 Comparison between DRUM and filter data ................................................. 24
   3.4 Comparisons between filter and high time resolved data ......................... 29
   3.5 Optec nephelometers and Radiance nephelometers comparison .................... 33
   3.6 Comparison between Optec nephelometer measured and reconstructed aerosol
       light scattering coefficients ............................................................................ 36
   3.7 Comparison between Radiance nephelometer measured and IMPROVE
       reconstructed dry (RH<=50%) aerosol light scattering coefficients ................... 40
   3.8 Relationship between high time resolution chemical measurements and aerosol
       light scattering coefficient .............................................................................. 40
   3.9 Relationship between Aethalometer EC and Sunset Laboratory EC ............... 45
   3.10 Ion balance ..................................................................................................... 48
   3.11 Data Quality Summary Table ....................................................................... 52
4. Attribution ..................................................................................................................... 55
   4.1 PMF analysis ...................................................................................................... 55
      4.1.1 Methodology .............................................................................................. 55
      4.1.2 PMF Results for Mt. Zion (COGO1) ..................................................... 56
      4.1.3 PMF Results for Wishram (C0RII) ...................................................... 58
      4.1.4 PMF attribution by chemical compound and to light extinction ............ 67
      4.1.5 PMF analysis results by wind pattern (cluster) ......................................... 69
      4.1.5.a Sulfate attribution by wind field type .................................................. 71
      4.1.6 PMF analysis using cation data during 2004 ........................................... 72
   4.2 Episode analysis ................................................................................................. 74
      4.2.1 November 2004 Episode ....................................................................... 74
         4.2.1.a PMF results for episode ................................................................ 81
      4.2.2 February 2004 episode ........................................................................... 81
      4.2.3 August 2004 episode .............................................................................. 84
      4.2.4 July 2004 episode .................................................................................. 88
   4.3 Summary of Episode Analyses ....................................................................... 95
5. Brief discussion of hypotheses tested ........................................................................... 96
6. Brief answers to Causes of Haze in the Gorge Questions ............................................ 98
   6.1 What aerosol components are responsible for haze? .................................... 98
      6.1.1 What are the major components for best, worst, and average days and how
            do they compare? ................................................................................... 98
6.1.2 How variable were the major components episodically, seasonally, inter-annually, spatially? ................................................................. 98
6.1.3 How do the relative concentrations of the major components compare with the relative emission rates nearby and regionally? .................. 98
6.2 What is meteorology’s role in the causes of haze? ......................................................... 99
6.2.1 How do meteorological conditions differ for best, worst and typical haze conditions? .................................................................................. 99
6.2.2 What empirical relationships are there between meteorological conditions and haziness? ................................................................................. 99
6.2.3 How does the spatial difference in meteorology and climate between west and east Scenic Area account for the haze differences observed between west and east Scenic Area? ................................................................. 99
6.2.4 How well can haze conditions be predicted solely using meteorological factors? ......................................................................................... 99
6.2.5 How well can inter-annual variations in haze be accounted for by variations in meteorological conditions? ......................................................... 99
6.3 What are the emission sources responsible for haze? ..................................................... 100
6.3.1 What geographic areas are associated with transported air that arrives at sites on best, typical and worst haze days? .............................. 100
6.3.2 Are the emission characteristics of the transport areas consistent with the aerosol components responsible for haze? ........................................ 100
6.3.3 What do the aerosol characteristics on best, typical and worst days indicate about the sources? ................................................................. 100
6.3.4 What does the spatial and temporal pattern analysis indicate about the locations and time periods associated with sources responsible for haze? 100
6.3.5 What evidence is there for urban impacts on haze and what is the magnitude and frequency when evident? .............................................. 100
6.3.6 What connections can be made between sample periods with unusual species concentrations and activity of highly sporadic sources (e.g., major fires and dust storms, point source activity changes such as aluminum plant shut-downs, etc.)? ............................................................... 100
6.3.7 What can be inferred about impacts from sources in other regions? .................. 101
6.4 Are there detectable and/or statistically significant multi-year trends in the causes of haze? ......................................................................................... 101
6.4.1 Are the aerosol components responsible for haze changing? .................................. 101
6.4.2 Where aerosol component changes are seen, are they the result of meteorological or emissions changes? ........................................ 101
6.4.3 Where emissions are known to have changed, are there corresponding changes in haze levels? (e.g., aluminum plant shutdowns or emission controls on the Centralia Power Plant)? ..................................................... 101
7. Conceptual Model for Haze in the Columbia River Gorge .......................................... 102
7.1 Meteorological relationship to transport of pollutants and haze levels ................. 102
7.2 Aerosol species and source contributions to haze levels ........................................... 103
8. References .................................................................................................................. 105
List of Tables

Table 1-1. Percentage of days in each month assigned to each cluster type. ............... 13
Table 2-1. Summary of Measurement Program. .............................................................. 19
Table 3-1. Aerosol major chemical components. ............................................................. 21
Table 3-2. f(RH) for small and large size distribution sulfate and nitrate (a sea salt). .... 37
Table 3-3. Annual average estimated sulfate and nitrate compound concentrations and percentage of total. Concentrations include the sulfate or nitrate mass only and do not include the mass of associated compounds such as ammonium, etc. Note that some sulfate is likely sodium sulfate directly emitted from Kraft recovery boilers.. 52
Table 3-4. Recommended uses and limitations of study measurements. ...................... 53
Table 4-1. Percentage of PM$_{2.5}$ mass attributed to each source factor by wind pattern type (cluster) at Wishram................................................................. 70
Table 4-2. Percentage of PM$_{2.5}$ mass attributed to each source factor by wind pattern type (cluster) at Mt. Zion................................................................. 70
Table 4-3. Percentage of sulfate attribution at Wishram by PMF factor and wind type. 72
Table 4-4. Percentage of sulfate attribution at Mt. Zion by PMF factor and wind type. 72
Table 4-5. Fraction of measurements that were below detection limits in 2004. .......... 73
Table 4-6. Comparison of PMF modeling results: percentage contributions of source factors to PM$_{2.5}$ mass concentrations................................................. 75
Table 4-7. Percentage of fine mass apportioned by PMF to each source factor at Wishram and Mt. Zion (for the samples on November 8, 11, and 14, 2004). ........ 81
Table 4-8. Percentage of fine mass apportioned by PMF to each source factor at Wishram and Mt. Zion (for the samples of February 12 adn 15, 2004). .......... 84
Table 4-9. Percentage of fine mass apportioned by PMF to each source factor at Mt. Zion and Wishram for the samples taken July 26 and 29, 2004. .......... 92
Table 6-1. Data available at Wishram........................................................................ 101
Table 7-1. Component contributions to reconstructed extinction using the new IMPROVE protocol at Mt. Zion and Wishram. ................................. 103
List of Figures

Figure 1-1. Regional setting of monitoring sites. ......................................................... 9
Figure 1-2. a) Western (Sauvie Island, Steigwald, Mt. Zion, and Strunk Road); b) Central (Bonneville, Memaloose State Park, and Sevenmile Hill); c) Eastern (Memaloose, Sevenmile Hill, Wishram, and Towal Road) monitoring sites in the Gorge. ........................................................................................................................ 10
Figure 1-3. 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). ........................................................................... 12
Figure 1-4. Daily average upgorge wind speed by cluster for each monitoring site (miles per hour). .................................................................................................................. 13
Figure 1-5. Frequency of occurrence of each cluster by month. ........................................ 14
Figure 1-6. Average $b_{sp}$ (Mm$^{-1}$) at each nephelometer site for each cluster. Average is over all hours for all days within each cluster. .................................................. 15
Figure 3-1. Comparison between measured and reconstructed PM$_{2.5}$ mass. ............ 21
Figure 3-2. Comparison between measured and reconstructed PM$_{2.5}$ mass after removing the three outliers. .................................................................................. 22
Figure 3-3. PM$_{2.5}$ chemical speciation based on IMPROVE-like samples. .................... 22
Figure 3-4. PM$_{2.5}$ chemical speciation ($\mu$g/m$^3$) based on IMPROVE data (7/2003 - 12/2004) collected at COGO1 (Mt. Zion) and CORI1 (Wishram). ....................... 24
Figure 3-5. Comparison of seasonally averaged IMPROVE and IAS data during: a) summer, b) fall, and c) winter ............................................................. 25
Figure 3-6. Comparison between DRUM and IAS filter measured: a) sulfur, b) silicon, and c) calcium concentrations for PM$_{2.5}$ at Bonneville. ........................................ 27
Figure 3-7. Comparison between DRUM and IMPROVE filter measured: a) sulfur, b) silicon, and c) calcium concentrations for PM$_{2.5}$ at Mt. Zion. .......................... 28
Figure 3-8. Comparison between 24-hour averages of high time-resolved: a) SO$_4^{2-}$, b) NO$_3^-$, c) OC, d) EC, and e) TC and measurements and IMPROVE daily filter measurements at Mt. Zion. ................................................................. 30
Figure 3-9. Comparison between 24-hour averages of high time-resolved: a) SO$_4^{2-}$, b) NO$_3^-$, c) OC, d) EC, and e) TC measurements and IMPROVE daily filter measurements at Wishram. ................................................................. 31
Figure 3-10. Comparison between 24-hour average of high time-resolved: a) SO$_4^{2-}$, b) NO$_3^-$, c) OC, d) EC, and e) TC measurements and daily IAS filter measurements at Bonneville. .............................................................................. 32
Figure 3-11. Average ratio of Optec nephelometer light scattering to Radiance Research nephelometer light scattering by integer-relative humidity value. ............ 34
Figure 3-12. Example time series comparison of Optec and Radiance Research light scattering at Mt. Zion ................................................................. 34
Figure 3-13. Scatterplot of Optec light scattering versus Radiance Research light scattering adjusted by RH, Mt. Zion ................................................................. 35
Figure 3-14. Scatterplot of Optec light scattering versus Radiance Research light scattering adjusted by RH, Wishram. ................................................................. 35
Figure 3-15. Calculated wet light scattering coefficient of PM$_{10}$ using IMPROVE aerosol data from Wishram versus daily average Optec nephelometer measured aerosol light scattering coefficient at Wishram. .......................................................... 38
Figure 3-16. Contribution of major chemical components to aerosol light extinction (light scattering + light absorption by LAC) coefficient at Wishram.......................... 38
Figure 3-17. Calculated wet light scattering coefficient of PM$_{10}$ using IMPROVE aerosol data from Mt. Zion versus daily average Optec nephelometer measured aerosol light extinction coefficient at Mt. Zion. .......................................................... 39
Figure 3-18. Contribution of major chemical components to aerosol light extinction (light scattering + light absorption by LAC) coefficient at Mt. Zion. ...................... 39
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.......................................................... 41
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 .......................................................... 41
Figure 3-21. Calculated "dry" light scattering coefficient of PM$_{10}$ using IMPROVE aerosol data from Mt. Zion versus daily average measured aerosol light extinction coefficient at Mt. Zion. .......................................................... 42
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.......................................................... 42
Figure 3-23. Relationship between measured aerosol light scattering coefficient ($b_{sp}$, Mm$^{-1}$) and sum of light scattering due to OC, sulfate, and nitrate in Bonneville........ 43
Figure 3-24. Average contribution to aerosol light scattering at Bonneville ................. 43
Figure 3-25. Relationship between measured aerosol light scattering coefficient ($b_{sp}$, Mm$^{-1}$) and sum of light scattering due to OC, sulfate, and nitrate at Mt. Zion ....... 44
Figure 3-26. Relationship between measured aerosol light scattering coefficient ($b_{sp}$, Mm$^{-1}$) and sum of light scattering due to OC, sulfate, and nitrate at Wishram ........ 45
Figure 3-27. Relationship between Optec measured aerosol light scattering coefficient ($b_{sp}$, Mm$^{-1}$) and sum of light scattering due to OC, sulfate, and nitrate at Mt. Zion.. 46
Figure 3-28. Relationship between Optec measured aerosol light scattering coefficient ($b_{sp}$, Mm$^{-1}$) and sum of light scattering due to OC, sulfate, and nitrate at Wishram. 46
Figure 3-29. Sunset Laboratory EC concentration ($\mu$g/m$^3$) versus aethalometer-derived EC ($\mu$g/m$^3$) at Mt. Zion.......................................................... 47
Figure 3-30. Sunset Laboratory EC concentration ($\mu$g/m$^3$) versus aethalometer-derived EC ($\mu$g/m$^3$) at Wishram .......................................................... 47
Figure 3-31. Monthly average ratio of positive to negative charge at Mt. Zion and Wishram....................................................................................... 48
Figure 3-32. Estimated monthly average concentration of sulfate in the form of ammonium bisulfate, ammonium sulfate, and unexplained sulfate for Mt. Zion, 2004. For Figures 3-32 to 3-35, estimates are done individually by sample and then averaged over the number of samples per month. .............................................. 50
Figure 3-33. Estimated monthly average concentration of sulfate in the form of ammonium bisulfate, ammonium sulfate, and unexplained sulfate for Mt. Zion, 2004. .......................... 50
Figure 3-34. Estimated monthly average concentration of nitrate in the form of ammonium nitrate, sodium nitrate, potassium nitrate, and unexplained nitrate for Wishram, 2004.

