Technical Report: Port of Tacoma Source Apportionment Study

By

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For the

Air Quality Program

Washington State Department of Ecology
Olympia, Washington

June, 2023, Publication 23-02-075

Publication Information

This document is available on the Department of Ecology's website at:
https://apps.ecology.wa.gov/publications/summarypages/2302075.html

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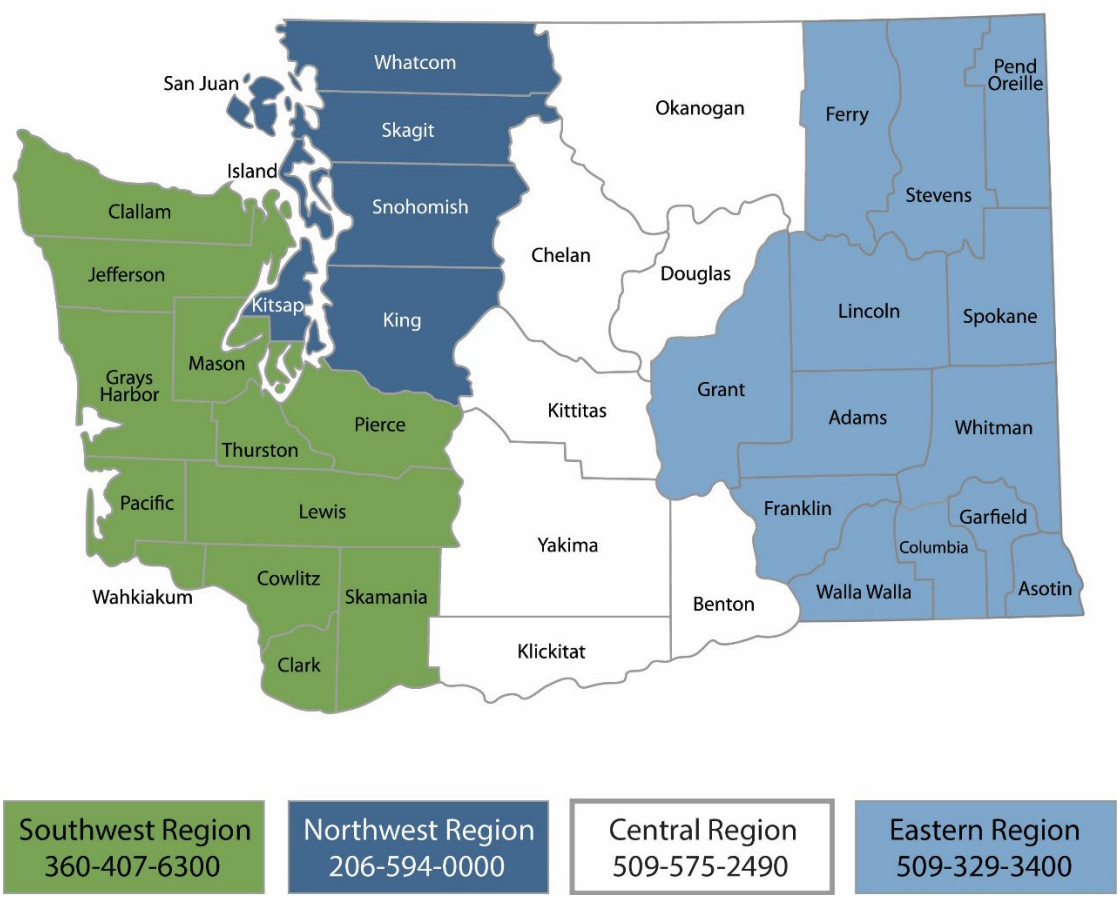

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Acknowledgements

The authors of this report thank the following people for their contribution to this study:

- Technical Services Section, Ecology Air Quality Program
- Puget Sound Clean Air Agency
- Robert Kotchenruther, EPA

Executive Summary

Receptor modeling was applied to Chemical Speciation Network $PM_{2.5}$ data collected from 2018-2022 at a monitoring site adjacent to the Port of Tacoma in order to quantify the contribution of sources to the measured $PM_{2.5}$ concentration.

Main findings include:

- Ten factor categories of $PM_{2.5}$ were identified. These ten factors explain 90% of the measured $PM_{2.5}$ mass. $PM_{2.5}$ associated with wood smoke was the highest contributing source to the annual average $PM_{2.5}$ mass concentration.
- A single factor associated with diesel $PM_{2.5}$ was not identified. Instead, components of diesel $PM_{2.5}$ were identified in multiple factors, including $PM_{2.5}$ associated with vehicles, high concentrations of zinc, unidentified urban, and high concentrations of iron. Together, these four factors comprised about 29% of the annual average $PM_{2.5}$ mass concentration.
- Many factors exhibited significant seasonal differences. $PM_{2.5}$ associated with wood smoke, vehicles, nitrate, and iron were significantly higher in the fall and winter months, while $PM_{2.5}$ associated with sulfate, fugitive dust, and fireworks were significantly higher during the spring and summer months.
- Significantly different weekend and weekday distributions were observed for $PM_{2.5}$ associated with iron and fugitive dust.
- Days with higher $PM_{2.5}$ concentrations mostly occurred during the winter and were characterized by contributions from $PM_{2.5}$ associated with wood smoke.
- $PM_{2.5}$ associated with vehicles significantly increased during the measurement period.

Introduction

Section 302 (16) of the 2018 Supplemental Operating Budget directed the Department of Ecology (Ecology) to conduct a "multiyear study to distinguish the sources of emissions of the toxic air pollutant that poses the greatest cancer risk at the air monitoring station that is located closest to a port in the state with the highest volume of container traffic in domestic and foreign waterborne trade." To address this directive, Ecology designed a three-year monitoring study of fine particulate matter ($PM_{2.5}$) and its chemical components at Puget Sound Clean Air Agency's (PSCAA) Alexander Avenue monitoring site adjacent to the Port of Tacoma. Receptor modeling was applied to the full dataset to quantity the contribution of sources to the measured $PM_{2.5}$ concentrations.

Receptor-based source apportionment methods, such as Positive Matrix Factorization (PMF) have been utilized extensively to determine sources of ambient $PM_{2.5}$.[2,3] Source apportionment studies in the Pacific Northwest have focused on identifying $PM_{2.5}$ sources in remote and urban areas, marine vessel $PM_{2.5}$ impacts, and recent changes in wintertime $PM_{2.5}$ sources.[4,5,6,7]

This study applied PMF to $PM_{2.5}$ Chemical Speciation Network (CSN) data collected from 2018-2022 at the Alexander Avenue monitoring site. PMF modeling output identified ten $PM_{2.5}$ source categories that explain the majority of $PM_{2.5}$ data measured at the monitoring site. Source categories were further analyzed based on seasonal trends, daily trends, and meteorology in order to understand their impacts on total $PM_{2.5}$ concentrations and any contributions to elevated $PM_{2.5}$ concentrations observed during the study period.

[2] Hopke, P. K. 2016. Review of Receptor Modeling Methods for Source Apportionment. *J. Air Waste Manage. Assoc.* 66 (3):237–59. doi:10.1080/10962247.2016.1140693.
[3] Reff, A., S. I. Eberly, and P. V. Bhave. 2007. Receptor modeling of ambient particulate matter data using positive matrix factoriation: Review of existing methods. *J. Air Waste Manage. Assoc.* 57 (2):146–54.
[4] Kotchenruther, R.A. 2020. Recent changes in winter PM2.5 contributions from wood smoke, motor vehicles, and other sources in the Northwest US. *Atmos. Environ.* 237, 117724.
[5] Hadley, O.L. 2017. Background PM2.5 source apportionment in the remote Northwestern United States. *Atmos. Environ.* 167.
[6] Kotchenruther, R.A.. 2013. A regional assessment of marine vessel PM2.5 impacts in the U.S. Pacific Northwest using a receptor-based source apportionment method. *Atmos. Environ.* 68.
[7] Friedman, B. 2020. Source apportionment of $PM_{2.5}$ at two Seattle chemical speciation sites. *J. Air Waste Manage. Assoc.* 70(7):687-699.

Methodology

Port of Tacoma Monitoring Site

CSN samples were collected at PSCAA's Alexander Avenue monitoring site adjacent to the Port of Tacoma (47.2656, -122.3850).

The Port of Tacoma comprises 2,500 acres within the area referred to as the Tacoma Tideflats and is among the top ten largest container ports in North America. With five major container terminals, the Port of Tacoma is a major center for containers, bulk, breakbulk, heavy-lift cargoes, automobiles, and trucks. Industry operations at the Port of Tacoma include manufacturing, warehousing, distributing, and shipping, as well as metal fabrication and machinery, paper milling, concrete and steel manufacturing, lumber, and oil refining. The Port is served by the BNSF Railway and Union Pacific railroads, and major roadways include Highway 509 to the south and east of the monitoring site and Interstate-5 to the south of the monitoring site.[8]

Figure 1. Map of the Port of Tacoma. The location of Puget Sound Clean Air Agency's Alexander Ave monitoring site is shown by the red triangle. Source: City of Tacoma.

CSN samplers use polytetrafluoroethylene, nylon, and quartz filters to collect 24-hour samples every six days. Offline analysis of chemical components is conducted at the contract laboratory

[8] https://www.cityoftacoma.org/government/city_departments/community_and_economic_development/economic_development_services/port_of_tacoma

by energy-dispersive X-ray fluorescence, ion chromatography, and thermal optical analysis to determine concentrations of metals, ions, and carbon fractions.[9]

Samples were collected from August 2018 to February 2022, with a break in sampling from March to August 2020 due to the COVID-19 pandemic, resulting in 187 total samples. Nephelometer $PM_{2.5}$ concentrations, black carbon concentrations, and meteorological parameters were also measured at the monitoring site. The wind rose from the duration of the study is shown in Figure 2. The highest concentration of winds originated from the southeast, with contributions from every direction. The highest wind speeds were generally from the southwest, south, and southeast directions.

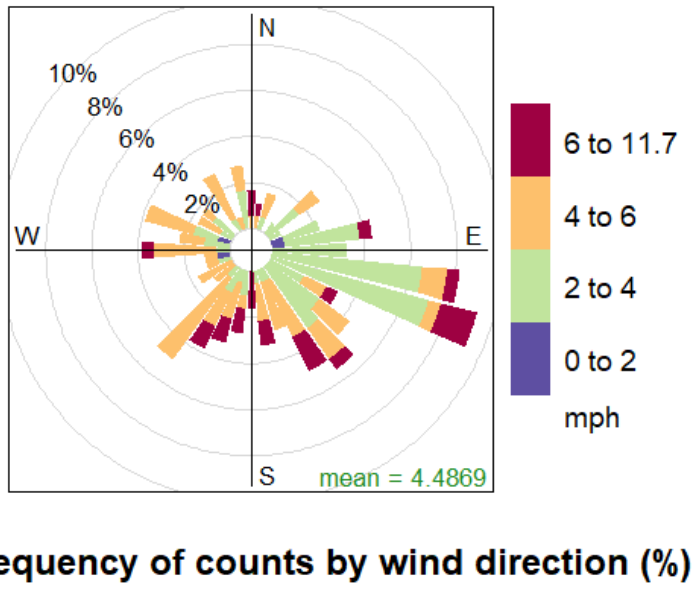


Figure 2. Wind rose during the sampling period.

