

Wapato Hills-Puyallup River Valley PM_{2.5} Nonattainment Area

PMF Analysis of Speciation Data

David Ogulei

April 1, 2010

The team

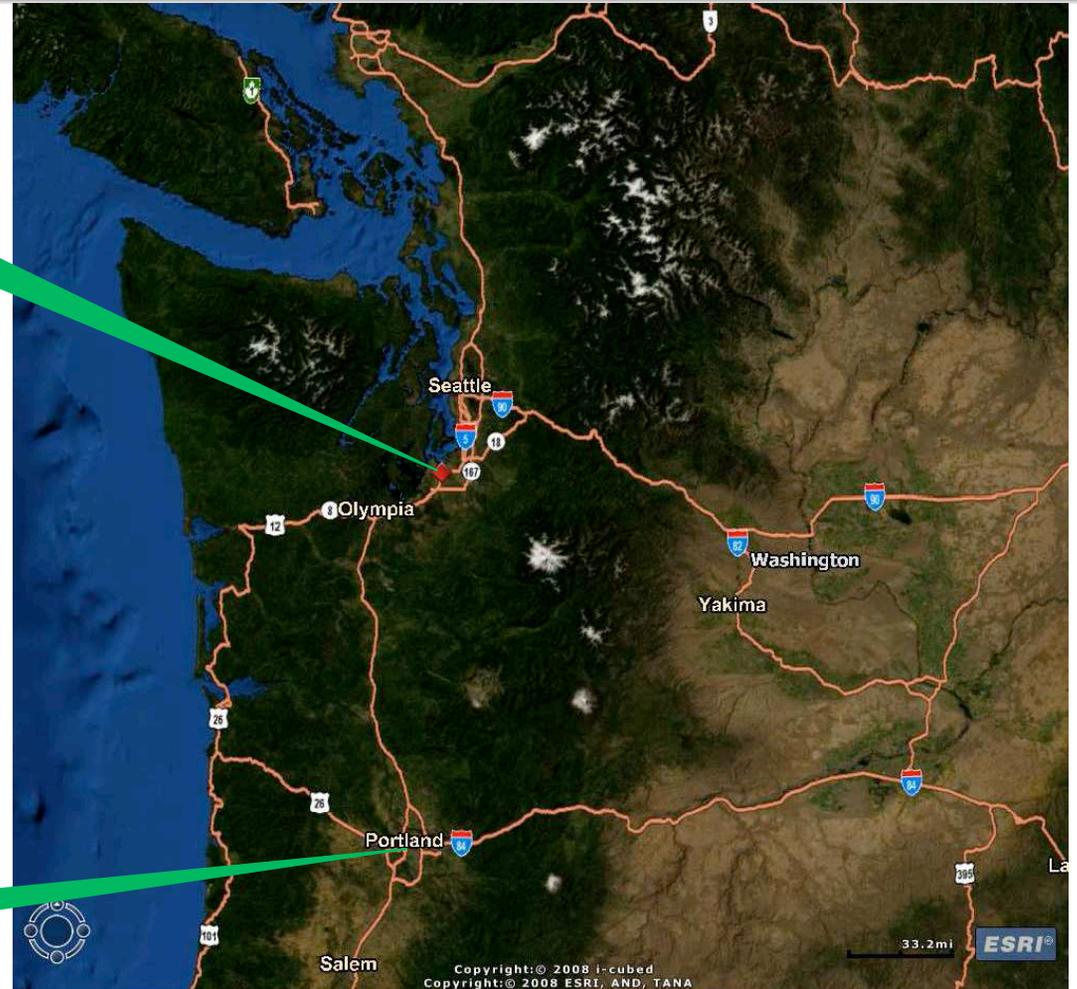
- Washington State Dept. of Ecology
 - Ranil Dhammapala, Jeff Johnston, Sarah Rees, Doug Schneider, among others.
- Puget Sound Clean Air Agency (PSCAA)
 - Katherine Himes /Strange
- Multiple reviewers /observers
 - Incl. EPA Region X