Figure 3-35. Estimated monthly average concentration of nitrate in the form of ammonium nitrate, sodium nitrate, potassium nitrate, and unexplained nitrate for Mt. Zion, 2004.

Figure 4-1. Factor profiles (µg/µg) 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. Time series of: a) paper mill, b) oil combustion, c) nitrate-rich secondary, d) sulfate-rich secondary, e) mobile, f) dust, and g) biomass smoke source contributions at Mt. Zion.

Figure 4-4. Factor profiles (µg/µg) 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: a) secondary sulfate, b) smoke, c) mobile, d) dust, and e) secondary nitrate source contributions at Wishram.

Figure 4-7. Contribution of each source factor to organic mass, sulfate, nitrate, and reconstructed light extinction at: a) Mt. Zion and b) Wishram.

Figure 4-8. Source profiles for Mt. Zion based on PMF modeling for 2004 only.

Figure 4-9. Source profiles for Wishram based on PMF modeling for 2004 only.

Figure 4-10. Daily average particle light scattering for the November 2004 episode.

Figure 4-11. Particle light scattering and high time-resolved sulfate, nitrate, and organic carbon at: a) Bonneville and b) Mt. Zion for the November 2004 episode.

Figure 4-12. Time series of high time-resolved nitrate at Mt. Zion and Bonneville for the November 2004 episode.

Figure 4-13. Time series of b$_{sp}$ and upgorge wind component at Sevenmile Hill during the November 2004 episode.

Figure 4-14. Time series of light scattering (Mm$^{-1}$) for the February 2004 episode.

Figure 4-15. Upgorge wind component for the February 2004 episode at selected sites.

Figure 4-16. Time series of light scattering, NO$_3$, and SO$_4$ at Bonneville during the February 2004 episode.

Figure 4-17. Time series of light scattering, NO$_3$, SO$_4$, and OC at Wishram during the February 2004 episode.

Figure 4-18. Time series of b$_{sp}$ at selected sites for the August 2004 episode.

Figure 4-19. Pressure at The Dalles minus pressure at Portland International Airport (mb) for the August 2004 episode. Values greater than zero suggest flow from west to east (upgorge).

Figure 4-20. B$_{sp}$, reconstructed b$_{sp}$, and estimated b$_{sp}$ due to sulfate, nitrate, and organic carbon during the August 2004 episode.

Figure 4-21. Organic carbon concentrations at IMPROVE sites in the Pacific Northwest on August 13, 2004.

Figure 4-22. Sulfate concentrations at IMPROVE sites in the Pacific Northwest on August 16, 2004.

Figure 4-23. Pressure at Portland International Airport minus pressure at The Dalles during the July 2004 episode.
Figure 4-24. Time series of $b_s$ (Mm$^{-1}$) and sulfate, nitrate, and organic carbon concentrations ($\mu$g/m$^3$) at Bonneville during the July 2004 episode......................... 89
Figure 4-25. Time series of $b_s$ (Mm$^{-1}$) and sulfate, nitrate, and organic carbon concentrations at Mt. Zion during the July 2004 episode........................................ 90
Figure 4-26. Time series of light scattering (Mm$^{-1}$) at Bonneville and Mt. Zion during the July 2004 episode.................................................................................. 90
Figure 4-27. Time series of organic carbon at Bonneville and Mt. Zion during the July 2004 episode. ............................................................................................................. 91
Figure 4-28. Time series of sulfate at Bonneville and Mt. Zion during the July 2004 episode. ................................................................................................................. 91
Figure 4-29. Time series of DRUM 0.34-0.56 µm particulate sulfur and sodium concentrations for the July-August 2004 DRUM samples. ........................................ 92
Figure 4-30. Time series of measured and reconstructed scattering and scattering by major components at Bonneville during the July 2004 episode. Reconstructed light scattering is computed for sulfate, nitrate, and organic carbon compounds only. .................................................................................................................. 93
Figure 4-31. Time series of measured and reconstructed scattering and scattering by major components at Mt. Zion during the July 2004 episode. Reconstructed light scattering is computed for sulfate, nitrate, and organic carbon compounds only. 93
Figure 4-32. Organic carbon concentrations at IMPROVE sites in the Pacific northwest on July 29, 2004. ............................................................................................................. 94
Figure 4-33. Sulfate concentrations at IMPROVE sites in the Pacific northwest on July 29, 2004. .................................................................................................................... 95
Figure 5-1. Diurnal pattern of particle light scattering in summer in the western Gorge. 96
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.

1.1 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. Nephelometers directly measured light scattering by particles ($b_{sp}$), typically the largest component of haze, 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 1-2 and 1-2. Meteorological measurements were taken at all sites except one (Memaloose).

![Figure 1-1. Regional setting of monitoring sites.](image-url)
Figure 1-2.  a) Western (Sauvie Island, Steirgwald, Mt. Zion, and Strunk Road); b) Central (Bonneville, Memaloose State Park, and Sevenmile Hill); c) Eastern (Memaloose, Sevenmile Hill, Wishram, and Towal Road) monitoring sites in the Gorge.
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 ($b_{sp}$), 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 1-3). 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.

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 1-4.
Figure 1-3. 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.
Figure 1-4. Daily average upgorge wind speed by cluster for each monitoring site (miles per hour).

The percentage frequency of occurrence of each cluster by month is shown tabularly in Table 1-1 and graphically in Figure 1-5.

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

<table>
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<tr>
<th>Cluster</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
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</tr>
</tbody>
</table>
Figure 1-5. 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 May 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 $b_{sp}$ at all sites except Sauvie Island and Steigerwald (Figure 1-6). Highest $b_{sp}$ for winter downgorge was at the eastern sites, with a decrease with distance downgorge. $b_{sp}$ increased again at Sauvie Island as the flow exited the Gorge and crossed the Portland/Vancouver area. This transport and $b_{sp}$ 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 $b_{sp}$ 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 $b_{sp}$ at Mt. Zion and a decreasing $b_{sp}$ with distance into the Gorge. Light upgorge (1) and moderate upgorge (2) showed diurnal patterns of increasing $b_{sp}$ progressing upgorge to the Bonneville site during the day. $b_{sp}$ 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 $b_{sp}$ 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 \( b_{\text{sp}} \) (when the direction is from The Dalles).

![Figure 1-6. Average \( b_{\text{sp}} \) (Mm\(^{-1}\)) at each nephelometer site for each cluster. Average is over all hours for all days within each cluster.](image)

At Mt. Zion and Wishram, measurements of particle light scattering and light absorption indicated that light absorption was a minor contributor (less than 3%) to haze.

### 1.2 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.

IMPROVE (Interagency Monitoring of Protected Visual Environments) samplers (http://vista.cira.colostate.edu/improve/) have been operating long-term at Wishram and Mt. Zion. They provide for chemical speciation of PM$_{2.5}$ (particulate matter less than 2.5 microns in diameter) and mass of PM$_{10}$ (particulate matter less than 10 microns in diameter)(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 (NH$_4^+$, K$^+$, Na$^+$, Mg$^{++}$, Ca$^{++}$) as well as anions (in the standard analysis).

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.

For some days corresponding to IMPROVE sampling days, PM$_{2.5}$ 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 collected 24-hour time-integrated aerosol samples in the PM$_{2.5}$ mode on three independent channels for analysis of mass, 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 (i.e. ~7.7 liters/minute) and consequently one-third as much sample is collected on each filter compared to the IMPROVE sampler.

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 nearly continuous concentrations of organic and elemental carbon (OC/EC) for 2 hour periods (1 hour 45 minutes sampling followed by 15 minutes of analysis time each 2 hours). The analysis uses thermal optical transmittance to account for pyrolized carbon. This is in contrast to the thermal optical reflectance method used for the filter samples (from the IMPROVE and IAS samplers). Due to the use of transmittance and a different temperature program used, the method is expected to give lower elemental carbon than from the IMPROVE
and IAS samples but similar total (organic plus elemental) carbon (Chow et al., 2001, Chow et al., 2004).

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).

Surface meteorology (wind speed and direction, temperature, and relative humidity) was measured at all nephelometer sites except Memaloose State Park.

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 DRUM sampler allows for analysis of chemical composition of collected particles in 3 hour time increments and 8 different sizes. 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 µm 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 Proton Elastic scattering Analysis (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.

For the DRUM analysis, the accuracy is approximately 5% (set by the accuracy of the standards and correlation with those). Uncertainty reported in the database incorporates analytical uncertainty, flowrate uncertainty, etc.). The analytical precision is roughly 10% (comparing reruns).
Table 2-1. Summary of Measurement Program.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Sauvie Is</th>
<th>Steigerwald</th>
<th>Mt Zion</th>
<th>Strunk Rd</th>
<th>Bonneville</th>
<th>Memaloose</th>
<th>7 mile</th>
<th>Wishram</th>
<th>Towal Rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{sp}$ Optec</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7/1/03-2/28/05</td>
<td></td>
<td></td>
<td></td>
<td>7/1/03-2/28/05</td>
</tr>
<tr>
<td>$B_{sp}$ Radiance</td>
<td>8/5/03-2/28/05</td>
<td>7/1/03-2/28/05</td>
<td></td>
<td>7/1/03-2/28/05</td>
<td>8/7/03-2/28/05</td>
<td></td>
<td>8/14/03-2/28/05</td>
<td>7/1/03-2/28/05</td>
<td>7/17/03-2/28/05</td>
</tr>
<tr>
<td>Surface Meteorology</td>
<td>8/5/03-2/28/05</td>
<td>7/1/03-2/28/05</td>
<td></td>
<td>7/1/03-2/28/05</td>
<td>8/7/03-2/28/05</td>
<td>none</td>
<td>8/14/03-2/28/05</td>
<td>7/1/03-2/28/05</td>
<td>7/17/03-2/28/05</td>
</tr>
<tr>
<td>IMPROVE PM$<em>{2.5}$ speciation, PM$</em>{10}$ mass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7/1/03-2/28/05</td>
<td></td>
<td></td>
<td></td>
<td>7/1/03-2/28/05</td>
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<tr>
<td>Cation analysis of IMPROVE</td>
<td>Every 3rd day</td>
<td>1/04-2/05</td>
<td></td>
<td></td>
<td></td>
<td>Every third day</td>
<td>1/04-2/05</td>
<td></td>
<td></td>
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<tr>
<td>International Aerosol Sampler PM$_{2.5}$ speciation</td>
<td>Some days 7/04-11/04</td>
<td></td>
<td></td>
<td></td>
<td>Some days 12/03/04, 7/04-1/05</td>
<td>Some days 12/03/04, 7/04-1/05</td>
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<td></td>
<td></td>
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<td>Time resolved EC/OC</td>
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<td>6/30/04-2/28/05</td>
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<td></td>
<td>12/18/03-3/1/04, 12/1/04-2/28/05</td>
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<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>7/2/03-2/28/05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.