Positive Matrix Factorization

Positive Matrix Factorization (PMF) solves a receptor-only, unmixing model that assumes a measured dataset conforms to a mass balance of a specific number of constant source profiles that contribute varying concentrations over time.[10,11,12] PMF analysis parses a time series of measured chemical species into a number of user-prescribed factors, each with its own

[9]Solomon, P. A., D. Crumpler, J. B. Flanagan, R. K. M. Jayanty, E. E. Rickman, and C. E. McDade. 2014. U.S. National $PM_{2.5}$ chemical speciation monitoring networks—CSN and IMPROVE: Description of networks. *J. Air Waste Manage. Assoc.* 64 (12):1410–38. doi:10.1080/10962247.2014.956904.

[10] Paatero, P. 1997. Least squares formulation of robust non-negative factor analysis. *Chemometr. Intell. Lab.* 37 (1):23–35. doi:10.1016/S0169-7439(96)00044-5.

[11] Paatero, P., and P. K. Hopke. 2003. Discarding or Downweighing High-Noise Variables in Factor Analysis Models. *Analytica. Chimica. Acta.* 490 (1–2):277–89. doi:10.1016/S0003-2670(02)01643-4.

[12] Paatero, P., and U. Tapper. 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* 5 (2):111–26. doi:10.1002/env.3170050203.

chemical profile and mass contribution to the total measured dataset. No *a priori* information regarding temporal behavior or source trends is required. The optimal solution of PMF analysis describes the measured dataset with a number of factors such that the solution minimizes a quality of fit parameter (where a smaller value means a better fit). The PMF user utilizes error analysis and guidance for PMF solutions, knowledge of potential sources, and previously defined chemical fingerprints (i.e., from EPA's SPECIATE database) to determine the solution that best explains the measured dataset.

To determine the optimal solution and number of factors that explain the measured dataset, the PMF model was run multiple times, starting with a low number of factors. A solution with too few factors leads to solutions with factors representing mixtures of sources and compositions. With an increasing number of factors, the resulting factors become better resolved. A solution with too many factors is apparent by the model splitting a single source into multiple factors.

Once a solution was identified, bootstrapping, displacement, and BS-DISP error analyses were conducted to better understand the uncertainty of the PMF solution and impacts of random errors and rotational ambiguity. If the factor solution satisfied error estimation guidelines[13,14,15] then the solution was chosen as optimal. If not, the number of factors were reduced by one and/or constraints were applied, and error analysis methods were re-run. It is common for a PMF solution to have clearly delineated factors but not satisfy error estimation guidelines or satisfy error estimation guidelines with factors that are mixtures and not clearly delineated as single sources. A solution that satisfied mathematical error estimation guidelines was favored over a solution with clearly delineated factors that did not pass error estimation guidelines.

PMF analysis utilized EPA PMF Version 5.0.14.[15] The PMF model was run in robust mode with 20 repeat runs. The Rotational Fpeak variable was held at the default of 0.0.

Data Preparation for PMF Analysis

Data preparation for PMF analysis used the same methodology as previous analyses.[16] After the data treatment steps outlined below, the remaining species included in PMF analysis using the EPA PMF 5.0 model were $NH4^+$, As, Br, Ca, Cl^-, Fe, K, Si, Na^+, SO_4^{2-}, non-sulfate sulfur (NSS), Ti, NO_3^-, Zn, elemental carbon subfractions EC1, EC2, and EC3 (EC2 and EC3 were combined into one EC2_EC3 subfraction), and organic carbon subfractions OC1, OC2, OC3, OC4, and OP.

[13] Paatero, P, S. Eberly, S.G. Brown, G.A. Norris. 2014. Methods for estimating uncertainty in factor analytic solutions. *Atmos. Meas. Tech.* 7 (3) 781-797.
[14] Brown, S.G., S. Eberly, P. Paatero, G.A. Norris. 2015. Methods for estimating uncertainty in PMF solutions: Examples with a mbient air and water quality data and guidance on reporting PMF results. *Science of the Total Environ.* 518-519, 626-635.
[15] EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. https://www.epa.gov/sites/default/files/2015-02/documents/pmf_5.0_user_guide.pdf.
[16] Friedman, B. 2020. Source apportionment of $PM_{2.5}$ at two Seattle chemical speciation sites. *J. Air Waste Manage. Assoc.* 70(7):687-699.

Blank correction

CSN data obtained from EPA's Air Quality System (AQS) is not blank corrected or corrected to account for filter media content and sampling artifacts. Corresponding field blank data can be obtained from AQS. Field blank samples generally occur monthly. When field blanks were collected concurrently with sample data the blank concentrations were directly subtracted from the sample concentrations. Samples without a concurrent field blank measurement utilized the median value from the previous three field blank measurements.

Missing data

Missing data were replaced by the species' median concentration; the associated sample uncertainty was set to 4 times the species' median concentration. Chemical species with data completeness less than 50% were removed from the analysis.

Avoiding double counting

Including similar chemical species (i.e., sulfate and sulfur) can bias the PMF solution by over-weighting the contribution of a chemical species to the factor solution. PMF analysis used one of the duplicate species to avoid double counting; the retained species were based on signal-to-noise ratios and data completeness statistics. Cl^-, K, Na^+, and SO_4^{2-} were retained in this analysis while Cl, K^+, Na, and S were not. EC1 was recalculated as EC1-OP because the organic pyrolysis (OP) concentration is also a portion of the EC1 concentration. Non-sulfate sulfur (NSS) was calculated from the difference of the measured sulfur concentration and the sulfur component of the measured sulfate concentration.

Estimating uncertainty

PMF model input includes a concentration matrix and an associated uncertainty matrix. CSN data obtained from EPA's Air Quality System includes analytical uncertainties associated with sample measurements. The overall uncertainty for each species at each timestep was calculated using the associated analytical measurement uncertainty as well as the reported method detection limit (MDL). The uncertainties of measurements below the MDL were set to the largest of either ⅚ of the MDL or the reported uncertainty. Uncertainties of measurements above the MDL were set to the reported analytical uncertainty plus ⅓of the MDL.

Signal-to-noise data exclusion

Species were excluded from analysis if their signal-to-noise ratio was less than 0.2, where the signal-to-noise calculation takes into account analytical uncertainties associated with sample measurements.[17] The excluded species were aluminum, antimony, barium, cadmium, cerium, cesium, chromium, cobalt, copper, indium, lead, magnesium, manganese, phosphorus, nickel, rubidium, selenium, silver, strontium, tin, and vanadium.

[17] EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. https://www.epa.gov/sites/default/files/2015-02/documents/pmf_5.0_user_guide.pdf.

Excluded samples

Sampling days associated with wildfire smoke in August and September 2018, as well as, September 2020 were excluded from the analysis. When wildfire data was included, the model could not replicate the observed high $PM_{2.5}$ mass concentrations, and solutions did not pass the error analysis guidance. Excluded days include 8/18/2018, 8/24/2018, 9/5/2018, 9/12/2020, and 9/18/2020.

CSN carbon data shift after October 2018

In October 2018, the carbon analyzer used to report thermal subfractions changed from DRI model 2015 analyzers at the Desert Research Institute (DRI) to Sunset Laboratory model 5L analyzers at UC Davis.[18] A laboratory inter-comparison study found significant differences in the thermal subfraction data (OC1, OC2, OC3, OC4, EC1, EC2, EC3, OP) between the two analyzer models.[19] To account for the differences between the two analyzer models and thermal subfraction data, the thermal subfraction data prior to the analyzer change (9 samples) was adjusted to emulate the measured thermal subfraction data after the analyzer change. This adjustment was done based on CSN and Interagency Monitoring of Protected Visual Environments (IMPROVE) collocated datasets that were collected both before and after October 2018. Linear regressions of these collocated datasets provide slopes between the two analyzer models for thermal subfraction measurements for data before and after October 2018; ratios between these slopes were used to adjust the pre-October 2018 thermal subfraction data.[20]

[18] https://www.epa.gov/sites/default/files/2021-06/documents/csn_dataadvisory_carbon_transition.pdf
[19] Zhang, X., Trzepla, K., White, W., Raffuse, S., and Hyslop, N.P. 2021. Intercomparison of thermal-optical carbon measurements by Sunset and Desert Research Institute (DRI) analyzers using the IMPROVE_A protocol, *Atmos. Meas. Tech*. 14, 3217-3231, https://doi.org/10.5194/amt-14-3217-2021, 2021.
[20] Kotchenruther, R.A. 2021. Report on $PM_{2.5}$ receptor modeling for Fairbanks, Alaska.

Results

PMF solution

Based on factor composition, temporal behavior, source profiles from EPA's SPECIATE database, and error analysis, a ten-factor solution was chosen as the optimal PMF solution. The following factors were identified:

- Wood smoke
- Vehicles
- Fugitive dust
- Sea salt
- Fireworks
- Iron-rich
- Zinc-rich
- Unidentified urban
- Sulfate-rich
- Nitrate-rich

Factor composition and identification are described in detail at the end of this section. Similar factors identified from previous source apportionment work utilizing CSN data from 2008-2012 at the Alexander Avenue monitoring site include $PM_{2.5}$ associated with wood smoke, ammonium nitrate, motor vehicles, iron-rich, sea salt, and fugitive dust.[21]

To further differentiate the wood smoke and nitrate factors, which have similar seasonal patterns, the following model constraints were implemented:

- Potassium and OC1 in the nitrate-rich factor were pulled down[22]
- Nitrate in the wood smoke factor was pulled down

The base model displacement error estimation analysis reported no factor swaps at any displacement level, which indicates the solution is stable without significant rotational ambiguity. Bootstrapping analysis indicated that all factors mapped back to their original factor at least 90% of the time. BS-DISP error estimation with all strong species displaced utilized 94% of bootstrapping cases and reported zero factor swaps at the lowest displacement level, further indicating that significant rotational ambiguity does not exist, and the ten-factor solution is well constrained.

The ten-factor PMF solution captured on average 90% of the measured $PM_{2.5}$ mass (Figure 3). Mass not captured by the ten factor PMF solution could be associated with noise and

[21] Kotchenruther, R.A. 2016. Source apportionment of PM2.5 at multiple Northwest US Sites: Assessing regional winter wood smoke impacts from residential wood combustion. *Atmos. Env.* 142, 210-219.
[22] The user can constrain or "pull down" specific elements in a factor to minimize their contribution to that factor.

uncertainty in the measured dataset, insignificant or small $PM_{2.5}$ sources, and $PM_{2.5}$ sources that the PMF model was unable to separate into a unique factor.

