Estimation of the Effects of Ship Emissions Using Existing PM$_{2.5}$ Particle Compositions

Philip K. Hopke
Center for Air Resources Engineering and Science
Clarkson University
Potsdam, NY 13699-5708
hopkepk@clarkson.edu
Outline

• Introduction
  • Ship Emissions
  • Health Effects
• Data Issues
  • Availability
  • Data Issues
• Data Analysis Tools
  • PMF
  • CPF
• Results
• Conclusions
Acknowledgements

• The results being presented in this talk is the work of
  • In-Jo Hwang
  • Eugene Kim
  • Jong-Hoon Lee

• Their hard work and dedication to doing good data analyses is what has made it possible to complete this project.
Ship Emissions

• With the globalization of manufacturing and movement of natural resources such as crude oil, large transport ships (container ships, supertankers, etc) represent a major flow of goods and materials into and out from major ports.
Ship Emissions

• It can be seen that there is major ship traffic into
  • Seattle
  • San Francisco
  • Los Angeles/Long Beach
  • San Diego
Ship Emissions

• Ship diesels can utilize a wide range of quality fuels and will typically utilize the lowest cost fuels available.

• Thus, they utilize low volatility residual oil, often referred to No. 6 or bunker-C oil.

• These fuels are typically high in sulfur (~2%) and porphyrins that contain Ni and V.
Health Effects

• Recent unpublished work by Lippmann, Ito and others at NYU have examined the key FPM components from the speciation network and the NMMAPS PM10 daily mortality risk estimates.

• The PM10 mortality risk estimates (expressed as percent excess deaths per 10 µg/m³ increase in PM10) were then regressed on each of the log of the PM\textsubscript{2.5} components, with weights based on the standard error of the PM\textsubscript{10} risk estimates.
Health Effects
Health Effects

• As input to the health effect modeling that is planned for the SECA-related work, it may be worthwhile to contact Profs. Lippmann and/or Ito to get their input on the potential for enhanced effects of Ni on health outcomes.
Ship Emissions

• Any combustion source using residual oil will have emissions with similar characteristics, but there have been significant efforts to reduce the use of such fuels to reduce the sulfur emissions along the west coast.

• Thus, to a first approximation, Ni and V can be hypothesized as tracers of ship emissions.
Ship Emissions

• The ships generally burn fuel as they enter and leave the ports, but do not generally run their engines while docked for loading and unloading so there are limited emissions during this period. However, there would be significant emissions from support vehicles, trucks and railroad engines, as well as cargo handling systems during the loading/unloading operations.
Ship Emissions

• Thus, to estimate the impacts of the ship emissions, it is necessary to be able to separate and apportion the residual oil combustion primary particulate matter as well as estimate the amount of related secondary particles that would arise from the oxidation of the co-emitted SO$_2$
Ship Emissions

• Our project objectives were to
  • Use existing databases of particle compositions for fine particulate matter (PM$_{2.5}$) and apply positive matrix factorization (PMF) to these data to identify and apportion primary ship emissions
  • Through the examination of the resulting apportioned sources, estimate the contribution of the ship emissions to the secondary PM$_{2.5}$ measured at these locations.
Data Availability

• Sampling and Analysis of PM2.5 samples along the west coast of the United States
  • IMPROVE
  • STN
Cities with Multiple Sites

• Seattle
  • Lake Forrest
  • Olive St
  • Duwamish
  • Beacon Hill
  • Georgetown

• Los Angeles
  • Simi Valley
  • Downtown
  • Rubidoux
Data Analysis Methods

- Positive Matrix Factorization
  - Solve the mass balance problem

- Conditional Probability Function
  - Relate the sources to specific wind directions to provide information on likely local sources.
Mass Balance

The analysis is based on the mass balance equation. The mass balance can be written to account for all \( m \) chemical species in the \( n \) samples as contributions from \( p \) independent sources

\[
x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}
\]

Where \( i = 1, \ldots, n \) samples, \( j = 1, \ldots, m \) species and \( k = 1, \ldots, p \) sources. The \( f \) values are the concentrations of species \( j \) in particles from source \( k \) and the \( g \) values are the mass contributions of source \( k \) to sample \( i \).
Mass Balance

- The question is then what is known \textit{a priori} to solve this equation.