Before proceeding with the data comparisons it is helpful to note that the only data used explicitly in source attribution analysis was the IMPROVE data at Wishram and Mt. Zion. Other data such as the IAS data, high-time resolved sulfate, nitrate, OC/EC, and nephelometer data were used qualitatively to help form conceptual models of the causes of haze in the gorge and to give additional information on spatial and temporal patterns. As will be seen in the comparisons that follow, some of the data was not as consistent as we hoped for and should be considered semi-quantitative. However, it is still useful, especially during for analysis of episodes of high-light scattering conditions. At the end of this section, we present a table that summarizes the authors opinions regarding quality of the data and appropriate uses.

3.1 Summary of the International Aerosol Sampler (IAS) 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 new 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 3-1). As it indicates, measured PM$_{2.5}$ mass concentrations were over 100 \(\mu g/m^3\) for three data points, much higher than the reconstructed mass. This may be due to mistakes in filter weighing. 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 squared correlation coefficient (r$^2$) 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). Because the IAS sampler had a low flow rate of about 7 l/min, the gravimetric mass (measured PM$_{2.5}$) has high uncertainty. Another potential issue is relative humidity growth during filter weighing. Because RH was not controlled in the weighing lab, water growth of hygroscopic particles could add to the measured PM$_{2.5}$ mass. Additionally, field blanks were high (about 1 \(\mu g/m^3\) each) for Cl$, Na$, and OC.

EC1, EC2, EC3, and OP are derived from the IMPROVE thermal optical reflectance (TOR) analysis. The EC fractions are thought to be elemental carbon compounds and the OP is thought to be pyrolyzed (charred) organic carbon compounds.
### Table 3-1. Aerosol major chemical components.

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Assumption</th>
<th>Possible Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate in PM$_{2.5}$</td>
<td>4.125[S]</td>
<td>All elemental S is from sulfate. All sulfate is from ammonium sulfate.</td>
<td>Fossil fuel combustion</td>
</tr>
<tr>
<td>Nitrate in PM$_{2.5}$</td>
<td>1.29[NO$_3$]</td>
<td>Denuder efficiency is close to 100%. All nitrate is from ammonium nitrate.</td>
<td>Industrial and automobile emissions, organic decomposition</td>
</tr>
<tr>
<td>Organic Mass by Carbon (OMC) in PM$_{2.5}$</td>
<td>1.8 * OC</td>
<td>Average organic molecule is 56% carbon.</td>
<td>Biomass burning, automobile emissions, fossil fuel combustion, gas-to-particle conversion of hydrocarbons</td>
</tr>
<tr>
<td>Light absorbing Carbon (LAC)</td>
<td>EC1+EC2+EC3-OP</td>
<td></td>
<td>Incomplete combustion of fossil and biomass fuels</td>
</tr>
<tr>
<td>Soil (Soil) in PM$_{2.5}$</td>
<td>2.2[Al]+2.49[Si]+1.63[Ca]+2.42[Fe]+1.94[Ti]</td>
<td>[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$_2$.</td>
<td>Desert dust, construction, road dust</td>
</tr>
<tr>
<td>Sea Salt</td>
<td>1.8*[Cl]</td>
<td>Sea salt is calculated as 1.8 x [Chloride], or 1.8 x [Chlorine] if the chloride measurement is below detection limits, missing or invalid</td>
<td></td>
</tr>
<tr>
<td>Coarse Mass (CM)</td>
<td>[PM$<em>{10}$] - [PM$</em>{2.5}$]</td>
<td>Consists only of insoluble soil particles.</td>
<td>Crushing or grinding operations, dust from paved or unpaved roads</td>
</tr>
</tbody>
</table>

![Figure 3-1. Comparison between measured and reconstructed PM$_{2.5}$ mass.](image-url)
\[ y = 0.72x + 2.82 \]
\[ R^2 = 0.62 \]

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

**Figure 3-3.** PM$_{2.5}$ chemical speciation based on IMPROVE-like samples.
Figure 3-3 summarizes 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 shows that sulfate and organics are the major aerosol components at Bonneville and Sauvie Island during the summer. Sulfate contributes about 36% and 41% to PM$_{2.5}$ mass in Bonneville and Sauvie Island during the summer, and OMC contributes 42% and 37%, respectively. During the fall, 52% and 40% of PM$_{2.5}$ is organics in Bonneville and Sauvie Island, and sulfate contributes 22% and 35%, respectively. In the winter, OMC contributes 38% and 42% to PM$_{2.5}$ mass at Bonn2 and BonnDam, and sulfate and nitrate each contributes about 20-25% at both sites. Nitrate is the largest contributor to PM$_{2.5}$ at Towal road in winter, with a contribution of 39%. OMC and sulfate each contributes about 25% during winter at Towal road.

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. It should be noted that the sea salt values have high uncertainty because of the large field blank values for chlorine.

3.2 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 during each season although nitrate is about equal to OMC in 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 slightly higher at Mt. Zion during the summer and nitrate is higher at Wishram during the winter.

Figure 3-5 shows the comparison of seasonally averaged IMPROVE and IAS filter data during the time periods when IAS samples were collected. The sites are ordered from west to east in the figures. It is emphasized that the seasonal averages are not for the same set of days for each site listed so that direct comparisons are not presented here. The aerosol loading at Sauvie Island is generally lower than other sites in summer and fall. Sauvie Island did have some anomalously low concentration days in November 2004 that calls in to doubt the lower average concentrations there. In general, there is relatively more organic mass on the west side of gorge during the summer and fall, and more nitrate on the east side of the gorge during the winter. Calculated PM$_{2.5}$ light scattering versus measured light scattering at Bonneville showed them to be highly correlated ($r^2=0.86$) while low correlations existed for Sauvie Island and Towal Road suggesting measurement problems at these two IAS sampler sites.
3.3 Comparison between DRUM and filter data

DRUM and filter data comparisons are known to have some limitations. A significant limitation is that the particles counted as PM$_{2.5}$ may well be different for the different methods. The filter samplers use cyclones which offer a less sharp cut-point than impactors as used in the DRUM. The cut-point for the DRUM samplers used for this study have been calculated, not calibrated. Here we compare DRUM and filter based S, Si, and Ca measurements. Sodium measurements by XRF (used for both DRUM and filter samplers) are highly uncertain and thus would not be expected to correlate well; thus they are not shown here.

As shown in Figures 3-6 and 3-7, daily PM$_{2.5}$ filter measured S is about twice the DRUM (0.09 – 2.5 µm) measured S at both sites. DRUM data is averaged over 3 hour periods. At Bonneville, IAS filter measured Si and Ca are of similar magnitude as the DRUM data. But at Mt. Zion, IMPROVE filter measured Si and Ca are much lower than the DRUM values.
Figure 3-5. Comparison of seasonally averaged IMPROVE and IAS data during: a) summer, b) fall, and c) winter.
Figure 3-5. Continued.
Figure 3-6. Comparison between DRUM and IAS filter measured: a) sulfur, b) silicon, and c) calcium concentrations for PM$_{2.5}$ at Bonneville.
Figure 3-7. Comparison between DRUM and IMPROVE filter measured: a) sulfur, b) silicon, and c) calcium concentrations for PM$_{2.5}$ at Mt. Zion.
3.4 Comparisons between filter and high time resolved data

High time resolved measurements of SO4, NO3, OC, EC, and total carbon (OC+EC) are compared to the 24-hour 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 ½ the concentration of the filter based measurements at Mt. Zion and Bonneville and about three-eighths at Wishram. This is expected to result from both the different temperature programs applied to the Sunset Carbon analyzer compared to the IMPROVE temperature program and the use of transmittance rather than reflectance for determining the split between OC and EC (Chow et al., 2004). The correlations ranged from $r^2=0.46$ at Bonneville to $r^2=0.62$ at Wishram.

For total carbon, at Mt. Zion and Wishram the Sunset analyzer total carbon is about two-thirds the IMPROVE filter carbon. The reason for this is not known. The Sunset analyzer has an organic gas denuder designed to remove organic gases that may absorb onto the sample and cause a positive artifact. The IMPROVE sampler does not have an organic gas denuder; there are considered to be positive artifacts from condensation of organic gases onto the filter and negative artifacts from desorption of particulate organics from the filter. For the Sunset analyzer, desorption of organic particulate is of less concern than for the IMPROVE samples because the analysis is performed every two hours in the field, presumably limiting the loss or organic particulate. On the other hand, perhaps the organic gas denuder removed some organic particulate matter. Consequently, because of the sampling methodologies, the Sunset analyzer may be expected have a lower total carbon concentration than the IMPROVE samplers.

At Bonneville, except for two outliers, the Sunset analyzer has similar total carbon concentrations as the IAS sampler. The outliers contribute substantially to a lowered $r^2$, low slope, and high intercept.
**Figure 3-8.** Comparison between 24-hour averages of high time-resolved: a) $\text{SO}_4^{2-}$, b) $\text{NO}_3^-$, c) OC, d) EC, and e) TC and measurements and IMPROVE daily filter measurements at Mt. Zion.
Figure 3-9. Comparison between 24-hour averages of high time-resolved: a) SO$_4^{2-}$, b) NO$_3^-$, c) OC, d) EC, and e) TC measurements and IMPROVE daily filter measurements at Wishram.
Figure 3-10. Comparison between 24-hour average of high time-resolved: a) $\text{SO}_4^{2-}$, b) $\text{NO}_3^-$, c) OC, d) EC, and e) TC measurements and daily IAS filter measurements at Bonneville.
3.5 Optec nephelometers and Radiance nephelometers comparison

At Wishram and Mt. Zion both Optec and Radiance Research nephelometers were operated. The Optec nephelometers operate under ambient RH conditions, while the Radiance Research nephelometers are heated to control RH to 50 percent or less. At an RH value over 50 percent, the growth of hygroscopic aerosol increases the scattering so that an unheated nephelometer (e.g., Optec) will measure higher scattering. Figure 3-11 shows the ratio of average Optec b_{sp} to average Radiance b_{sp} at each site by ambient RH value (as measured with the Optec RH sensor). At an RH greater than 60 percent, the Optec nephelometer has higher average b_{sp} than does the Radiance nephelometer at each site; the ratio increases with RH due to water growth of the hygroscopic particles. At high RH, the Optec to Radiance scattering ratio is higher than at Mt. Zion. This would happen if the particles at Wishram are more hygroscopic than those at Mt. Zion under high humidity conditions. Values for RH above 90 percent were not computed, since the Optec nephelometer data is flagged when RH greater than 90 percent. At an RH value below about 55 percent, the Radiance nephelometer tends to have higher b_{sp} than the Optec nephelometer. This is because these nephelometers 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 percent higher than the Optec scattering. Thus, under low RH conditions, it is expected that the Radiance nephelometer would have higher bsp than the Optec instrument. However, the ratio is somewhat lower than would be expected at low RH, particularly at Wishram.