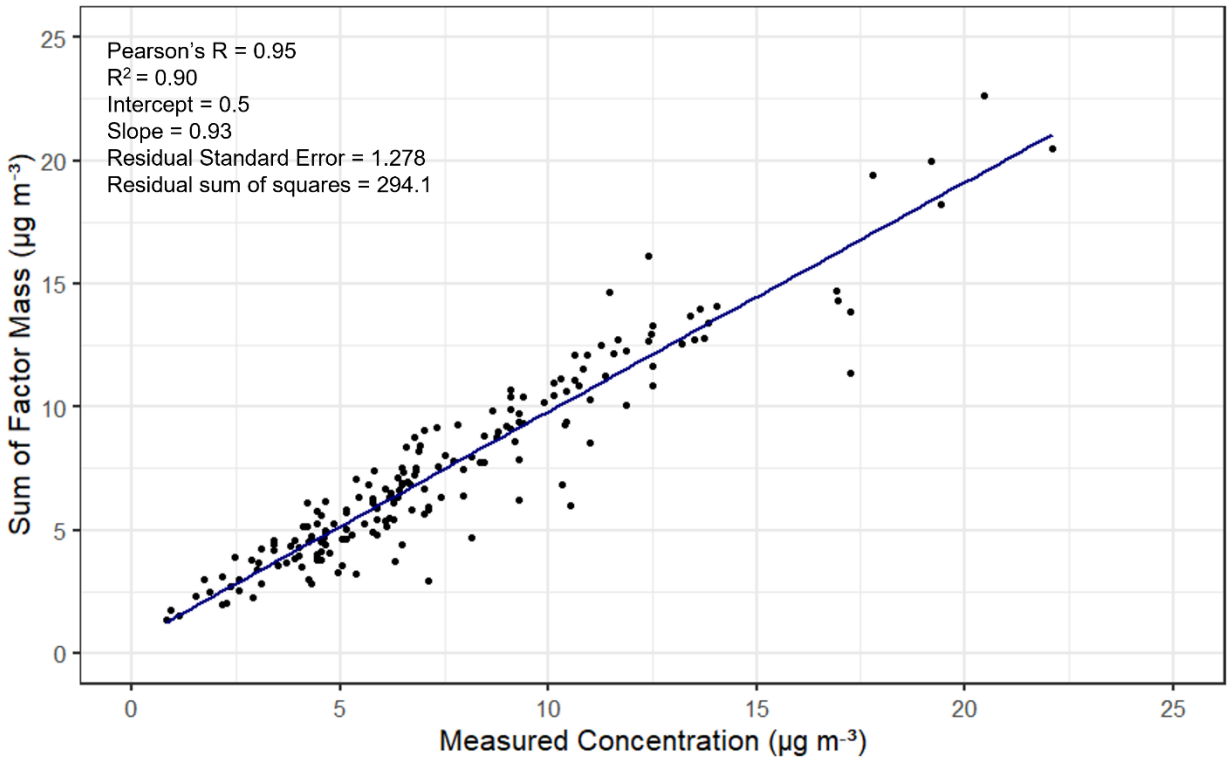


Figure 3. Modeled (PMF) vs. measured $PM_{2.5}$ mass.

Factor identification

Annual average concentrations and contributions to the total factor mass are shown in Figures 4 and 5, as well as Table 1. Annual averages were derived from monthly average mass concentrations since the data spanned multiple years as well as an uneven distribution of samples throughout different years. $PM_{2.5}$ associated with wood smoke contributed the most on average to total measured $PM_{2.5}$, followed by sulfate-rich, vehicles, nitrate-rich, unidentified urban, dust, zinc-rich, fireworks, iron-rich, and sea salt factors.

Table 1. Annual average concentrations of factors identified at the Port of Tacoma from PMF analysis and annual average $PM_{2.5}$ concentration. Annual average $PM_{2.5}$ concentration is based on CSN monitoring data.

Factor or Ambient Concentration	**Annual Average $PM_{2.5}$ Factor Mass ($\mu g\ m^{-3}$) and annual average $PM_{2.5}$ mass ($\mu g\ m^{-3}$)**
Wood smoke	2.0
Sulfate-rich	1.4
Vehicles	1.0
Nitrate-rich	0.65
Unidentified urban	0.62
Fugitive dust	0.53
Fireworks	0.38
Zinc-rich	0.30
Sea salt	0.23
Iron-rich	0.21
$PM_{2.5}$ (ambient concentration)	7.3

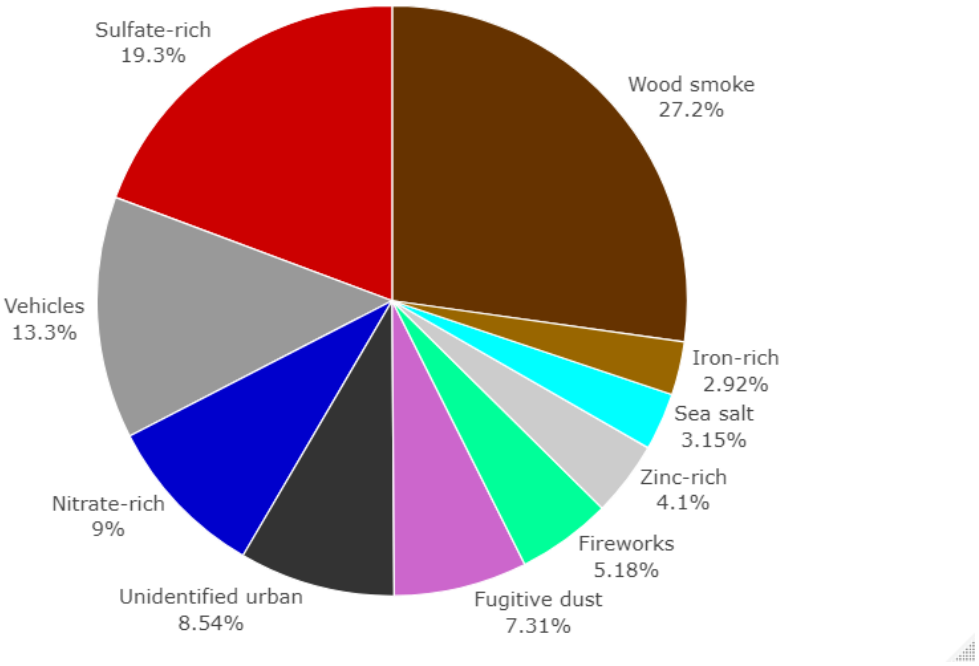


Figure 4. Average contribution of each factor identified to the total factor mass.

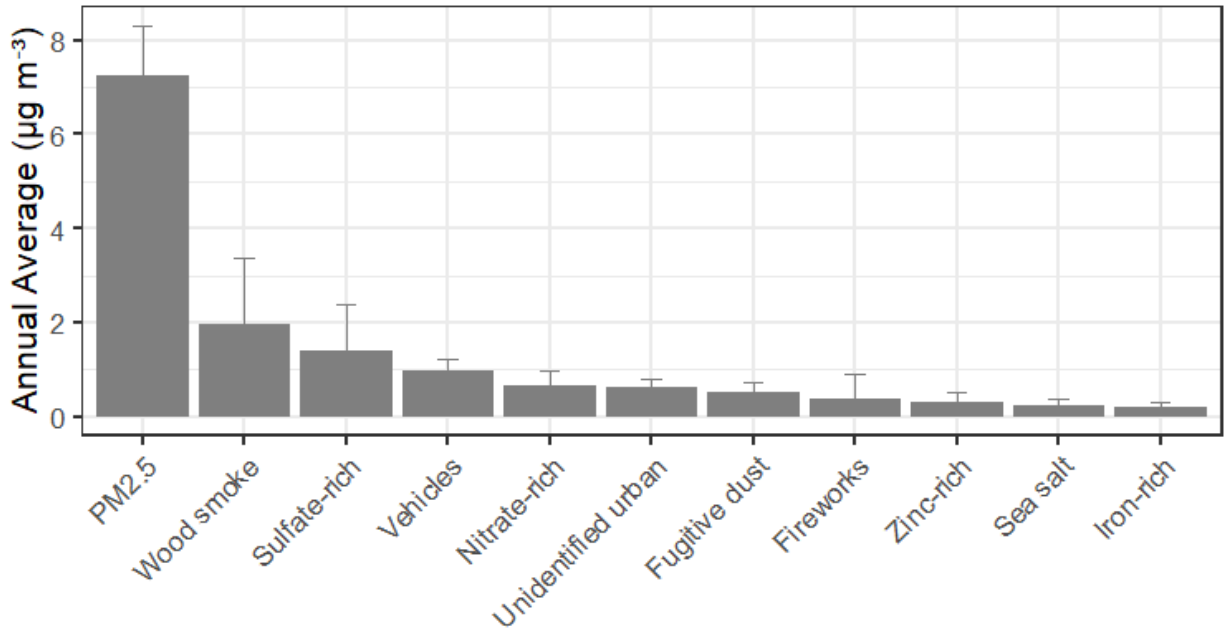


Figure 5. Annual average concentration of each identified factor and ambient $PM_{2.5}$. Error bars represent the standard deviation of the mean.

Impacts of the sampling break on data representativeness

The COVID-19 pandemic led to a pause in CSN sampling from March to August 2020, resulting in 27 missed samples. However, the nephelometer at the monitoring site continued collecting data during this sampling pause. Average nephelometer $PM_{2.5}$ concentrations can provide insight into whether the break in sampling introduced challenges regarding the representativeness of the dataset. The average nephelometer $PM_{2.5}$ concentration during the entire study period (including March-August 2020 data) was 7.1 µg m^{-3}, while the average nephelometer $PM_{2.5}$ concentration accounting for the sampling pause (omitting March-August 2020 data) was 7.5 µg m^{-3}. As there isn't a large change in average $PM_{2.5}$ concentrations accounting for the break in sampling, it's likely that including data from the sampling break would not have substantially changed the results of this study. While a continuous dataset is more desirable for PMF modeling and analysis, the early months of the COVID-19 pandemic were likely not representative of typical conditions at the monitoring site due to reduced interstate and container traffic. The interrupted dataset is likely more representative of typical conditions observed at the monitoring site.

Factors associated with diesel $PM_{2.5}$

Components of diesel $PM_{2.5}$ were identified in multiple PMF factors, including vehicles, zinc-rich, iron-rich, and unidentified urban. Together, these three factors comprised about 29% of the annual average $PM_{2.5}$ mass concentration. A timeseries of the sum of the factors associated with diesel compared to the total factor sum is shown in Figure 6. The sum of factors associated with diesel were also aggregated into one pollution rose shown in Figure 7. The highest

concentrations of $PM_{2.5}$ associated with diesel are from the southeast, east, and northeast directions, which corresponds to directions associated with major nearby roadways.

The chemical profiles of $PM_{2.5}$ associated with diesel exhaust are generally enriched in elemental carbon, magnesium, calcium, nickel, copper, zinc, manganese, iron, and vanadium.[23] However, many of the metals present in $PM_{2.5}$ associated with diesel were not included in this PMF analysis due to their low signal to noise ratios. This likely contributed to PMF having difficulties distinguishing and identifying distinct diesel $PM_{2.5}$ sources (i.e., on-road vehicles vs. industry vs. commercial ships), which resulted in identifying multiple factors associated with common chemical components of diesel $PM_{2.5}$.