- Divide the problem into two classes
  - Source Profiles Known
  - Source Profiles Unknown
Source Profiles Known

• There has been limited work on chemical characterization of source emissions
• Work is on-going to measure the composition of ship emission and other sources (e.g., railroad diesel)
• Emitted particles change in the atmosphere over relatively short distances and time intervals.
Source Profiles Unknown

• Thus, we have focused on the development and application of methods that do not require the detailed knowledge of the source profiles.

• Understanding the likely species emitted by various sources is essential to be able to interpret the results of the methods that resolve both the profiles and contributions from the ambient concentration data.
Receptor Modeling

• SOURCES PROFILES UNKNOWN
  • Factor Analysis
    • Principal Components Analysis
    • Absolute Principal Components Analysis
    • SAFER/UNMIX
    • Positive Matrix Factorization
Factor Analysis

- Most factor analysis (PCA, APCA, Unmix) use an eigenvector analysis. In an eigenvector analysis, it can be shown [Lawson and Hanson, 1974; Malinowski, 1991] that the equation estimates $X$ in the least-squares sense that it gives the lowest possible value for

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij})^2 = \sum_{i=1}^{n} \sum_{j=1}^{m} (x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj})^2$$
Factor Analysis

• Thus, most factor analysis use an unrealistic unweighted least-squares fit to the data.
Positive Matrix Factorization

- Explicit least-squares approach to solving the factor analysis problem
- Individual data point weights
- Imposition of natural and other constraints, and
- Flexibility to build more complicated models
Positive Matrix Factorization

• The Objective Function, $Q$, is defined by

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{\sigma_{ij}} \right]^2$$

where $\sigma_{ij}$ is an estimate of the uncertainty in $x_{ij}$
Conditional Probability Function (CPF)

- Analyzing source contribution vs wind direction
- Probability that a given factor contribution from a given wind direction will exceed a predetermined threshold criterion (upper 25 % of contribution)

\[
CPF_{\Delta \theta} = \frac{m_{\Delta \theta}}{n_{\Delta \theta}}
\]

- \(m_{\Delta \theta}\) : number of occurrence from wind sector \(\Delta \theta\) that are upper 25 % of source contributions
- \(n_{\Delta \theta}\) : total number of occurrence from the same wind sector

- Sources are likely to be located in the directions that have high CPF values
Data Issues

• Data from the IMPROVE and STN networks have some important differences
  • IMPROVE measures a dynamic blank value for OC and subtracts these blanks from the data before reporting it.
  • STN measures static field and laboratory blanks, but these values were not made publicly available and the reported values are NOT blank corrected.
Data Issues

• Data from the IMPROVE and STN networks have some important differences
  • IMPROVE samples are all measured in the same laboratory for a given species
    • Elements and mass at UC Davis
    • OC/EC at DRI
    • Ions at RTI
  • STN samples have been analyzed for elements in up to 3 laboratories with different error reporting procedures and no errors were reported for the first three years of network operation.
Data Issues

• PMF requires an estimate of uncertainty in each data value.

• The “uncertainty” needs to include both the measurement error and some measure of the potential variability in the source profile over time.

• We have developed empirical protocols to deal with the data from both networks that permit reasonable results to be obtained from the data.
Data Issues


Data Issues

• These approaches have now been applied to a large number of data sets by both the Clarkson group and others.