Figure 3-12 is an example time series plot of hourly averaged b_{sp} at Mt. Zion from the Optec and Radiance nephelometers from January 14 through April 23, 2004. It can be noted that they track closely, but that the Optec values tend to be higher, due to the high winter and spring RH values.

Figures 3-13 and 3-14 show scatterplots of Optec b_{sp} versus an adjusted Radiance b_{sp} at each site. The radiance b_{sp} for each hour was adjusted by multiplying its value by the average ratio of Optec/Radiance b_{sp} 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 3-11.** Average ratio of Optec nephelometer light scattering to Radiance Research nephelometer light scattering by integer-relative humidity value.

**Figure 3-12.** Example time series comparison of Optec and Radiance Research light scattering at Mt. Zion.
Figure 3-13. Scatterplot of Optec light scattering versus Radiance Research light scattering adjusted by RH, Mt. Zion.

Figure 3-14. Scatterplot of Optec light scattering versus Radiance Research light scattering adjusted by RH, Wishram.
3.6 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 under high RH conditions the heated Radiance Research nephelometers underestimate true light scattering.

Figures 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 of PM$_{10}$ based on IMPROVE aerosol data from Wishram and Mt. Zion, respectively, using the new IMPROVE equation shown below (with relative humidity (RH) adjustment factors f(RH) based on daily average of hourly f(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 are in agreement with each other very well. As shown in Figures 3-16 and 3-18, OMC is the largest aerosol contributor to light extinction at both sites.

$$B_{sp} = 2.2 * f_s(RH) * [\text{small sulfate}] + 4.8 * f_l(RH) * [\text{large sulfate}] + 2.4 * f_s (RH) * [\text{small nitrate}] + 5.1 * f_l(RH) * [\text{large nitrate}] + 2.8 * f_S(RH) * [\text{small organic mass}] + 6.1 * f_L(RH) * [\text{large organic mass}] + 10 * [\text{elemental carbon}] + 1 * [\text{fine soil}] + 1.7 * f_{SS}(RH) * [\text{sea salt}] + 0.6 * [\text{coarse mass}]$$

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

The apportionment of the total concentration of sulfate compounds into the concentrations of the small and large size fractions is accomplished using the following equations.

$$[\text{Large Sulfate}] = \frac{[\text{Total Sulfate}]}{20 \mu g / m^3} \times [\text{Total Sulfate}], \text{ for } [\text{Total Sulfate}] < 20 \mu g / m^3$$

$$[\text{Large Sulfate}] = [\text{Total Sulfate}], \text{ for } [\text{Total Sulfate}] \geq 20 \mu g / m^3$$

$$[\text{Small Sulfate}] = [\text{Total Sulfate}] - [\text{Large Sulfate}]$$

The same equations are used to apportion total nitrate and total organic mass concentrations into the small and large size fractions.
The algorithm uses three water growth adjustment terms as shown in the Table 3-2. They are for use with the small size distribution and the large size distribution sulfate and nitrate compounds and for sea salt \( f_S(RH), f_L(RH) \) and \( f_{SS}(RH) \) respectively.

**Table 3-2.** \( f(RH) \) for small and large size distribution sulfate and nitrate (a sea salt).

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>( f_S(RH) )</th>
<th>( f_L(RH) )</th>
<th>( f_{SS}(RH) )</th>
<th>RH (%)</th>
<th>( f_S(RH) )</th>
<th>( f_L(RH) )</th>
<th>( f_{SS}(RH) )</th>
<th>RH (%)</th>
<th>( f_S(RH) )</th>
<th>( f_L(RH) )</th>
<th>( f_{SS}(RH) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 36</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>56</td>
<td>1.78</td>
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Figure 3-15. Calculated wet light scattering coefficient of PM$_{10}$ using IMPROVE aerosol data from Wishram versus daily average Optec nephelometer measured aerosol light scattering 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 versus 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.
3.7 Comparison between Radiance nephelometer measured and IMPROVE reconstructed dry (RH<=50%) aerosol light scattering coefficients

It should be remembered under high RH conditions, the heated Radiance Research nephelometers underestimate true light scattering.

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 or equal to 50%) at Wishram and Mt. Zion, and calculated “dry” light scattering coefficients. All calculations were the same as for the Optec nephelometer comparison except that RH was limited to 50% in applying the f(RH) factors to the reconstructed scattering equations. This is because the Radiance nephelometers are heated to maintain a relative humidity not to exceed 50%. In general, the measured and reconstructed light scattering coefficients agree with each other very well (R^2 ~ 0.9).

Figures 3-20 and 3-22 illustrate 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 11% to 18% each.

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

High time resolution chemical measurements including sulfate, nitrate, and OC/EC were taken at 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, as were the aerosol light scattering coefficients measured by Radiance Research nephelometers at the three sites. Then light scattering coefficients of OMC, sulfate and nitrate were calculated (based on measured RH when RH<50%, otherwise f(RH) = f(RH=50%)) and compared with Radiance Research nephelometer measured “dry” aerosol light scattering coefficients (RH<=50%) using the new IMPROVE methodology as shown earlier in this section.

Figure 3-23 illustrates that a good correlation exists 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. The analysis suggests that other components such as fine soil and sea salt, and particles bigger than 2.5 µm had little contribution to light extinction during this time period. Figure 3-24 shows that, in average, OMC, LAC, sulfate and nitrate contribute 46%, 10%, 36% and 8% to light extinction during June to November 2004.
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 versus 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.
Figure 3-23. Relationship between measured aerosol light scattering coefficient \( b_{sp} \) (Mm\(^{-1}\)) 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 in average the sum of the calculated OMC, sulfate and nitrate light scattering is only about 50% 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 as well in Wishram based on 607 data points during the winter of 2004 and 2005 as shown in Figure 3-26. The reason for this lack of correlation is not known. Most of the data compared at Wishram was in February 2005 during which the reconstructed to measured scattering ratio was consistently high. This is believed to be caused by unrealistically low $b_{sp}$ measurements from the Radiance research nephelometer at Wishram during this time period. As will be shown below, reconstructed scattering at Wishram versus Optec nephelometer measured scattering was much better than compared to the Radiance Research nephelometer measured scattering.

![Figure 3-25. Relationship between measured aerosol light scattering coefficient ($b_{sp}$, Mm$^{-1}$) and sum of light scattering due to OC, sulfate, and nitrate at Mt. Zion.](image)
Figure 3-26. Relationship between measured aerosol light scattering coefficient \((b_{sp}, \text{Mm}^{-1})\) and sum of light scattering due to OC, sulfate, and nitrate at Wishram.

As discussed earlier, Optec nephelometers were also used at Mt. Zion and Wishram to measure light scattering at ambient RH. Figures 3-27 and 3-28 show the comparison between daily averages of Optec nephelometer measured aerosol light scattering coefficients at Mt. Zion and Wishram, and calculated light scattering coefficients based on real time OMC, sulfate and nitrate data using the new IMPROVE equation. The Optec and Radiance nephelometers give similar results at Mt. Zion, although the Optec has a slightly greater \(r^2\) and slope closer to 1. At Wishram, a much better correlation \((r^2=0.75)\) and slope \((0.75)\) has been found for Optec nephelometer measurements than for Radiance Research nephelometer measurements, suggesting possible problems (generally too low \(b_{sp}\)) with the Radiance Research nephelometer measurements during the winter of 2004-2005.

3.9 Relationship between Aethalometer EC and Sunset Laboratory EC

Figures 3-29 and 3-30 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.
Figure 3-27. Relationship between Optec measured aerosol light scattering coefficient (b_{sp}, Mm^{-1}) and sum of light scattering due to OC, sulfate, and nitrate at Mt. Zion.

Figure 3-28. Relationship between Optec measured aerosol light scattering coefficient (b_{sp}, Mm^{-1}) and sum of light scattering due to OC, sulfate, and nitrate at Wishram.
Mt. Zion Sunset Laboratory EC and Aethalometer EC comparison

\[ y = 0.64x - 0.01 \]
\[ R^2 = 0.83 \]

-0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0

Sunset EC (ug/m³)

Aethalometer EC (ug/m³)

Figure 3-29. Sunset Laboratory EC concentration (µg/m³) versus aethalometer-derived EC (µg/m³) at Mt. Zion.

Wishram Sunset EC and Aethalometer EC comparison

\[ y = 0.45x + 0.04 \]
\[ R^2 = 0.60 \]

-0.2 0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2

Sunset Laboratory EC (µg/m³)

Aethalometer EC (520 nm) (µg/m³)

Figure 3-30. Sunset Laboratory EC concentration (µg/m³) versus aethalometer-derived EC (µg/m³) at Wishram.
3.10 Ion balance

For the year 2004, cation analysis was done for the IMPROVE sites at Wishram and Mt. Zion. This included ion chromatography for NH$_4^+$, Na$^+$, K$^+$, Ca$^{++}$, and Mg$^{++}$. The cation analysis was used in conjunction with the anion analysis (SO$_4^{=}$, NO$_3^-$, and Cl$^-$) to estimate the forms of sulfate and nitrate.

The sum of positive and negative charges were computed and are plotted by monthly average in Figure 3-31.

![Cation/Anion ratios MT Zion and Wishram 2004](image)

**Figure 3-31.** Monthly average ratio of positive to negative charge at Mt. Zion and Wishram.

For the yearly average, the positive to negative charge ratio was 0.82 at Wishram and 0.87 at Mt. Zion. As H$^+$ is not measured, this may account for the deficit of cations at both sites. Figure 1 indicates that during the cold season (i.e. January to March), there is more deficit in cations, indicating more acidity. This may be due to having more nitric acid in the particle phase because of the lower temperature (also see Figure 3-34 and 3-35). It may also be due in part to volatilization of a portion of the NH$_4^+$ from the nylon filter used for analysis by ion chromatography. The fact that the sulfuric and nitric acid are more hygroscopic than ammonium sulfate and nitrate suggests that a higher f(RH) value may be needed to estimate the light scattering coefficient during this time of year. Acidic deposition may be an environmental concern in the area during winter. Generally, the particles are more neutralized during the warm season. More SO$_2$ is converted into sulfate during the warm weather, and at the same time, more ammonium, Na$^+$ and K$^+$ are also emitted. K$^+$ is mostly from fires which are more frequent during summer. Both Na$^+$ and K$^+$ are higher at Mt. Zion than Wishram which may due to paper mill emissions close to Mt. Zion (see PMF modeling results).
Without having analysis of individual particles, it is not possible to know the composition of ions; however some estimates can be made regarding composition. We estimated the partitioning of SO$_4$ and NO$_3$ into compounds such as ammonium sulfate, ammonium nitrate, etc.

The following methodology was used:

1) Assign Na$^+$ to NaCl to the extent that Cl$^-$ was available.
2) Assign NH$_4^+$ to NH$_4$HSO$_4$ based on SO$_4^{2-}$ concentration.
3) Assign NH$_4^+$ as available, to complete the neutralization of SO$_4$ in (NH$_4$)$_2$SO$_4$
4) Assign any remaining NH$_4$ to NH$_4$NO$_3$ based on NO$_3$ concentration.
5) Assign any remaining Na$^+$ from 1) to NaNO$_3$
6) Assign K$^+$ to KNO$_3$.
7) Determine remaining or unexplained SO$_4^{2-}$ and NO$_3^-$.

Mg$^{++}$ and Ca$^{++}$ concentrations were negligible and Ca$^{++}$ uncertainties were greater than their concentrations, so Mg$^{++}$ and Ca$^{++}$ were not used. It should be noted that a large fraction of primary particles from Kraft recovery boilers (associated with Kraft pulp and paper mills) are sodium sulfate (Na$_2$SO$_4$) (Lind, et al., 2006). Thus, particularly at Mt. Zion, which is in close proximity to a Kraft paper mill and in summer typically downwind of additional mills, some of the sodium assigned first to chlorine and then to nitrate may have been directly emitted as Na$_2$SO$_4$.