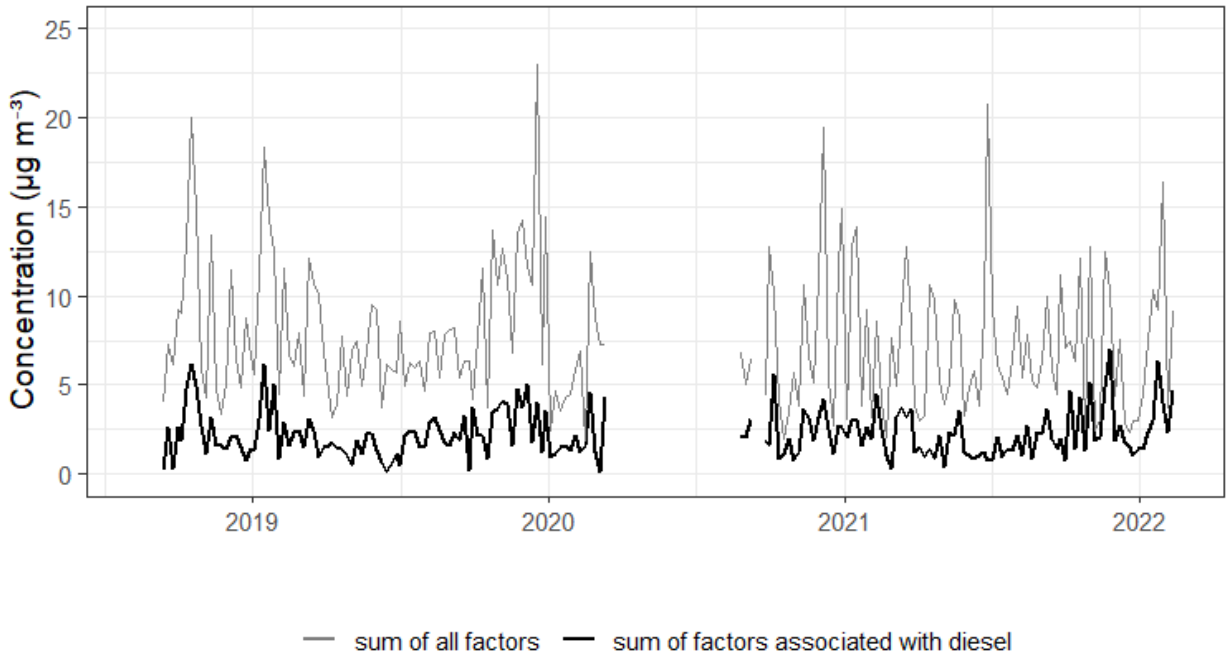


Figure 6. Timeseries of the sum of all PMF factors (gray line) and the sum of PMF factors associated with diesel (black line).

[23] Squizzato, S., M. Masiol, D.Q. Rich, P.K. Hopke. 2018. A long-term source apportionment of PM2.5 in New York State during 2005-2016. *Atmos. Env.* 192, 35-47.

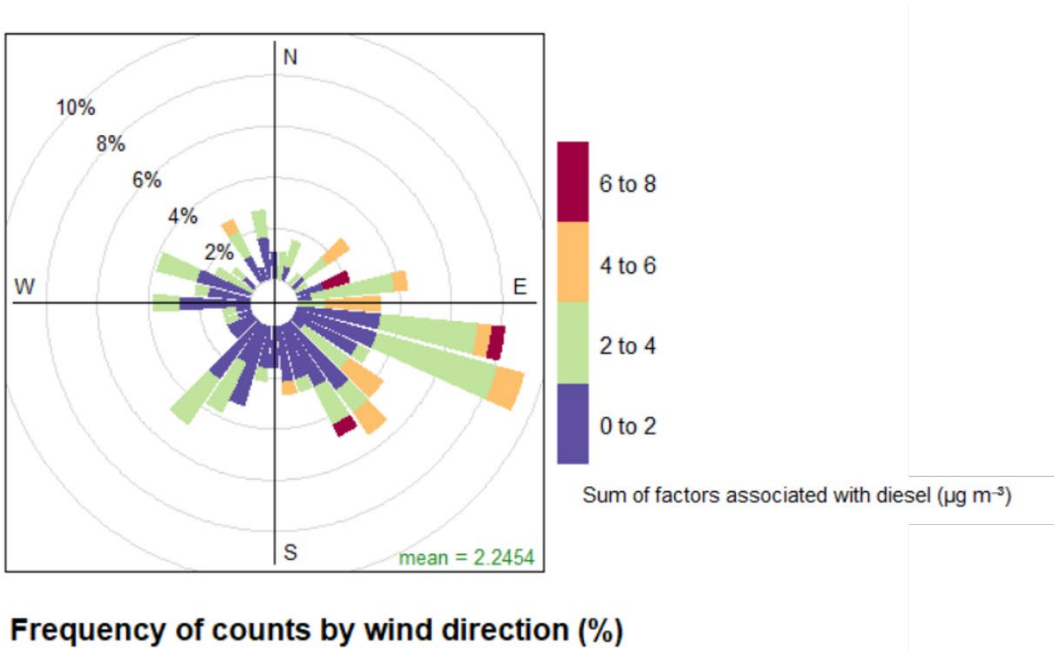


Figure 7. Pollution rose of the sum of PMF factors associated with diesel.

Temporal variability

Daily concentrations of each factor and their contributions to the total modeled $PM_{2.5}$ concentration are shown in Figure 6. Factors contributed various amounts to the total modeled $PM_{2.5}$ based on seasonality and day of week emission patterns. In general, the highest modeled $PM_{2.5}$ concentrations occurred during the fall and winter, where $PM_{2.5}$ associated with wood smoke and motor vehicles contributed on average 33% and 25%, respectively. Highest summertime $PM_{2.5}$ concentrations were associated with the sulfate-rich factor, which contributed on average 40% to the total modeled $PM_{2.5}$ during the summer months.

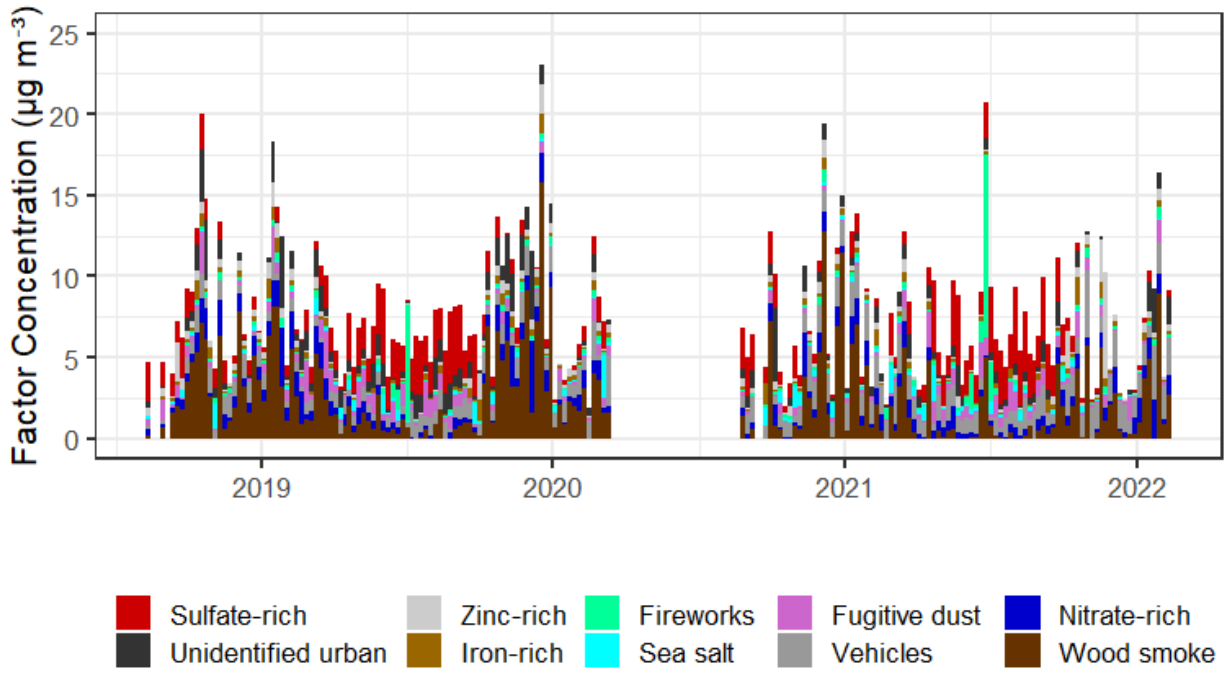


Figure 8. Daily concentrations of each factor. Note that days impacted by wildfires were excluded.

Monthly and Seasonal Contributions

To better understand the contributions of individual sources, factor concentrations were averaged both monthly and seasonally. Monthly factor contributions (Figures 7 and 8) show that $PM_{2.5}$ associated with wood smoke and sulfate contribute the most to modeled $PM_{2.5}$ during the wintertime and summertime months, respectively.

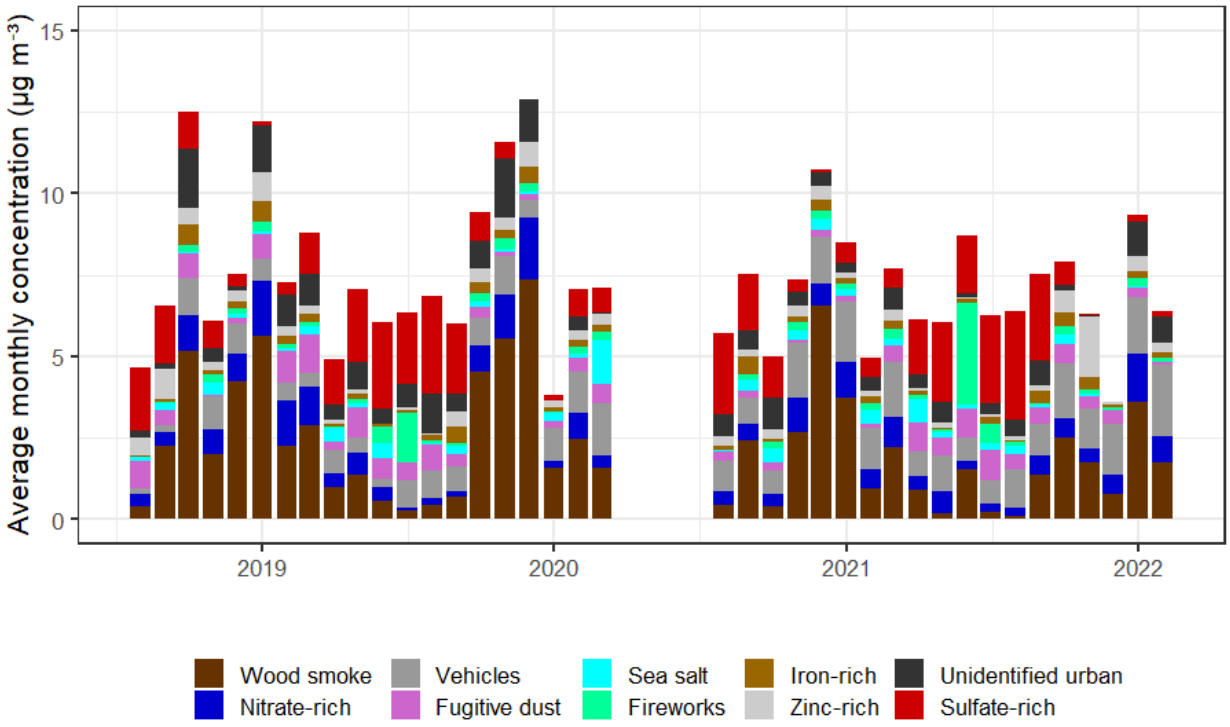


Figure 9. Monthly average concentrations of each factor.