• We have also recently made more detailed comparisons between estimated and actual errors for the STN network data and found that there was relatively little differences in the results and the differences are probably due to the underestimation of the XRF errors reported by one of the STN laboratories.
Results

• Residual Oil Profiles could be resolved using the data from:
  • Seattle
    • Beacon Hill
    • Olive St.
    • Duwamish
  • San Diego
    • Escondido
    • El Cajon
  • Point Reyes National Seashore
Results

- Illustrate the results by looking at two sites where the residual oil profile is seen
  - STN (Seattle – Beacon Hill)
  - IMPROVE (Point Reyes National Seashore)
- Site where residual oil is not resolved
  - STN (Rubidoux)
  - Kalmiopsis
Results – Beacon Hill

Concentration (µg/µg)
Results – Beacon Hill

![Graph showing results for Beacon Hill with different substances and time periods.](image)
Results – Beacon Hill

<table>
<thead>
<tr>
<th>Source</th>
<th>Weekday</th>
<th>Weekend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline vehicle</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sec. sulfate</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sec. nitrate</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Metal processing</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Oil combustion</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Diesel emissions</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Aged sea salt</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Airborne soil</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Sea salt</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Concentration (µg/m³)
Results – Beacon Hill

- Gasoline vehicle
- Secondary sulfate
- Secondary nitrate
- Wood smoke
- Metal processing
- Aged sea salt
- Oil combustion
- Airborne soil
- Diesel emissions
- Sea salt
Results – Beacon Hill
Results – Seattle CPF for Residual Oil
Results – Point Reyes National Seashore

[Bar charts showing concentration of various substances]
Results – Point Reyes National Seashore

Average contributions (µg/m³)

- Fresh Sea Salt
- Aged Sea Salt
- Salt
- Sec. Nitrate
- Gasoline Traffic
- Oil Combustion
- Wood Smoke
- Asian Dust
- Diesel Traffic

Summer
Winter
Results – Point Reyes National Seashore

- Fresh Sea Salt
- Aged Sea Salt
- Sec. Nitrate
- Gasoline Traffic
- Oil Combustion
- Wood Smoke
- Asian Dust
- Diesel Traffic

Concentration (µg/m³)
Results – Point Reyes National Seashore
Results – Rubidoux
Results – Rubidoux

• The Ni and V are distributed between the secondary sulfate and aged sea salt profiles.

• Yet there is V and Ni present at Rubidoux and in concentrations approximately 2/3 of those seen at the downtown LA site.

• Results from the past summer at Riverside also see clear evidence of a V/Ni source whose nature is not yet known.
Results – Kalmiopsis
Results – Kalmiopsis

• The Ni and V are again distributed between the secondary sulfate and aged sea salt profiles.

• Ni and V concentrations are much lower than seen in urban areas.
Results – Kalmiopsis

![Graph showing the results of Kalmiopsis with bars for different categories and seasons: Summer, Winter, and Annual. The categories include Field Burning, Secondary Sulfate, Airborne Soil, Nitrate, Fresh Sea Salt, OP + Sulfate, Aged Sea Salt, Gasoline Vehicles, and Diesel Emission. The x-axis represents the categories, and the y-axis represents the values.](image-url)
Results – Kalmiopsis

- **Weekday** vs **Weekend**

  - **Wood/Field Burning**
  - **Airborne Soil**
  - **Fresh Sea Salt**
  - **Aged Sea Salt**
  - **Diesel Emission**
  - **Secondary Sulfate**
  - **Nitrate**
  - **OP + Sulfate**
  - **Gasoline Vehicle**
  - **PM2.5 Mass**

Concentration (µg/m³)
Biscuit Fire Episode

- 8/9/2002
- 8/27/2002
- 9/2/2002
- 9/11/2002

Wood/Field Burning

K Concentration

Sampling Date
Biscuit Fire Episode

- Biscuit wildfire periods → Wood/Field Burning
- TC Concentration
- K Concentration
- \( \text{SO}_4^{2-} \) Concentration