The partitioning of sulfate into ammonium bisulfate, ammonium sulfate, and unexplained sulfate is by month and site is shown in Figures 3-32 and 3-33.

In winter, there is sufficient ammonium to fully neutralize the SO$_4$ most of the time. In spring and summer, there is typically only enough ammonium to fully neutralize a minority of the sulfate so ammonium bisulfate is more common than ammonium sulfate. Spring tends to have some periods without sufficient ammonium to form ammonium bisulfate from all the sulfate. Remaining sulfate could be in the form of sulfuric acid (H$_2$SO$_4$) or combined with sodium, potassium, etc. The methodology used here first assigned sodium and potassium to nitrate.

The results of the nitrate analysis are shown in Figures 3-34 and 3-35.
Figure 3-32. Estimated monthly average concentration of sulfate in the form of ammonium bisulfate, ammonium sulfate, and unexplained sulfate for Wishram, 2004. For Figures 3-32 to 3-35, estimates are done individually by sample and then averaged over the number of samples per month.

Figure 3-33. Estimated monthly average concentration of sulfate in the form of ammonium bisulfate, ammonium sulfate, and unexplained sulfate for Mt. Zion, 2004.
Figure 3-34. Estimated monthly average concentration of nitrate in the form of ammonium nitrate, sodium nitrate, potassium nitrate, and unexplained nitrate for Wishram, 2004.

Figure 3-35. Estimated monthly average concentration of nitrate in the form of ammonium nitrate, sodium nitrate, potassium nitrate, and unexplained nitrate for Mt. Zion, 2004.
Ammonium nitrate dominates the nitrate budget in winter and is greater at Wishram than Mt. Zion. From March- September, sodium nitrate and unexplained nitrate (possibly nitric acid - HNO₃) are the largest components. Ammonium nitrate averages higher at Wishram than Mt. Zion. Sodium nitrate is higher at Mt. Zion than Wishram. Potassium nitrate is highest in late summer – early fall and is higher at Mt. Zion than Wishram. Annual average concentrations of each component of nitrate and sulfate and their percentage of the total is given in Table 3-3. These results suggest that sources of ammonia affect Wishram more than Mt. Zion (especially in winter) and sources of sodium and potassium affect Mt. Zion more than Wishram (especially in summer).

Table 3-3. Annual average estimated sulfate and nitrate compound concentrations and percentage of total. Concentrations include the sulfate or nitrate mass only and do not include the mass of associated compounds such as ammonium, etc. Note that some sulfate is likely sodium sulfate directly emitted from Kraft recovery boilers.

<table>
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<th>Compound</th>
<th>Wishram</th>
<th>Mt. Zion</th>
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</thead>
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<tr>
<td></td>
<td>Concentration of SO₄ or NO₃ (ng/m³)</td>
<td>Percent</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
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<tr>
<td>(NH₄)₂SO₄</td>
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<tr>
<td>NH₄NO₃</td>
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3.11 Data Quality Summary Table
Table 3-4 presents the authors opinions regarding relative quality of the data collected for the study and its appropriate uses.
Table 3-4. Recommended uses and limitations of study measurements.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measurement</th>
<th>Sites deployed</th>
<th>Appropriate Uses</th>
<th>Limitations</th>
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</thead>
<tbody>
<tr>
<td>Radiance Research nephelometer</td>
<td>RH controlled Light scattering by particles (Bsp)</td>
<td>9 sites</td>
<td>Vertical and horizontal Gradients in haze, temporal patterns</td>
<td>Underestimates haze during higher RH conditions</td>
</tr>
<tr>
<td>Optec nephelometer</td>
<td>Light scattering by particles (Bsp)</td>
<td>Wishram, Mt. Zion</td>
<td>Temporal patterns in haze at east and west ends of gorge</td>
<td>Data flagged under high RH conditions (&gt;90%)</td>
</tr>
<tr>
<td>Surface meteorology sensors</td>
<td>Temperature, RH, wind speed, wind direction</td>
<td>All nephelometer sites except Memaloose</td>
<td>Relate nephelometer and aerosol data to source directions, compute f(RH)</td>
<td>Data only every third day. Some elements poorly measured (e.g. Na, Cl). No routine cation analysis (e.g. NH₄⁺)</td>
</tr>
<tr>
<td>IMPROVE sampler</td>
<td>PM₂.₅ mass and chemical speciation, PM₁₀ mass</td>
<td>Wishram, Mt. Zion</td>
<td>Estimated chemical component contributions to haze, PMF modeling</td>
<td>Limited number of samples, low flow rates, high blank concentrations Not useful with IMPROVE samples to determine gradients</td>
</tr>
<tr>
<td>IAS sampler</td>
<td>PM₂.₅ mass and chemical speciation</td>
<td>Sauvie Island, Bonneville Dam, Towal Road</td>
<td>Determine major components contributing to haze at sites with IAS samplers</td>
<td>Comparability with filter measurements of EC/OC</td>
</tr>
<tr>
<td>Sunset laboratory EC/OC analyzer</td>
<td>About 2 hour average EC/OC</td>
<td>Bonneville Dam, Wishram (winter), Mt. Zion (summer-fall)</td>
<td>Time resolved concentration of EC and OC, high time resolved reconstructed extinction, episode analysis</td>
<td>Poor comparison to filter data at Wishram, but tracks nephelometer scattering during episodes</td>
</tr>
<tr>
<td>Rupprect &amp; Patashnick sulfate analyzer</td>
<td>High time resolved sulfate (1-hour averages used)</td>
<td>Bonneville Dam, Wishram (winter), Mt. Zion (summer-fall)</td>
<td>Sulfate contributions to haze in episode analysis</td>
<td>Poor comparison to filter data at Wishram, but tracks nephelometer scattering during episodes</td>
</tr>
<tr>
<td>Rupprect &amp; Patashnick nitrate analyzer</td>
<td>High time resolved nitrate (1-hour averages used)</td>
<td>Bonneville Dam, Wishram (winter), Mt. Zion (summer-fall)</td>
<td>Nitrate contributions to haze in episode analysis</td>
<td>Poor comparison to filter data at Wishram, but tracks nephelometer scattering during episodes</td>
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<tr>
<td>DRUM sampler</td>
<td>Size and time (3 hr) resolved PM₂.₅ chemical composition</td>
<td>Bonneville Dam, Wishram (winter), Mt. Zion (summer-fall)</td>
<td>Time resolved elements for episode analysis, size distribution analysis</td>
<td>Compare poorly with filter data, limited periods of analysis</td>
</tr>
<tr>
<td>Aethalometer</td>
<td>Light absorbing (elemental) carbon</td>
<td>Wishram, Mt. Zion</td>
<td>High time resolved EC for episode analysis, continuous EC</td>
<td>Calibration issues, scattering particle interference</td>
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</tbody>
</table>
The surface meteorology data, the nephelometer data and the IMPROVE data are of sufficiently high quality for quantitative use to determine extinction budgets, source-receptor relationships, and to evaluate meteorological and air quality model performance.

The other measurements should be considered more semi-quantitative and are useful for timing of changes in aerosol components and determination of main components contributing to high nephelometer measurements. They are most useful for episode analysis. The high-time resolution data did an adequate job of reconstructing light scattering measured by the nephelometers.
4. Attribution

4.1 PMF analysis

To help 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.

4.1.1 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.

\[ X = GF + E \]  \hspace{1cm} (1)

where: \( X \) \((n * Sp)\) = 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 \( (S_i, \mu g/\mu g) \).

\[ S_i = \frac{F_{ij}}{FM_i} \]  \hspace{1cm} (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 \( i \)

\[ C_i = G_{ki} * FM_i \]  \hspace{1cm} (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.

4.1.2 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 µg/m³ over all 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 Kraft paper mill emissions. Emissions from Kraft recovery boilers are shown to consist largely of sodium and sulfate particles (i.e. Na_2SO_4) with lesser but significant amounts of Chlorine and Potassium (Watson, 1979, Lind et al., 2006). 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 (µg/µg) 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.

4.1.3 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. The sulfate factor contributes most during the summer season, while nitrate contributes most in the winter. Smoke and dust are episodic sources with big peaks during dust and fire pollution events, while the contribution of mobile sources is relatively constant throughout the year.
Figure 4-3. Time series of: a) paper mill, b) oil combustion, c) nitrate-rich secondary, d) sulfate-rich secondary, e) mobile, f) dust, and g) biomass smoke source contributions at Mt. Zion.
Figure 4-3. Continued.
Figure 4-3. Continued.
Figure 4-3. Continued.
Figure 4-4. Factor profiles (µg/µg) 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: a) secondary sulfate, b) smoke, c) mobile, d) dust, and e) secondary nitrate source contributions at Wishram.
Figure 4-6. Continued.
4.1.4 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).

About ½ of organic mass was attributed 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.
Figure 4-7. Contribution of each source factor to organic mass, sulfate, nitrate, and reconstructed light extinction at: a) Mt. Zion and b) 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 m²g⁻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.

### 4.1.5 PMF analysis results by wind pattern (cluster)

Percentage of PM$_{2.5}$ 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 PM$_{2.5}$ mass for the light and moderate upgorge and winter downgorge patterns. The mobile factor is most important for light upgorge and light 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 pattern, is also substantial for light downgorge, and is minor for the upgorge patterns. It should be noted that the upgorge wind patterns have slightly higher PM$_{2.5}$ mass at Mt. Zion than Wishram and the downgorge patterns have higher PM mass at Wishram- thus a higher percentage at one site may or may not imply a higher concentration of PM$_{2.5}$ mass.

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.

**Table 4-1.** Percentage of PM$_{2.5}$ mass attributed to each source factor by wind pattern type (cluster) at Wishram.

<table>
<thead>
<tr>
<th>Percentage of PM$_{2.5}$</th>
<th>Light upgorge (1)</th>
<th>Moderate upgorge (2)</th>
<th>Strong upgorge (3)</th>
<th>Light downgorge (4)</th>
<th>Winter downgorge (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate-rich secondary</td>
<td>33</td>
<td>33</td>
<td>44</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>Biomass smoke</td>
<td>31</td>
<td>28</td>
<td>19</td>
<td>37</td>
<td>33</td>
</tr>
<tr>
<td>Mobile</td>
<td>17</td>
<td>12</td>
<td>10</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>Dust</td>
<td>15</td>
<td>22</td>
<td>22</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Nitrate-rich secondary</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>19</td>
<td>44</td>
</tr>
</tbody>
</table>

**Table 4-2.** Percentage of PM$_{2.5}$ mass attributed to each source factor by wind pattern type (cluster) at Mt. Zion.

<table>
<thead>
<tr>
<th>Percentage of PM$_{2.5}$</th>
<th>Light upgorge (1)</th>
<th>Moderate upgorge (2)</th>
<th>Strong upgorge (3)</th>
<th>Light downgorge (4)</th>
<th>Winter downgorge (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper Mill</td>
<td>14</td>
<td>15</td>
<td>19</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Oil Combustion</td>
<td>8</td>
<td>14</td>
<td>14</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Nitrate-rich secondary</td>
<td>10</td>
<td>7</td>
<td>9</td>
<td>12</td>
<td>34</td>
</tr>
<tr>
<td>Sulfate-rich secondary</td>
<td>17</td>
<td>13</td>
<td>16</td>
<td>10</td>
<td>19</td>
</tr>
<tr>
<td>Mobile</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Dust</td>
<td>14</td>
<td>18</td>
<td>12</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>Biomass smoke</td>
<td>32</td>
<td>29</td>
<td>25</td>
<td>43</td>
<td>32</td>
</tr>
</tbody>
</table>
At Mt. Zion, the biomass smoke factor has the largest contribution to PM$_{2.5}$ 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 multiple paper mills are 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 SO$_2$ upwind of the gorge have not converted a large fraction of the SO$_2$ 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.