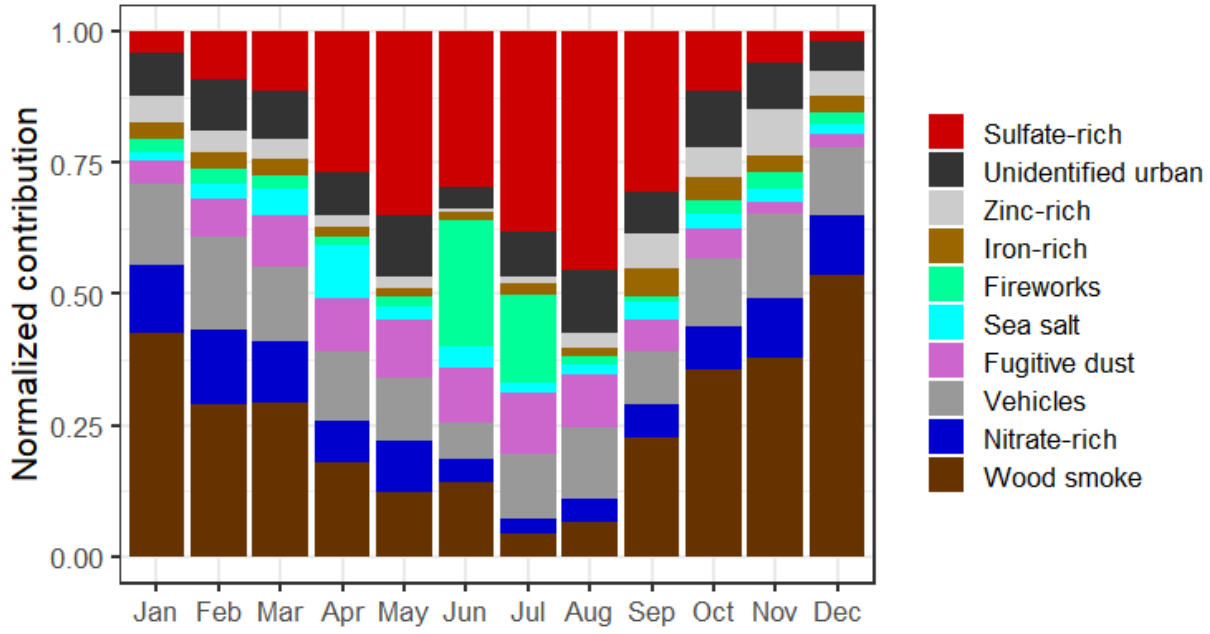


Figure 10. Contributions of each factor to total monthly concentrations.

To further distinguish sources based on their temporal variability, seasonal concentrations were investigated by defining a residential heating season as October-March and a non-residential heating season as April-September. Average seasonal concentrations are shown in Figure 8. Note that because of the pause in sampling in 2020, the dataset resulted in 3 residential heating seasons (110 total samples) and 2 non-residential heating seasons (77 total samples).

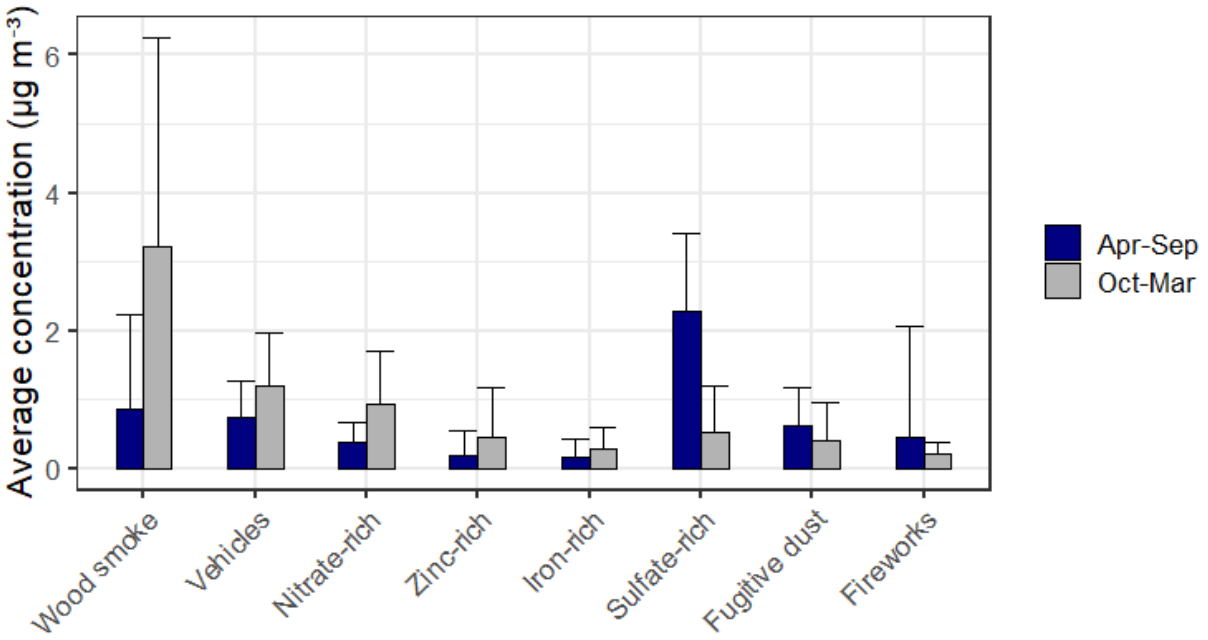


Figure 11. Average seasonal concentrations for each factor. Only factors with significant differences between their Apr-Sep and Oct-Mar distributions are shown.

Mann-Whitney U tests were run on each factor to test for significant differences in factor concentrations between the residential heating (October-March) and non-heating (April-September) seasons. Wood smoke, motor vehicles, fugitive dust, fireworks, iron-rich, zinc-rich, sulfate-rich, and nitrate-rich all had p-values less than 0.05, indicating significant differences between their respective April-September and October-March distributions.

Wood smoke and nitrate-rich factors were both significantly higher during residential heating season. This is consistent with emission patterns of wood smoke, as colder temperatures lead to increased residential home heating. Colder temperatures and higher relative humidity during the wintertime also favors formation of secondary nitrate. There are multiple reasons why the vehicles, zinc-rich, and iron-rich factors are significantly higher during the winter. The highest concentrations for the zinc-rich and iron-rich factors occurred during the winter; the significant difference between April-September and October-March concentrations could be due to wintertime emissions. There are multiple explanations for higher concentrations of $PM_{2.5}$ associated with vehicles in the colder months: 1) an increase in cold-starts from vehicles; 2) wintertime meteorological conditions and temperature inversions leading to increased surface pollutant concentrations; 3) the chemical profile of $PM_{2.5}$ associated with motor vehicles

included components that are also present in the wood smoke factor, which may artificially increase the seasonality of $PM_{2.5}$ associated with motor vehicles; 4) an increase in running PM emissions from vehicles with colder temperatures.

The higher concentrations observed in the non-residential heating season for $PM_{2.5}$ associated with fireworks are driven by a few high points that occurred in June and July. $PM_{2.5}$ associated with the fugitive dust and sulfate-rich factors exhibited higher concentrations in April-September compared to October-March. Increased photochemistry, regional emissions, and mixing in the warmer months likely contributes to increases in the sulfate-rich factor, while drier soil and less precipitation leads to increases in $PM_{2.5}$ associated with fugitive dust.

Day of week

To test for significant differences in factor concentrations between their weekday and weekend distributions, Mann-Whitney U tests were also run on each factor. Weekend and weekday distributions are shown in Figure 9. Significant differences (p-values < 0.05) were exhibited by $PM_{2.5}$ associated with fugitive dust and iron-rich emissions, suggesting an association with local industrial activities at the Port of Tacoma.

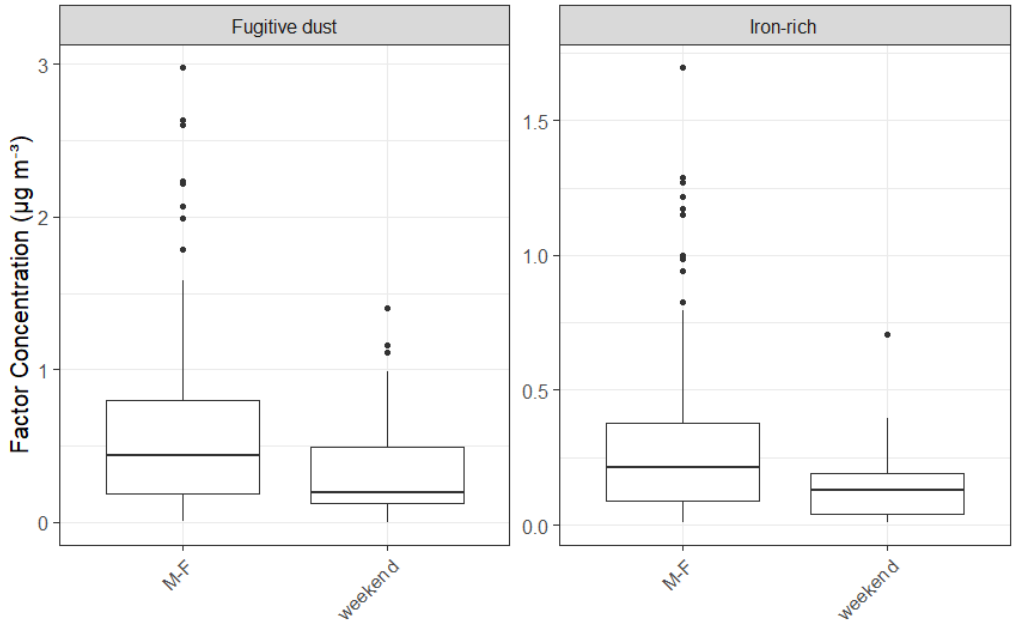


Figure 12. Day of week variability for each factor. Only factors with significant differences between their weekday and weekend distributions are shown.

Contribution to highest ambient $PM_{2.5}$

With wildfire data excluded, there were no exceedances of the daily $PM_{2.5}$ national ambient air quality standard of 35 µg m^{-3} during the study. However, there were multiple days characterized by elevated $PM_{2.5}$ concentrations, which are defined here as days observing daily $PM_{2.5}$ concentrations greater than 16 µg m^{-3}.

The majority of days over 16 µg m^{-3} occurred during the residential heating season, and many were associated with lower wind speeds, suggesting an association with wintertime inversion conditions. Figure 10 describes factor contributions to these higher observed concentration days. These higher concentrations were characterized by high contributions associated with wood smoke. One exception occurred on June 27, 2021, with a large contribution from $PM_{2.5}$ associated with fireworks to the total $PM_{2.5}$ concentration (June 27 was the Sunday prior to the 4th of July).