Sampling Date
## Impact of Primary Ship Emissions

<table>
<thead>
<tr>
<th>Site</th>
<th>Type</th>
<th>Mean Residual Oil Contribution (µg/m3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seattle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olive Street</td>
<td>STN</td>
<td>0.39</td>
</tr>
<tr>
<td>Beacon Hill</td>
<td>STN</td>
<td>0.43</td>
</tr>
<tr>
<td>Beacon Hill</td>
<td>IMPROVE</td>
<td>0.60</td>
</tr>
<tr>
<td>Duwamish</td>
<td>STN</td>
<td>0.43</td>
</tr>
<tr>
<td>San Diego</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Escondido</td>
<td>STN</td>
<td>0.57</td>
</tr>
<tr>
<td>El Cajon</td>
<td>STN</td>
<td>0.43</td>
</tr>
</tbody>
</table>
# Impact of Primary Ship Emissions

<table>
<thead>
<tr>
<th>Site</th>
<th>Type</th>
<th>Mean Residual Oil Contribution (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqua Tibia</td>
<td>IMPROVE</td>
<td>0.13</td>
</tr>
<tr>
<td>San Rafael</td>
<td>IMPROVE</td>
<td>0.26</td>
</tr>
<tr>
<td>Point Reyes National Seashore</td>
<td>IMPROVE</td>
<td>0.66</td>
</tr>
<tr>
<td>Olympic National Park</td>
<td>IMPROVE</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Impact of Primary Ship Emissions

Ships are also expected to emit SO$_2$ as well as the primary V-Ni particles. The SO$_2$ will be oxidized into sulfate particles so we might expect to observe a correlation between the residual oil combustion contributions and the amount of secondary sulfate particles. We can look for such correlations by plotting the contributions from one factor against the other.
Secondary Impacts of Ship Emissions

Beacon Hill

![Graph showing the relationship between oil combustion and secondary sulfate emissions.](Image)
Secondary Impacts of Ship Emissions

The upper edge in this plot is a measure of the maximum amount of oil combustion particles per unit contribution of sulfate. The slope of this line is 1.213 so that there appears to be $0.82 \, \mu g/m^3$ of sulfate for every $1 \, \mu g/m^3$ of primary oil combustion particles.

We can look for a similar pattern at other sites.
Secondary Impacts of Ship Emissions

Seattle

Olive Street

Duwamish
## Ship Diesel Contribution in Seattle

<table>
<thead>
<tr>
<th>Seattle</th>
<th>Primary</th>
<th>$\text{SO}_4$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive Street</td>
<td>0.39</td>
<td>0.32</td>
<td>0.71</td>
</tr>
<tr>
<td>Beacon Hill STN</td>
<td>0.43</td>
<td>0.35</td>
<td>0.78</td>
</tr>
<tr>
<td>Beacon Hill IMPROVE</td>
<td>0.60</td>
<td>0.49</td>
<td>1.09</td>
</tr>
<tr>
<td>Duwamish</td>
<td>0.43</td>
<td>0.35</td>
<td>0.78</td>
</tr>
</tbody>
</table>
Secondary Impacts of Ship Emissions

San Diego

Escondido

El Cajon
Clearly, there is no obvious relationship between the residual oil factor and secondary sulfate in San Diego. It may be that there is insufficient time to permit significant oxidation of $\text{SO}_2$ to sulfate.

We can also look at the results from IMPROVE Sites like Point Reyes National Seashore and Olympic National Park.
Secondary Impacts of Ship Emissions

IMPROVE

Point Reyes

Olympic

![Graph showing residuals of oil combustion against secondary sulfate for Point Reyes and Olympic.](image)
Conclusions

• There appears to be some impact of ship emissions, both primary and secondary. At most sites, these impacts are small. The mean primary emission mass contributions of the order of 0.13 to 0.66 µg/m³.

• At some sites, a relationship with the secondary sulfate factor was observed that would roughly double the directly observable contribution of ship emissions to ambient PM₂.₅.
Conclusions

• The maximum attributable contribution of ship emissions to any site is approximately 1.2 μg/m³. There may be additional secondary sulfate and nitrate arising from their emissions, but they have become disassociated with the primary particulate emissions.
QUESTIONS?