4.1.5.a 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 during downgorge flow. An interesting finding is that for wind type 5, winter downgorge, over one-half of the sulfate at Wishram 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 SO$_2$ and NO$_X$ (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 analysis does not “prove” that Boardman is responsible for a large fraction of the haze in the gorge in winter. Measurements that may have lead to much stronger evidence of impact were not funded. However, it should be noted that Boardman emits 66% of the SO$_2$ by point sources in Oregon and 34% of the NOx. The most typical winter flow patterns would transport the Boardman emissions through the gorge. Thus, it is not unreasonable to expect that Boardman contributes substantially to winter time sulfate and nitrate in the gorge.

The sulfate attribution at Mt. Zion (Table 4-4) also shows a nitrate-rich secondary factor containing some sulfate that is most important for downgorge flows. The mass contribution to sulfate for this factor is about $\frac{1}{2}$ 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 of SO$_2$ to sulfate 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).

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

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

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

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

4.1.6 PMF analysis using cation data during 2004

Filter measurements for major cations, including Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$, are available in 2004. We also ran the PMF model using only data from 2004 including the cation concentrations available. Table 4-5 lists the fraction of measurements that were below the detection limit in 2004. The chemical components that were below the detection limits more than 50% of the time in any site were not included in the PMF modeling.
Table 4-5. Fraction of measurements that were below detection limits in 2004.

<table>
<thead>
<tr>
<th>Code</th>
<th>Elements</th>
<th>Mt. Zion</th>
<th>Wishram</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>Aluminum</td>
<td>0.55</td>
<td>0.41</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>AS</td>
<td>Arsenic</td>
<td>0.22</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>BR</td>
<td>Bromine</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>Calcium</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>EC1</td>
<td>Elemental Carbon 1</td>
<td>0.03</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>EC2</td>
<td>Elemental Carbon 2</td>
<td>0.18</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>EC3</td>
<td>Elemental Carbon 3</td>
<td>0.80</td>
<td>0.76</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>OC1</td>
<td>Organic Carbon 1</td>
<td>0.44</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>OC2</td>
<td>Organic Carbon 2</td>
<td>0.04</td>
<td>0.07</td>
<td></td>
</tr>
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<td>OC3</td>
<td>Organic Carbon 3</td>
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<td>OC4</td>
<td>Organic Carbon 4</td>
<td>0.00</td>
<td>0.05</td>
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</tr>
<tr>
<td>OP</td>
<td>Organic Carbon Pyrolized</td>
<td>0.73</td>
<td>0.59</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>CHL</td>
<td>Chloride</td>
<td>0.02</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>CL</td>
<td>Chlorine</td>
<td>0.69</td>
<td>0.61</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>CR</td>
<td>Chromium</td>
<td>0.37</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>CU</td>
<td>Copper</td>
<td>0.02</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>FE</td>
<td>Iron</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>PB</td>
<td>Lead</td>
<td>0.02</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>MG</td>
<td>Magnesium</td>
<td>0.78</td>
<td>0.79</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>MN</td>
<td>Manganese</td>
<td>0.06</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>Nickel</td>
<td>0.35</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>NO3</td>
<td>Nitrate</td>
<td>0.00</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>Phosphorus</td>
<td>0.96</td>
<td>0.99</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>K</td>
<td>Potassium</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>RB</td>
<td>Rubidium</td>
<td>0.51</td>
<td>0.48</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>SE</td>
<td>Selenium</td>
<td>0.22</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>SI</td>
<td>Silicon</td>
<td>0.10</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>NA</td>
<td>Sodium</td>
<td>0.72</td>
<td>0.76</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>SR</td>
<td>Strontium</td>
<td>0.15</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>Sulfur</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>TI</td>
<td>Titanium</td>
<td>0.03</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Vanadium</td>
<td>0.19</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>ZN</td>
<td>Zinc</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>ZR</td>
<td>Zirconium</td>
<td>0.95</td>
<td>0.87</td>
<td>Not included in PMF</td>
</tr>
<tr>
<td>NA+</td>
<td>Sodium Ion</td>
<td>0.04</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>NH4+</td>
<td>Ammonium</td>
<td>0.08</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>K+</td>
<td>Potassium Ion</td>
<td>0.02</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>MG++</td>
<td>Magnesium Ion</td>
<td>0.38</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>CA++</td>
<td>Calcium Ion</td>
<td>0.95</td>
<td>0.92</td>
<td>Not included in PMF</td>
</tr>
</tbody>
</table>

Figure 4-8 and 4-9 show the source profiles resolved by PMF using only data from 2004. Table 4-6 lists the PMF results using data from 2003 and 2004, results based on data from 2004 only including cations Na\(^+\), NH\(_4^+\), K\(^+\), and Mg\(^{2+}\), as well as results from Dr. Keith Rose’s analysis using data from 1996-1998. Similar results were found from these different modeling runs. Secondary sulfate contributions were lower using only 2004’s data mainly due to the reason that some measured NH\(_4^+\) concentrations were quite low (close or equal to zero). It is not clear if this is due to analysis problems. A paper mill factor, which has an almost identical source profile as for Mt. Zion, was identified for
Wishram using only 2004’s data. It was blended with other factors using data from 2003-2004 without cations. This may be due to the reason that there are large uncertainties in XRF sodium measurements (which is used in PMF modeling for 2003-2004), while the IC sodium ion (Na⁺) measurement (used in PMF modeling for 2004 only) is more accurate. The paper mill factor at Wishram was associated with winds from the west. A mixed combustion factor was identified for Mt. Zion based on 2004 only modeling, which includes emissions from both mobile and oil combustion sources. An unknown factor with very high K⁺ concentration was identified for 2004 only modeling in Mt. Zion. We are not sure if this is due to measurement uncertainties. But the total K concentrations based on XRF measurements were much lower than IC measured K⁺ during the days when this factor was important.

The 2004 with cation PMF results and the 2003-2004 (no cation) results do not lead to substantial differences in source contributions. The main differences are: 1) blending of the mobile and oil combustion sources at Mt. Zion and 2) appearance of a paper mill factor at Wishram, probably containing primary sodium sulfate, coincident with a reduced secondary sulfate factor.

4.2 Episode analysis

4.2.1 November 2004 Episode

An extended episode of high bsp at all sites occurred during early-mid November 2004. Daily averaged bsp for all nephelometers (Radiance Research heated nephelometers) is shown in Figure 4-10. Unless noted otherwise all nephelometer data in the episode analysis section is from the heated Radiance Research nephelometers. 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 upgorge 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 4-11a and 4-11b.

This episode had elevated concentrations of sulfate, nitrate, and organic carbon. Sulfate concentrations were as high as 10 µg/m³ at Mt Zion and 8 µg/m³ at Bonneville. Nitrate reached hourly average concentrations of over 9 µg/m³ at both locations. Peak OC concentrations were about 8 µg/m³ at Bonneville and 7 µg/m³ at Mt. Zion and concentrations were generally higher at Bonneville than at Mt. Zion.
Table 4-6. Comparison of PMF modeling results: percentage contributions of source factors to PM$_{2.5}$ mass concentrations.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass Smoke</td>
<td>31</td>
<td>30</td>
<td>26.4</td>
<td>29</td>
</tr>
<tr>
<td>Sulfate-rich Secondary</td>
<td>17</td>
<td>14</td>
<td>25.7</td>
<td>28</td>
</tr>
<tr>
<td>Nitrate-rich Secondary</td>
<td>14</td>
<td>19</td>
<td>10.5</td>
<td>16</td>
</tr>
<tr>
<td>Dust</td>
<td>13</td>
<td>10</td>
<td>8.9</td>
<td>14</td>
</tr>
<tr>
<td>Mobile</td>
<td>6</td>
<td>6</td>
<td>5.2</td>
<td>13</td>
</tr>
<tr>
<td>Diesel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil Combustion</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paper Mill</td>
<td>12</td>
<td>9</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>Marine Aerosols</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unidentified Combustion</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combustion Mixture (Mobile, Oil Combustion)</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum Reduction - Combustion Mix</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-8. Source profiles for Mt. Zion based on PMF modeling for 2004 only.
Figure 4-9. Source profiles for Wishram based on PMF modeling for 2004 only.
Figure 4-10. Daily average particle light scattering for the November 2004 episode. Also shown in wind pattern type.

Figure 4-12 compares Mt Zion and Bonneville NO\textsubscript{3} during the episode. Mt. Zion experienced peak nitrate on November 8, Bonneville on November 10.

Next we will compare upgorge wind component (essentially wind from the west) with b\textsubscript{sp} at the sites.

Figure 4-13 uses the Sevenmile Hill site as an example for trends in b\textsubscript{sp} 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 in b\textsubscript{sp} 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 b\textsubscript{sp} from over 180 Mm\textsuperscript{-1} to less than 40 Mm\textsuperscript{-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 b\textsubscript{sp} to over 200 Mm\textsuperscript{-1}. B\textsubscript{sp} remained high but gradually decreased under continued light dowgorge flow over the next few days, then dropped rapidly to under 20 Mm\textsuperscript{-1} on November 15 as winds became upgorge at 10-15 mph.

This wind/b\textsubscript{sp} pattern was common at other sites and indicates sources to the east of the Gorge as being sources of the high b\textsubscript{sp}. As levels of b\textsubscript{sp} decreased from east to west, this suggests that most impact was due to sources east of the Gorge rather than within the Gorge.
Figure 4-11. Particle light scattering and high time-resolved sulfate, nitrate, and organic carbon at: a) Bonneville and b) Mt. Zion for the November 2004 episode.
Figure 4-12. Time series of high time-resolved nitrate at Mt. Zion and Bonneville for the November 2004 episode.

Figure 4-13. Time series of b_{sp} and upgorge wind component at Sevenmile Hill during the November 2004 episode.
4.2.1.a PMF results for episode

PMF results are available for Wishram and Mt. Zion. Table 4-7 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 4-7.** Percentage of fine mass apportioned by PMF to each source factor at Wishram and Mt. Zion (for the samples on November 8, 11, and 14, 2004).

<table>
<thead>
<tr>
<th></th>
<th>Sulfate rich</th>
<th>Biomass burning</th>
<th>Mobile</th>
<th>Dust</th>
<th>Nitrate rich</th>
<th>Oil combustion</th>
<th>Paper mill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt. Zion</td>
<td>9.8</td>
<td>41.1</td>
<td>3.1</td>
<td>3.3</td>
<td>37.4</td>
<td>1.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Wishram</td>
<td>2.4</td>
<td>43.3</td>
<td>7.4</td>
<td>1.6</td>
<td>45.3</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

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

4.2.2 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 downgore flow (cluster 5) every day from February 10-17, 2004. The downgore flow varied in strength with variations in the pressure gradients. Figure 4-14 shows the time series of hourly averaged light scattering at the nephelometer sites.

$B_{sp}$ rose rapidly (from $<20 \text{ Mm}^{-1}$ to 80-100 $\text{ Mm}^{-1}$) 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 downgore at the sites, suggesting transport down gorge from the east (Figure 4-15). $B_{sp}$ at all but the easternmost sites decreased substantially from the morning of February 11 to midday February 12. This decrease in $b_{sp}$ occurred while downgore winds were strong (Figure 4-15), suggesting a dilution of aerosol. A rise in $b_{sp}$ 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 downgore winds eased, possibly reducing the dilution effect. At the eastern sites of Towal Road, Wishram, and Memaloose, $b_{sp}$ 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 $b_{sp}$ throughout the gorge and while later in the episode, large gradients existed.
Figure 4-14. Time series of light scattering (Mm⁻¹) for the February 2004 episode.