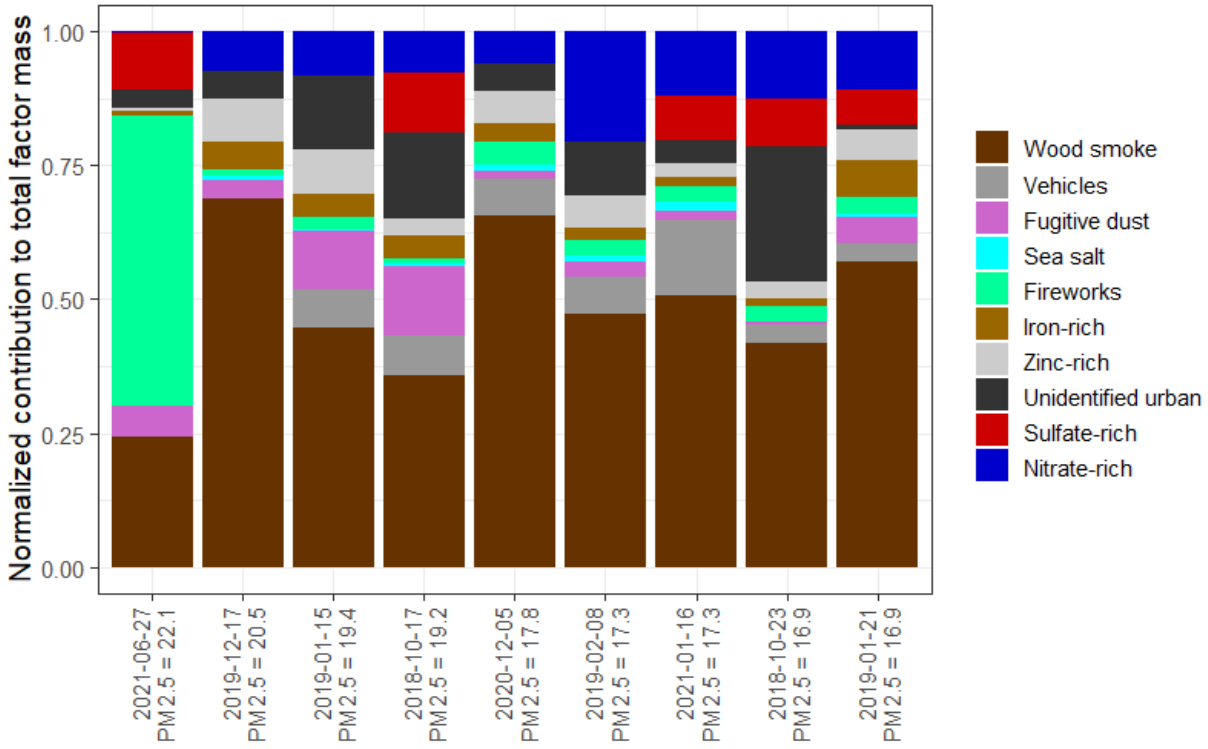


Figure 13. Factor contributions to the highest observed $PM_{2.5}$ daily concentrations during the study period.

Short-term trends

While it is difficult to substantiate a trend from a three-year dataset, trend analysis can provide insight into short-term temporal changes. Theil-Sen trend analysis identified a significant increasing trend (0.28 µg m^{-3} per year) only for the vehicles factor (p-value < 0.01). However, annual average daily traffic data from the Washington State Department of Transportation for major roadways near the Port of Tacoma (I-5 and I-509) do not show increases from 2018-2021, although trends analysis is complicated by the atypical traffic patterns that arose from the COVID-19 pandemic.[24] This increase in $PM_{2.5}$ associated with vehicles could possibly be due to local on-road vehicle activity in the vicinity of the Port of Tacoma. An upward trend of $PM_{2.5}$

[24] https://wsdot.wa.gov/about/transportation-data/travel-data/traffic-count-data

associated with motor vehicles was also identified in a long-term trend study across New York State.[25]

No other factors or total $PM_{2.5}$ exhibited significant increasing or decreasing trends.

Detailed Factor Descriptions

Factor timeseries, chemical profiles, and pollution roses are shown in Figures 12-14.

Wood smoke

$PM_{2.5}$ associated with wood smoke is dominated by EC and lower-temperature OC subfraction components and accounted for 27% of the total factor mass. The factor composition also indicates trace contributions from K and Cl, similar to previous analyses.[26] Concentrations were also significantly higher in the residential heating season compared to the non-residential heating season. The highest concentrations were from east of the Port of Tacoma, consistent with population centers (Figure 15). The factor also was highly correlated (R^2 = 0.83) with aethalometer UV-BC measurements, which is a marker for woodsmoke.[27] $PM_{2.5}$ concentrations associated with wood smoke are similar to a previous analysis of 2008-2012 CSN data at the Alexander Ave monitoring site, which reported about 35.3% of PM2.5 mass was attributed to $PM_{2.5}$ associated with primary wood smoke.[28]

Sulfate-rich

Sulfate-rich $PM_{2.5}$ ($PM_{2.5}$ associated with high concentrations of sulfate) comprised 19% of the total factor mass. While NH_4 was not present in this factor, higher concentrations in the summer months due to increased photochemical activity is consistent with secondary sulfate, which is produced from atmospheric oxidation of multiple SO_2 sources. The presence of OC components is also consistent with secondary sulfate, as reaction pathways that favor the production of secondary sulfate may also lead to the formation of secondary organic aerosol.

Trace amounts of EC in the factor profile indicate a potential contribution from industrial sources and fuel combustion. Given the presence of sodium (indicative of $PM_{2.5}$ associated with sea salt) in the chemical profile, $PM_{2.5}$ emissions from commercial marine vessels (due to burning of residual fuel oil, which has a high sulfur content), could be contributing to this sulfate-rich factor. The pollution rose (Figure 15) shows the highest concentrations from the southwest and west, consistent with nearby ships. Vanadium and nickel are markers for residual fuel oil combustion emissions yet were not included in PMF analysis due to their low

[25] Masiol, M., S. Squizzato, D.Q. Rich, P.K. Hopke. 2019. Long-term trends (2005-2016) of source apportioned PM2.5 across New York State. *Atmos. Environ.* 201, 110-120.
[26] Friedman, B. 2020. Source apportionment of $PM_{2.5}$ at two Seattle chemical speciation sites. *J. Air Waste Manage. Assoc.* 70(7):687-699.
[27] Wang, Y., P.K. Hopke, O.V. Rattigan, X. Xia, D.C. Chalupa, M.J. Utell. 2011. *Environ. Sci. Technol.* 45, 17, 7387-7393.
[28] Kotchenruther, R.A. 2016. Source apportionment of PM2.5 at multiple Northwest U.S. sites: Assessing regional winter wood smoke impacts from residential wood combustion. *Atmos. Environ.* 142, 210-219.

signal-to-noise ratios. While there were days where the raw concentrations of vanadium and nickel increased above their respective detection limits, these days were not associated with higher concentrations of the sulfate-rich factor. Further, 2015 regulations have dramatically decreased burning of high-sulfur fuels and their associated $PM_{2.5}$ emissions.[29] This PMF analysis did not identify a distinct $PM_{2.5}$ source associated with marine vessel burning of residual fuel oil.

Vehicles

The $PM_{2.5}$ factor associated with motor vehicles accounted for about 13.6% of the total factor mass. The source profile was dominated by EC1, OC2, OC3, and OC4, with small contributions from NO_3 and SO_4. Given the presence of elemental carbon subfractions, it is likely that this factor includes both gasoline and diesel vehicles. Higher factor concentrations in the fall and winter months could be due to a variety of reasons, including more cold starts in winter, higher running emissions with colder temperatures, meteorological conditions, or a modeling artifact. Cl and OP are present in the gasoline factor profile in trace amounts, and these pollutants are also present in the factor associated with wood smoke, which also has significant observed seasonality. Attempts to constrain the modeling further did not resolve this seasonal difference.

Nitrate-rich

$PM_{2.5}$ associated with high concentrations of nitrate contributed 9% of the total $PM_{2.5}$ at the Port of Tacoma monitoring site. The factor composition also included trace amounts of OC, EC, and NH_4. Despite the factor only having trace amounts of NH_4, concentrations are consistent with the seasonal pattern of secondary nitrate, as low temperatures and high relative humidity favor higher ammonium nitrate concentrations in the wintertime. Thus, it is likely that this factor is a mix of primary and secondary nitrate. Sources of NO_x at the Port of Tacoma potentially contributing to this factor include industrial boilers, cement kilns, and on-and off-road vehicles. It is also possible that there were difficulties separating NH_4 in this factor from the high contribution of NH_4 to the unidentified urban factor. Attempts to constrain the modeling further did not resolve this or generate a unique ammonium nitrate factor.

Unidentified urban

Ammonium, nitrate, and sulfate were the main components of $PM_{2.5}$ associated with this factor, with contributions from EC, OC, OP, Cl, and Si. It is likely that this factor is related to many different sources of ammonia, sulfate, and nitrate, such as oil refinery operations, burning, and primary sulfate production. Similar factors previously identified have been linked to fuel combustion activities and diesel sources.[30,31] The highest concentrations of this factor originate

[29] Kotchenruther, R.A. 2021. Source apportionment of PM2.5 at IMPROVE monitoring sites within and outside of marine vessel fuel sulfur emissions control areas. *J. Air Waste Manage. Assoc.* 71(9):1114-1126.
[30]Kotchenruther, R.A.. 2013. A regional assessment of marine vessel PM2.5 impacts in the U.S. Pacific Northwest using a receptor-based source apportionment method. *Atmos. Environ.* 68.
[31] Friedman, B. 2020. Source apportionment of $PM_{2.5}$ at two Seattle chemical speciation sites. *J. Air Waste Manage. Assoc.* 70(7):687-699.

from the east and northwest. However, contributions from this factor occur from all directions, suggesting this factor is a mixture of many sources. When increasing the number of factors in the PMF solution this factor was always present; increasing the factors did not split up NO_3 from SO_4. Another explanation for the presence of nitrate and sulfate together is that this factor is related to secondary $PM_{2.5}$. Ammonium nitrate, ammonium sulfate, and OP are linked to secondary $PM_{2.5}$ production, and the mixture of sources may reflect changes in atmospheric photochemical activity and oxidant capacity.

Fugitive dust

$PM_{2.5}$ associated with dust is characterized by Si, Ca, and trace amounts of Ti. This factor is most similar to SPECIATE unpaved and paved road dust profiles. Higher concentrations during the weekdays as well as the presence of EC and sulfate indicates that $PM_{2.5}$ associated with road dust is related to local industrial activities. Higher spring and summertime concentrations could also be due to drier ground conditions, which are more likely in the summer.

Fireworks

This factor profile is characterized by high concentrations of K and SO_4, with contributions from OC, OP, and Cl. The factor comprises similar chemical components to wood smoke but the seasonal pattern of $PM_{2.5}$ associated with wood smoke is not observed as well as no significant correlation with aethalometer wood smoke markers. Concentrations of this factor are relatively low with a few exceptions that occurred in June and July.

This factor was investigated further by looking at hourly PM2.5 concentrations and meteorological conditions on days when high concentrations of this factor were observed. Increases in hourly nephelometer $PM_{2.5}$ concentrations occurred primarily in the evenings (6-10pm) and were associated with winds from the west and southwest. Based on the transient nature of the concentration spikes and the factor profile, this factor is most likely associated with local firework activity.

Zinc-rich

This factor was associated with high concentrations of EC and a significant contribution of Zinc. Previous studies have linked Zinc-rich factors to diesel vehicles and industrial activities.[32] Zinc is also an additive in many engine lubricating oils as well as present in brake and tire wear profiles. 81% of the total Zinc mass was apportioned to this factor. Monthly concentrations of this factor were less than 1 $\mu g\ m^{-3}$, with the exception of November 2021. The highest observed concentration of this factor occurred on November 24, 2021 and was associated with wind speeds less than 2 mph from the northeast.

Sea salt

[32] Kotchenruther, R.A. 2013. A regional assessment of marine vessel PM2.5 impacts in the U.S. Pacific Northwest using a receptor-based source apportionment method. *Atmos. Environ.* 68, 103-111.

$PM_{2.5}$ associated with sea salt is dominated by sodium and chlorine. The presence of NO_3 indicates a contribution from aged sea salt, as aged sea salt is characterized by nitrate displacing chloride. This factor accounted for 3% of the total factor mass.

Iron-rich

This factor was dominated by elemental carbon and iron and accounted for only 3% of the total factor mass. All of the measured iron mass was apportioned to this factor. Previous work has linked iron-rich factors to diesel vehicles and industrial activities. Iron is also associated with brake and tire wear sources. This factor also was significantly higher during the week, suggesting $PM_{2.5}$ associated with EC and Fe is related to local industrial activities.

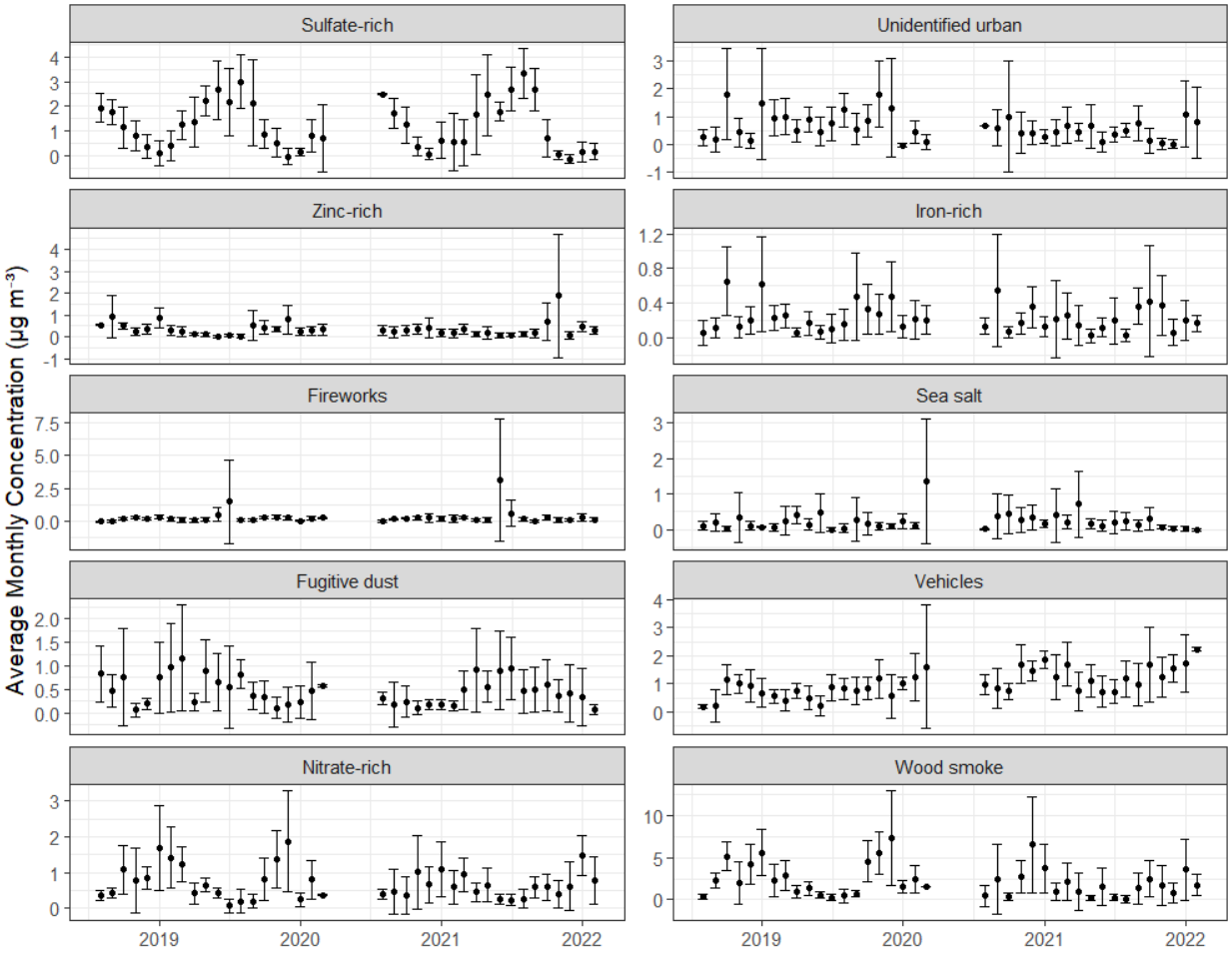


Figure 14. Average monthly concentrations of each factor. Error bars are the standard deviation of the mean.

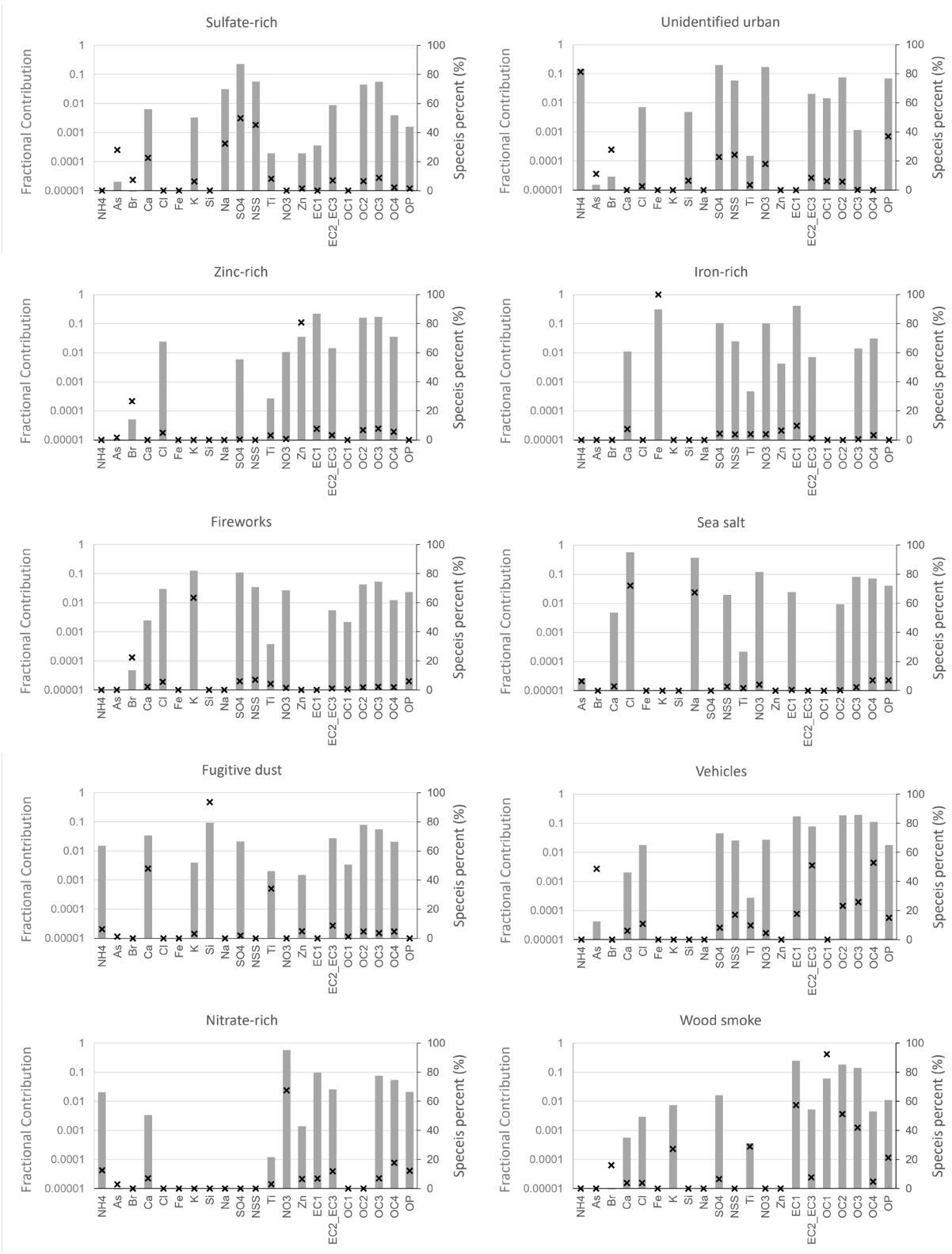
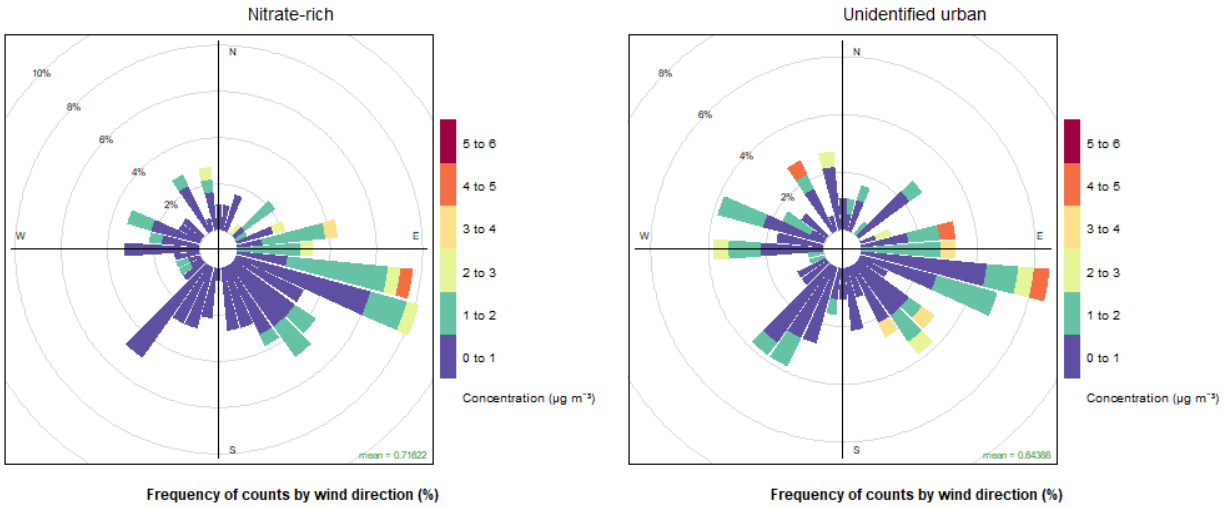
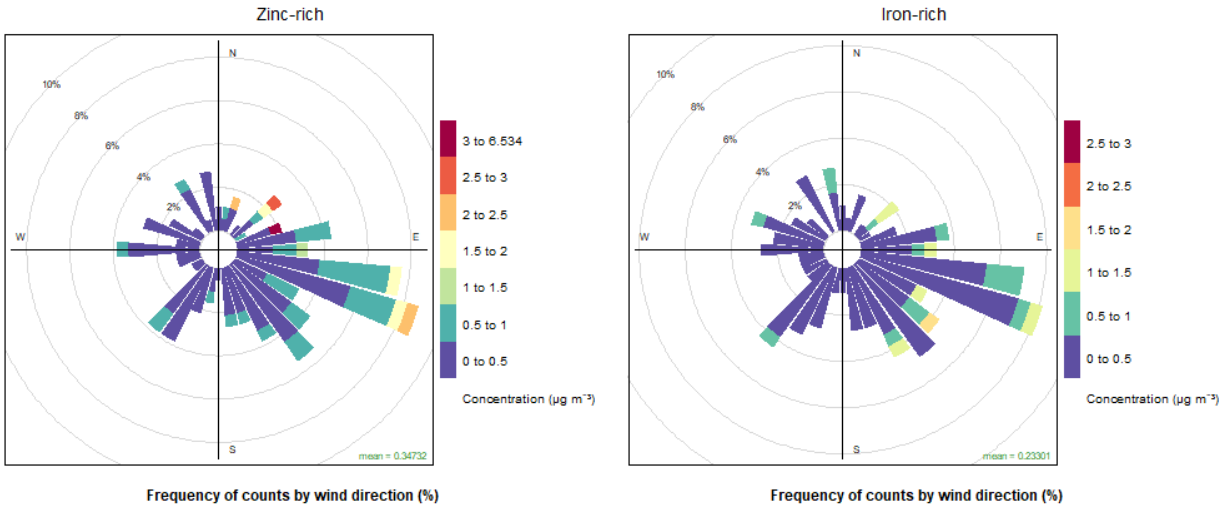
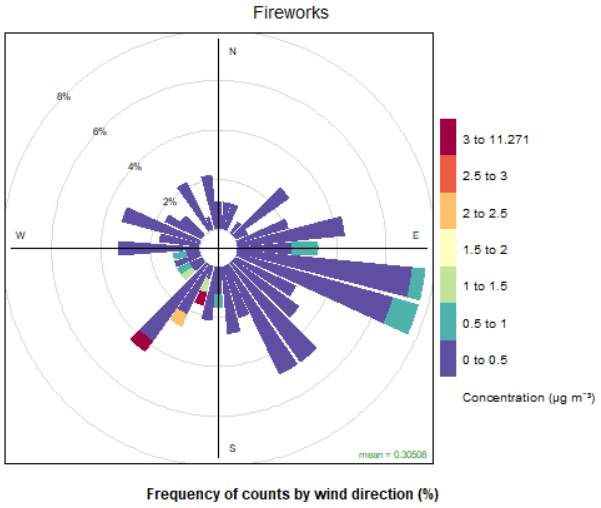
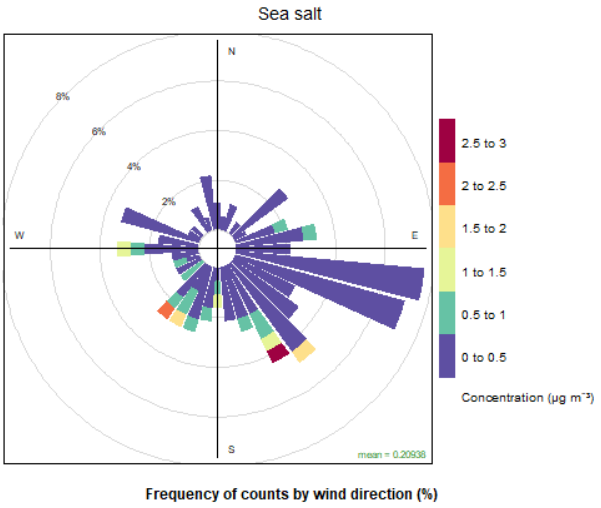