Hourly light scattering, NO₃ and SO₄ at Bonneville for the episode are shown in Figure 4-16. Time series of hourly light scattering, NO₃, SO₄, and OC at Wishram are shown in Figure 4-17. 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 µg/m³ on February 12 to 3.5 µg/m³ on February 15.
Figure 4-15. Upgorge wind component for the February 2004 episode at selected sites.

Figure 4-16. Time series of light scattering, NO₃, and SO₄ at Bonneville during the February 2004 episode.
Figure 4-17. Time series of light scattering, NO$_3$, SO$_4$, and OC at Wishram during the February 2004 episode.

Table 4-8 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 4-8. Percentage of fine mass apportioned by PMF to each source factor at Wishram and Mt. Zion (for the samples of February 12 and 15, 2004).

<table>
<thead>
<tr>
<th></th>
<th>Sulfate rich</th>
<th>Biomass burning</th>
<th>Mobile</th>
<th>Dust</th>
<th>Nitrate rich</th>
<th>Oil combustion</th>
<th>Paper mill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt. Zion</td>
<td>29.8</td>
<td>9.0</td>
<td>2.2</td>
<td>2.1</td>
<td>49.5</td>
<td>0.4</td>
<td>7</td>
</tr>
<tr>
<td>Wishram</td>
<td>14.0</td>
<td>11.2</td>
<td>2.4</td>
<td>1.6</td>
<td>70.9</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

4.2.3 August 2004 episode

The August 2004 episode had several days of continuously elevated b$_{sp}$ at the nephelometer sites. Figure 4-18 shows time series of b$_{sp}$ at representative sites. b$_{sp}$ 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 b$_{sp}$. 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 4-19.
**August 2004 episode hourly bsp at selected sites**

![Graph of August 2004 episode hourly bsp at selected sites](image)

**Figure 4-18.** Time series of \( b_{sp} \) at selected sites for the August 2004 episode.

**PDX-DLS pressure for August 2004 episode**

![Graph of PDX-DLS pressure for August 2004 episode](image)

**Figure 4-19.** Pressure at The Dalles minus pressure at Portland International Airport (mb) for the 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 $b_{sp}$ increased.

Figure 4-20 shows a time series of $b_{sp}$, reconstructed $b_{sp}$, and estimated $b_{sp}$ due to sulfate, nitrate, and organic carbon at Bonneville for the episode. Measured and reconstructed scattering compare well both in magnitude and trend. Reconstructed $b_{sp}$ was due about equally to sulfate and organic carbon, with a very minor contribution from nitrate.

Figure 4-20. $b_{sp}$, reconstructed $b_{sp}$, and estimated $b_{sp}$ due to sulfate, nitrate, and organic carbon during the August 2004 episode.

Figure 4-21 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 µg/m3, with over 8 µg/m3 at Sawtooth Wilderness Area. This suggests impacts from fires in the region. Figure 4-22 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 4-21. Organic carbon concentrations at IMPROVE sites in the Pacific Northwest on August 13, 2004.
Figure 4-22. Sulfate concentrations at IMPROVE sites in the Pacific Northwest on August 16, 2004.

4.2.4 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 $b_{sp}$, sulfate, organic carbon, and nitrate at Bonneville and Mt. Zion are shown in Figures 4-24 and 4-25.

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 $b_{sp}$, sulfate, and organic carbon at Bonneville and Mt. Zion are shown in Figures 4-26 to 4-28. $b_{sp}$, sulfate, and OC track well and are quite similar in magnitude for the two sites except for July 31 when sulfate and $b_{sp}$ are much higher at Mt. Zion. The DRUM data at Mt. Zion (Figure 4-29) and Bonneville show increases in fine sodium concurrent with increases in fine sulfur. From the PMF analysis and source profile data (which indicates that emissions from Kraft recovery boilers consist largely of sodium sulfate) this suggests significant paper mill impact to particulate sulfur (sulfate) at Mt. Zion and Bonneville during this time period.
Figure 4-23. Pressure at Portland International Airport minus pressure at The Dalles during the July 2004 episode.

Figure 4-24. Time series of $b_{sp}$ (Mm$^{-1}$) and sulfate, nitrate, and organic carbon concentrations ($\mu$g/m$^3$) at Bonneville during the July 2004 episode.
Figure 4-25. Time series of b_{sp} (Mm^{-1}) and sulfate, nitrate, and organic carbon concentrations at Mt. Zion during the July 2004 episode.

Figure 4-26. Time series of light scattering (Mm^{-1}) at Bonneville and Mt. Zion during the July 2004 episode.
Figure 4-27. Time series of organic carbon at Bonneville and Mt. Zion during the July 2004 episode.

Figure 4-28. Time series of sulfate at Bonneville and Mt. Zion during the July 2004 episode.
Mt Zion 0.34-0.56 um S vs Na July-Aug 2004

Figure 4-29. Time series of DRUM 0.34-0.56 µm particulate sulfur and sodium concentrations for the July-August 2004 DRUM samples.

In table 4-9, the PMF attribution for the samples of July 26 and July 29 are shown.

The largest source at Mt. Zion is paper mill, while biomass burning dominates at Wishram.

Table 4-9. Percentage of fine mass apportioned by PMF to each source factor at Mt. Zion and Wishram for the samples taken July 26 and 29, 2004.

<table>
<thead>
<tr>
<th></th>
<th>Sulfate rich</th>
<th>Biomass burning</th>
<th>Mobile</th>
<th>Dust</th>
<th>Nitrate rich</th>
<th>Oil combustion</th>
<th>Paper mill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt. Zion</td>
<td>16</td>
<td>12</td>
<td>2</td>
<td>20</td>
<td>8</td>
<td>17</td>
<td>25</td>
</tr>
<tr>
<td>Wishram</td>
<td>31</td>
<td>42</td>
<td>3</td>
<td>17</td>
<td>6</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Light scattering at Bonneville and Mt. Zion was dominated by sulfate and organic carbon (Figures 4-30 and 4-31). 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%.
**Figure 4-30.** Time series of measured and reconstructed scattering and scattering by major components at Bonneville during the July 2004 episode. Reconstructed light scattering is computed for sulfate, nitrate, and organic carbon compounds only.

**Figure 4-31.** Time series of measured and reconstructed scattering and scattering by major components at Mt. Zion during the 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 4-32 and 4-33. OC concentrations were high throughout the region ranging from about 4-7 $\mu$g/m$^3$, except less than 3 $\mu$g/m$^3$ at Mt. Zion. This widespread distribution of high OC suggest impacts from forest fires. Sulfate concentrations were less regionally consistent, highest near the Gorge and the Puget Sound area and low east of the Cascades.

Figure 4-32. Organic carbon concentrations at IMPROVE sites in the Pacific northwest on July 29, 2004.
4.3 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. Sources to the east of the Gorge were the main contributors to haze. The February 2004 episode was mainly nitrate-rich and sulfate-rich secondary and was also associated with transport from sources east of the Gorge.

The August 2004 episode was mainly SO$_4$ 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. 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) may be 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 PM$_{2.5}$ 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 from Wishram (upgorge from the Dalles) to Memaloose and Sevenmile Hill (downgorge 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 to fall, suggesting contributions from all the sources listed in the hypothesis.
6. Brief answers to Causes of Haze in the Gorge Questions

In the contract for the Causes of Haze in the Gorge analysis, a series of questions were listed that were to be addressed. Many of these questions are addressed in sections of this report and the Haze Gradient Study report. However, for convenience they are briefly addressed here as well.

6.1 What aerosol components are responsible for haze?

6.1.1 What are the major components for best, worst, and average days and how do they compare?

At Wishram, during the best and average days, sulfate is the major component contributing to aerosol light extinction, with a contribution of ~30% on both best and average days. OMC is the second largest contributor, with a contribution of ~20%. During the worst days, nitrate is the largest contributor to aerosol light extinction, with a contribution of 38%. Sulfate and OMC contribute 26% and 20%, respectively.

At Mt. Zion, during the best and average days, sulfate is the major component contributing to aerosol light extinction, with a contribution of ~30% on both best and average days. Nitrate and OMC each contributes about 20%. During the worst days, nitrate is the largest contributor to aerosol light extinction, with a contribution of 35%. Sulfate and OMC each contribute ~26%.

6.1.2 How variable were the major components episodically, seasonally, inter-annually, spatially?

No statistically significant multi-year trends are found in Wishram for major components except sulfate which showed a significant decreasing trend during 1994-2004. Seasonally, nitrate is the largest contributor to aerosol light extinction in the first and fourth quarter, and sulfate is the largest contributor in the second and third quarter, each with a contribution of ~35-40%.

In Mt. Zion, because only 3 years of aerosol data are available, no multi-year trend can be analyzed. Seasonally, similar as at Wishram, nitrate is the largest contributor to aerosol light extinction in the first and fourth quarter, and sulfate is the largest contributor in the second and third quarter, each also with a contribution of ~35-40%.

Similar aerosol speciation is found at Mt. Zion (west side of the gorge) and Wishram (east side) except that there are more dusts (CM and fine soil) at Wishram especially during the second and third quarter of the year.

6.1.3 How do the relative concentrations of the major components compare with the relative emission rates nearby and regionally?

This question is not straightforward to answer for the following reasons:

Good emissions inventories are not available for organic and elemental carbon and soil and coarse mass emissions. Sulfate and nitrate which contribute substantially to haze are
secondary pollutants and their formation is highly variable depending upon temperature, cloud cover, etc.

6.2 What is meteorology’s role in the causes of haze?

The relationship between meteorological conditions and haze levels was addressed extensively in the Haze Gradient Study Report. They are summarized here.

6.2.1 How do meteorological conditions differ for best, worst and typical haze conditions?

The best haze conditions were typically associated with summertime strong upgorge flow. These conditions led to particularly good visibility in the eastern Gorge. Days with precipitation were also associated with less haze than days without precipitation. Worst haze days were typically associated with winter downgorge flow. Under these conditions winds are light in the eastern Gorge and then increase in speed from the east in the western Gorge. Periods with regional wildland fires were also associated with high haze conditions. Meteorological conditions of hot, dry weather with lightning would thus be associated with forest fires and the resulting haze.

6.2.2 What empirical relationships are there between meteorological conditions and haziness?

The along-gorge wind component was associated with haziness. Precipitation was associated with decreased haziness.

6.2.3 How does the spatial difference in meteorology and climate between west and east Scenic Area account for the haze differences observed between west and east Scenic Area?

For the main summer wind pattern (strong upgorge), light scattering by particles (b_sp) is about twice in the western Gorge as in the eastern gorge. While some of this is due to closer proximity to upwind major sources/source areas in the western Gorge, the eastern Gorge has much greater dispersion than the western Gorge due to stronger winds and deeper mixing. For winter downgorge, winds and dispersion are light in the eastern gorge and winds and therefore, alongwind dispersion is greater in the western gorge. B_sp for this pattern is significantly higher in the eastern Gorge than the western Gorge.

6.2.4 How well can haze conditions be predicted solely using meteorological factors?

There were statistically significant differences in the haze levels for the five wind pattern types. However, there was substantial variability within each type as well.

6.2.5 How well can inter-annual variations in haze be accounted for by variations in meteorological conditions?

The study period lasted for less than two years so the relationship between inter-annual variations in haze and meteorology was not addressed.
6.3 What are the emission sources responsible for haze?

6.3.1 What geographic areas are associated with transported air that arrives at sites on best, typical and worst haze days?

Worst haze days are associated with wintertime transport from areas east of the gorge. Best haze days, particularly in the eastern gorge, were associated with strong flow from the west.

6.3.2 Are the emission characteristics of the transport areas consistent with the aerosol components responsible for haze?

Yes. Worst haze periods with wintertime transport from the east has significant sources of NOX, ammonia, SO2 as well as organic mass from residential wood burning. Good and average day haze is dominated by sulfate and organic mass and transport from the west to east. There are significant sources of SO2 and sulfate to the west (e.g. power production, pulp and paper mills, shipping). Significant organic sources include mobile sources in the Portland urban area, wildfires and agricultural burning.

6.3.3 What do the aerosol characteristics on best, typical and worst days indicate about the sources?

See the answer to the previous question.

6.3.4 What does the spatial and temporal pattern analysis indicate about the locations and time periods associated with sources responsible for haze?

Sources east of the gorge mainly contribute to haze in winter. Sources west of the gorge contribute all year, contributing essentially every day in summer (but usually at lower levels of haze). Sources within the gorge contribute most noticeably during periods of flow reversal in the gorge (typically autumn).

6.3.5 What evidence is there for urban impacts on haze and what is the magnitude and frequency when evident?

During summertime when winds are essentially always from the west, diurnal patterns in light scattering at the western and central gorge sites showed a “slug” of hazy air moving eastward through the gorge. This illustrates impacts from the Portland/Vancouver metropolitan area. For the most frequent summertime wind pattern (strong upgorge), daily average bsp increased from 14.8 mm\(^{-1}\) at Sauvie Island, upwind of the urban area to 22.7 Mm\(^{-1}\) at Mt. Zion, downwind of the cities. This represents about a 50% increase in particle light scattering across the urban area.

6.3.6 What connections can be made between sample periods with unusual species concentrations and activity of highly sporadic sources (e.g., major fires and dust storms, point source activity changes such as aluminum plant shut-downs, etc.)?

The July 2004 and August 2004 episodes considered in the episode analysis section occurred during periods of major wildfires in the Pacific Northwest.
6.3.7 What can be inferred about impacts from sources in other regions?

Forest fires outside of the Columbia River Gorge area contribute to haze in the region. Background levels of haze coming into the region and the source regions of this haze was not thoroughly investigated. Sites at the edges of the study region (e.g. Steigerwald to the west and Towal Road to the east) give some idea about outside source areas and background. Winds from the east and highest haze at the eastern sites during winter downgorge conditions implied impacts from source areas to the east of the gorge.

6.4 Are there detectable and/or statistically significant multi-year trends in the causes of haze?

6.4.1 Are the aerosol components responsible for haze changing?

Because only 3 years of aerosol data are available at Mt. Zion, no trends analysis can be done for this site. At Wishram, 8 years of data (as shown in the table below) are available (based on Regional Haze Rule) for trends analysis. The trends analyses using the Theil method shows no statistically significant trends (i.e. P-Value <0.05) in total light extinction and light extinction due to major aerosol components except sulfate which was significantly deceased during 1994-2004.

Table 6-1. Data available at Wishram.

<table>
<thead>
<tr>
<th>site</th>
<th>Year</th>
<th>aerosol_bext</th>
<th>ammSO4f_bext</th>
<th>ammNO3f_bext</th>
<th>OMCf_bext</th>
<th>ECf_bext</th>
<th>SOILf_bext</th>
<th>OMCf_bext</th>
</tr>
</thead>
<tbody>
<tr>
<td>CORI1</td>
<td>1994</td>
<td>46.98</td>
<td>14.57</td>
<td>10.24</td>
<td>10.83</td>
<td>4.47</td>
<td>0.66</td>
<td>10.83</td>
</tr>
<tr>
<td>CORI1</td>
<td>1995</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CORI1</td>
<td>1996</td>
<td>41.3</td>
<td>12.43</td>
<td>9.35</td>
<td>9.58</td>
<td>4.13</td>
<td>0.55</td>
<td>9.58</td>
</tr>
<tr>
<td>CORI1</td>
<td>1997</td>
<td>41.55</td>
<td>14.36</td>
<td>7.8</td>
<td>9.25</td>
<td>3.78</td>
<td>0.54</td>
<td>9.25</td>
</tr>
<tr>
<td>CORI1</td>
<td>1998</td>
<td>39.25</td>
<td>12.84</td>
<td>5.4</td>
<td>10.09</td>
<td>4.66</td>
<td>0.63</td>
<td>10.09</td>
</tr>
<tr>
<td>CORI1</td>
<td>1999</td>
<td>35.65</td>
<td>11.76</td>
<td>4.7</td>
<td>8.92</td>
<td>4.13</td>
<td>0.79</td>
<td>8.92</td>
</tr>
<tr>
<td>CORI1</td>
<td>2000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CORI1</td>
<td>2001</td>
<td>51.67</td>
<td>13.93</td>
<td>20.16</td>
<td>7.76</td>
<td>2.99</td>
<td>0.86</td>
<td>7.76</td>
</tr>
<tr>
<td>CORI1</td>
<td>2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CORI1</td>
<td>2003</td>
<td>43.35</td>
<td>11.52</td>
<td>14.18</td>
<td>10.19</td>
<td>3.3</td>
<td>0.6</td>
<td>10.19</td>
</tr>
<tr>
<td>CORI1</td>
<td>2004</td>
<td>48.12</td>
<td>11.48</td>
<td>18.74</td>
<td>10.57</td>
<td>3.55</td>
<td>0.78</td>
<td>10.57</td>
</tr>
<tr>
<td>Slope</td>
<td></td>
<td>0.271</td>
<td>-0.225</td>
<td>0.67</td>
<td>-0.049</td>
<td>-0.117</td>
<td>0.011</td>
<td>-0.049</td>
</tr>
<tr>
<td>P-Value</td>
<td></td>
<td>0.2742</td>
<td>0.0156</td>
<td>0.2742</td>
<td>0.4524</td>
<td>0.0894</td>
<td>0.1994</td>
<td>0.4524</td>
</tr>
</tbody>
</table>

6.4.2 Where aerosol component changes are seen, are they the result of meteorological or emissions changes?

The only statistically significant trend was for sulfate at Wishram. Regional SO2 emissions have decreased since 1999 as controls were installed at the Centralia Powerplant in 2001 and 2002 and some aluminum smelter and pulp and paper mills ceased operation.

6.4.3 Where emissions are known to have changed, are there corresponding changes in haze levels? (e.g., aluminum plant shutdowns or emission controls on the Centralia Power Plant)?

No. From the table above, decreases in sulfate scattering at Wishram due to regional decreases in SO2 emissions appears to have been offset by increases in nitrate scattering. However the increases in total aerosol light extinction and nitrate scattering were not statistically significant.
7. Conceptual Model for Haze in the Columbia River Gorge

7.1 Meteorological relationship to transport of pollutants and haze levels

Winds through the Columbia River Gorge are driven by pressure gradients across the gorge, blowing from high to low pressure. Significant sources near or within the gorge that affect visibility include a variety of sources in the Portland/Vancouver metropolitan area to the immediate west of the gorge, additional industrial sources west of the gorge, small cities and mobile sources (ships, trains, trucks, and automobiles) within the gorge, electricity generation, dairy operations, and small urban areas (e.g. Tri-Cities) upriver from the gorge.

During summer winds are nearly always from west to east (upriver or upgorge). This is in response to a coast to interior pressure gradient that develops from heating of the interior compared to coastal areas and higher pressure offshore due to the location of the Pacific High. Winds increase in speed during the day as the pressure gradient increases due to increased temperature gradients. These winds transport pollutants from the Portland/Vancouver metropolitan area and industrial sources west of the gorge eastward through the gorge. In the western and central gorge, haze (light scattering) increases in late morning as winds transport these urban/industrial caused aerosols deeper into the gorge. At the eastern gorge sites, there is less haze due to the increased vertical and along-wind dispersion of these aerosols as they travel through the gorge.

The main summer meteorological pattern with strong upgorge flow has the lowest level of haze, with highest levels at the western gorge sites nearest the Portland urban area and lowest haze levels at the eastern sites.

In winter there is typically higher pressure east of the gorge and lower to the west. This results from cold stable air to the east and the prevalence of Pacific low pressure systems to the west. Under the most common winter pattern (winter downgorge), winds are light from the east in the eastern gorge and increase in speed as the air travels westward through the gorge. Haze levels are highest east of the gorge and gradually decrease to the west. Thus sources to the east of the gorge (e.g. Boardman power plant, nearby dairy operation, and the Tri-Cities areas) are major contributors to haze-causing aerosols that are transported through the gorge from east to west. This pattern has the highest haze levels of the main meteorological patterns. Nitrate, sulfate, and organic aerosols are the main contributors to haze. The contrast in haze levels between the haziest (winter downgorge) and least hazy (strong upgorge) wind patterns is much greater in the eastern gorge than in the western gorge.

During spring and fall pressure gradients are generally weaker and flows tend to be frequently lighter and may change direction diurnally. Under these conditions aerosols can slosh back and forth within the gorge and sources within the gorge become relatively more important as transport is reduced. Some effect of The Dalles on haze was noted for the flow reversal conditions.

During late summer, the most common meteorological condition has moderately strong west to east winds that have a large increase in speed during the day.
7.2 Aerosol species and source contributions to haze levels

During the July 2003 through February 2005 study period, the major components responsible for haze in the gorge were organic carbon, sulfate, and nitrate. Coarse mass and light absorbing carbon were of lesser importance; fine soil and sea salt were minor contributors. Component contributions to reconstructed extinction using the new IMPROVE protocol is shown in Table 7-1.

Table 7-1. Component contributions to reconstructed extinction using the new IMPROVE protocol at Mt. Zion and Wishram.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mt. Zion</th>
<th>Wishram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic mass</td>
<td>35%</td>
<td>35%</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>24%</td>
<td>17%</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>16%</td>
<td>17%</td>
</tr>
<tr>
<td>Coarse mass</td>
<td>12%</td>
<td>15%</td>
</tr>
<tr>
<td>Light absorbing carbon</td>
<td>9%</td>
<td>10%</td>
</tr>
<tr>
<td>Sea salt</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Fine soil</td>
<td>1%</td>
<td>3%</td>
</tr>
</tbody>
</table>

Organic mass is a large contributor to haze in the gorge all seasons, with a peak in fall. The PMF analysis suggests that about half of the organic mass is biomass smoke, with mobile sources as the second largest contributor. The biomass smoke is substantial in all seasons with residential wood burning for heat in winter, agricultural burning in spring and fall, and wildfires/prescribed burning in summer and fall.

Nitrate is an important contributor to haze in fall and winter. PMF analysis showed nitrates mainly attributed to a generic secondary nitrate factor with the next largest contributor being oil combustion at Mt. Zion and mobile sources at Wishram. Sulfate is a significant contributor in all seasons, with peak sulfate concentrations in summer. Sulfate was more than half due to a generic secondary sulfate factor with significant contributions from oil combustion and paper mills at Mt. Zion and sources associated with secondary nitrate at Wishram. The PMF analysis utilizing cation data from 2004 also identified paper mill source affects at Wishram.
An unresolved issue is how well the PMF analysis accounts for mobile sources. Mobile sources may contribute in part to the secondary nitrate and oil combustion factors. The occurrence of a higher source attribution to mobile emissions at Mt. Zion compared to Wishram suggests that the effect of mobile emission impact at Mt. Zion may be underestimated by PMF.

Biomass smoke and secondary nitrate are the most important source factors for the most common winter pattern (winter downgorge). At Mt. Zion, paper mill and oil combustion impacts were associated with winds from the west (upgorge), consistent with locations of these emissions sources.
8. References