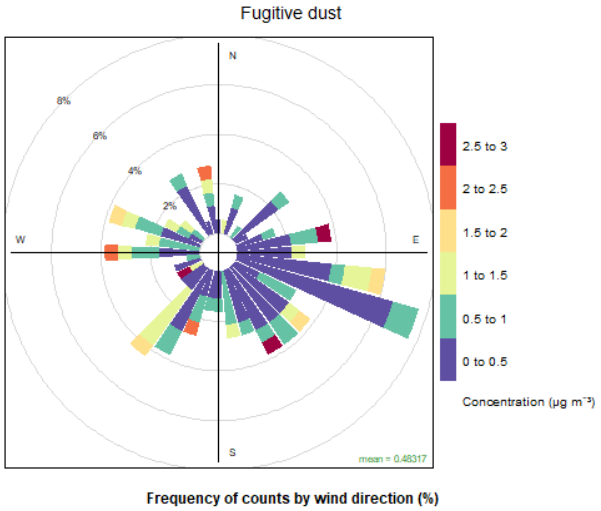
Figure 15. Chemical fingerprints of PMF factors. Bars refer to the fractional contribution of each species to the total chemical composition of the factor (left axis) and 'x' symbols refer to the percent contribution of each species to the factor (right axis).

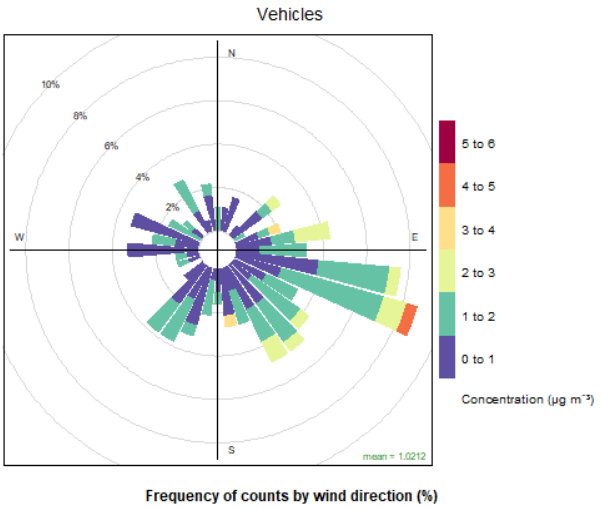

Nitrate-rich
N
E
S
W
10%
8%
6%
4%
2%
mean = 0.71622
5 to 6
4 to 5
3 to 4
2 to 3
1 to 2
0 to 1
Concentration (µg m⁻³)
Frequency of counts by wind direction (%)
Unidentified urban
N
E
S
W
8%
6%
4%
2%
mean = 0.64388
5 to 6
4 to 5
3 to 4
2 to 3
1 to 2
0 to 1
Concentration (µg m⁻³)
Frequency of counts by wind direction (%)


Zinc-rich
N
E
S
W
10%
8%
6%
4%
2%
mean = 0.34732
3 to 6.534
2.5 to 3
2 to 2.5
1.5 to 2
1 to 1.5
0.5 to 1
0 to 0.5
Concentration (µg m⁻³)
Frequency of counts by wind direction (%)
Iron-rich
N
E
S
W
10%
8%
6%
4%
2%
mean = 0.23301
2.5 to 3
2 to 2.5
1.5 to 2
1 to 1.5
0.5 to 1
0 to 0.5
Concentration (µg m⁻³)
Frequency of counts by wind direction (%)


Fireworks
N
E
S
W
8%
6%
4%
2%
3 to 11.271
2.5 to 3
2 to 2.5
1.5 to 2
1 to 1.5
0.5 to 1
0 to 0.5
Concentration (µg m⁻³)
mean = 0.30508
Frequency of counts by wind direction (%)


Sea salt
N
E
S
W
8%
6%
4%
2%
2.5 to 3
2 to 2.5
1.5 to 2
1 to 1.5
0.5 to 1
0 to 0.5
Concentration (µg m⁻³)
mean = 0.20938
Frequency of counts by wind direction (%)


Fugitive dust
N
E
S
W
8%
6%
4%
2%
2.5 to 3
2 to 2.5
1.5 to 2
1 to 1.5
0.5 to 1
0 to 0.5
Concentration (µg m⁻³)
mean = 0.48317
Frequency of counts by wind direction (%)


Vehicles
N
E
S
W
10%
8%
6%
4%
2%
5 to 6
4 to 5
3 to 4
2 to 3
1 to 2
0 to 1
Concentration (µg m⁻³)
mean = 1.0212
Frequency of counts by wind direction (%)

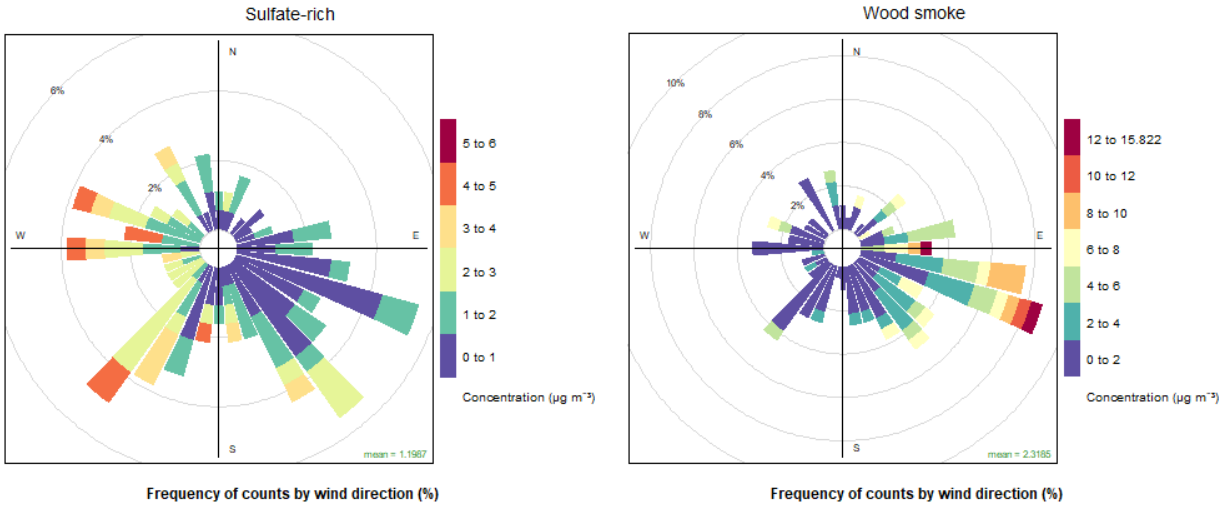


Figure 16. Pollution roses for each PMF factor.

Conclusions

Analysis of speciated $PM_{2.5}$ measurements by PMF from a monitoring site adjacent to the Port of Tacoma identified ten factors of $PM_{2.5}$. These ten factors included several that likely correspond to specific source types: $PM_{2.5}$ associated with wood smoke, vehicles, fugitive dust, sea salt, fireworks, and urban emissions, along with factors that captured high concentrations of sulfate, nitrate, zinc, and iron, whose source was less clear or not unique. $PM_{2.5}$ associated with wood smoke was the highest contributing source to the measured $PM_{2.5}$ mass concentration; this factor exhibited a significant seasonal pattern and contributed to days with high $PM_{2.5}$ concentrations that occurred during the wintertime. Other identified factors with significant seasonal differences include $PM_{2.5}$ associated with motor vehicles, nitrate, iron, sulfate, fugitive dust, and fireworks. These seasonal differences are mainly due to seasonal emission patterns and atmospheric processes.

Significantly different weekend and weekday distributions were observed by $PM_{2.5}$ associated with iron and fugitive dust, suggesting an association with local industrial activities.

Components of $PM_{2.5}$ associated with diesel were identified in multiple PMF factors, including $PM_{2.5}$ associated with vehicles, unidentified urban and high concentrations of iron and zinc.

Analysis identified a significant increasing short-term trend only for $PM_{2.5}$ associated with vehicles.