Tacoma, Washington

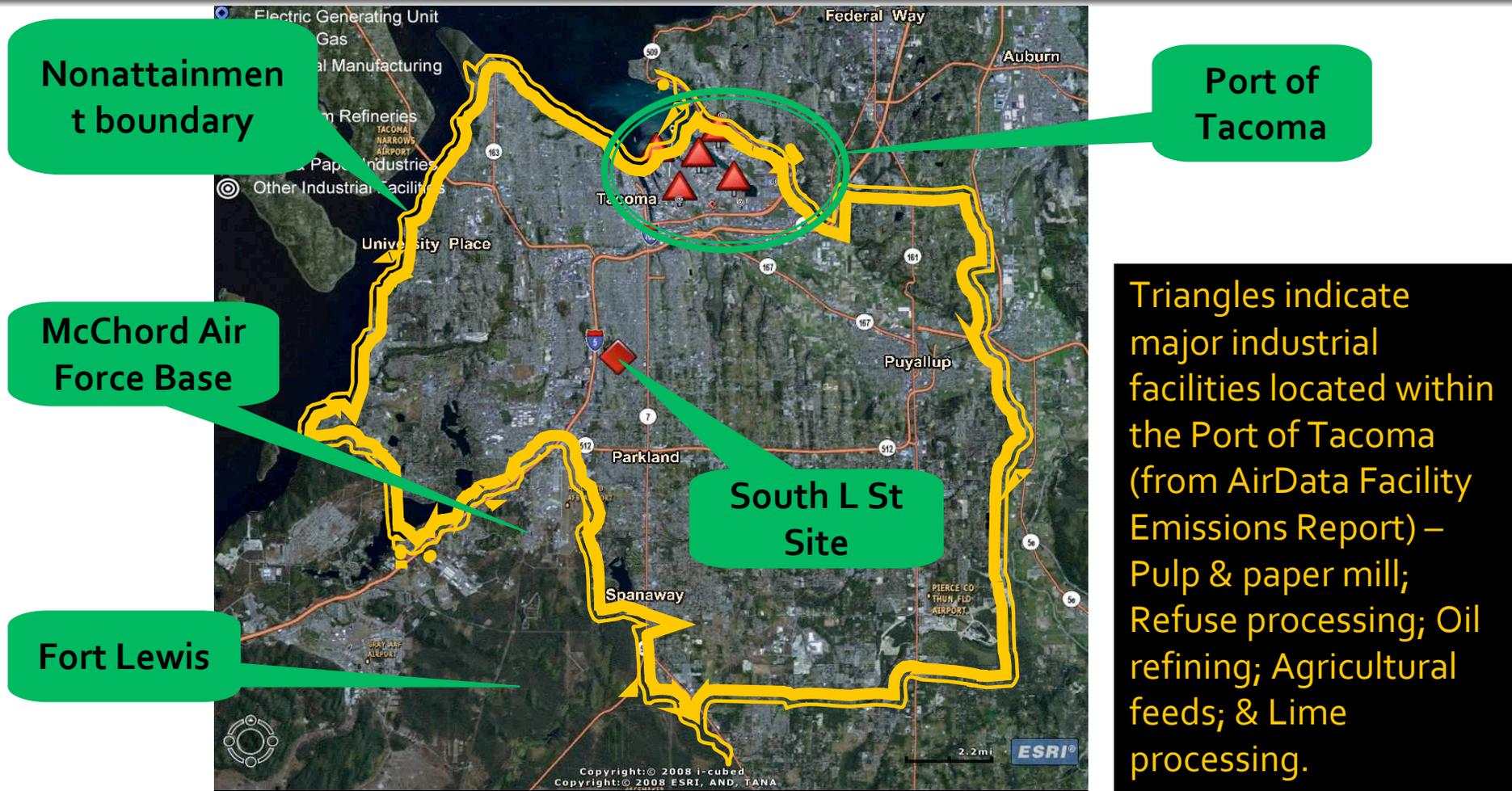
South L
Street
Sampling Site



Portland, OR



Wapato Hills-Puyallup River Valley PM_{2.5} Nonattainment Area



Modeling Tools Used

- **Positive Matrix Factorization (PMF)** – a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices: factor contributions and factor profiles. We used EPA PMF 3.0.
- **The Conditional Probability Function (CPF)** – a probabilistic tool that estimates the probable direction associated with ambient concentrations that exceed a pre-defined threshold.

Understanding PMF

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



- ✓ p independent sources. $i = 1, \dots, n$ samples; $j = 1, \dots, m$ species.
- ✓ PMF will estimate independent contributions (g) and species loadings (f) that explain matrix X .
- ✓ PMF equation assumes mass is conserved between the source & the receptor.
- ✓ The devil is in the details.

Understanding CPF

$$CPF_{\Delta\theta} = \frac{m_{\Delta\theta}}{n_{\Delta\theta}}$$

- $m_{\Delta\theta}$ = No. of occurrences of “high” concentrations in wind sector $\Delta\theta$.
- $n_{\Delta\theta}$ = Total no. of concentration occurrences in wind sector $\Delta\theta$.
- “High” = 75th percentile. $\Delta\theta$ = size bins of 20° starting at 0° (CPF_s for the species were calculated using 10° wind sectors) .
- CPF algorithm will estimate the probability that a given source contribution from a given wind direction will exceed a predetermined threshold criterion. (Set CPF = 0 if $CPF_{\Delta\theta} < 0.01$.)
- **Used all wind speeds in this PMF analysis!**

Data Description

- PM_{2.5} data from the Speciation Trends Network (STN). Every 6th day samples (1/11/06 – 5/7/09). Sampling site: 7802 S. L Street, Tacoma, WA – a low income residential neighborhood. Population of Tacoma, WA >~ 200,000.
- Species with $\geq 75\%$ of concentrations below detection, or missing, were omitted from modeling. Under this criterion, 25 species (i.e., 45%) were omitted: Sb, Ba, Cd, Ce, Cs, Eu, Ga, Au, Hf, In, Ir, La, Hg, Mo, Nb, P, Sm, Sc, Ag, Ta, Tb, Sn, W, Y, & Zr.
- S, K⁺ & Na were omitted because they were “repeat” species. Cr, Co, Hg, Rb and Se were flagged “bad” and excluded from further PMF analysis because they had low signal/noise ratios (≤ 1.0).
- On 5/12/07, STN began sampling and analysis for OC & EC using revised thermal optical transmittance (TOT) & thermal optical reflectance (TOR) protocols, while the previous protocols were continued up to 7/5/07. Modeling data includes total EC and total OC data using the old TOT protocol until 5/6/07. After 5/6/07 total EC and OC data are from the revised TOT protocol.

Data Description Continued

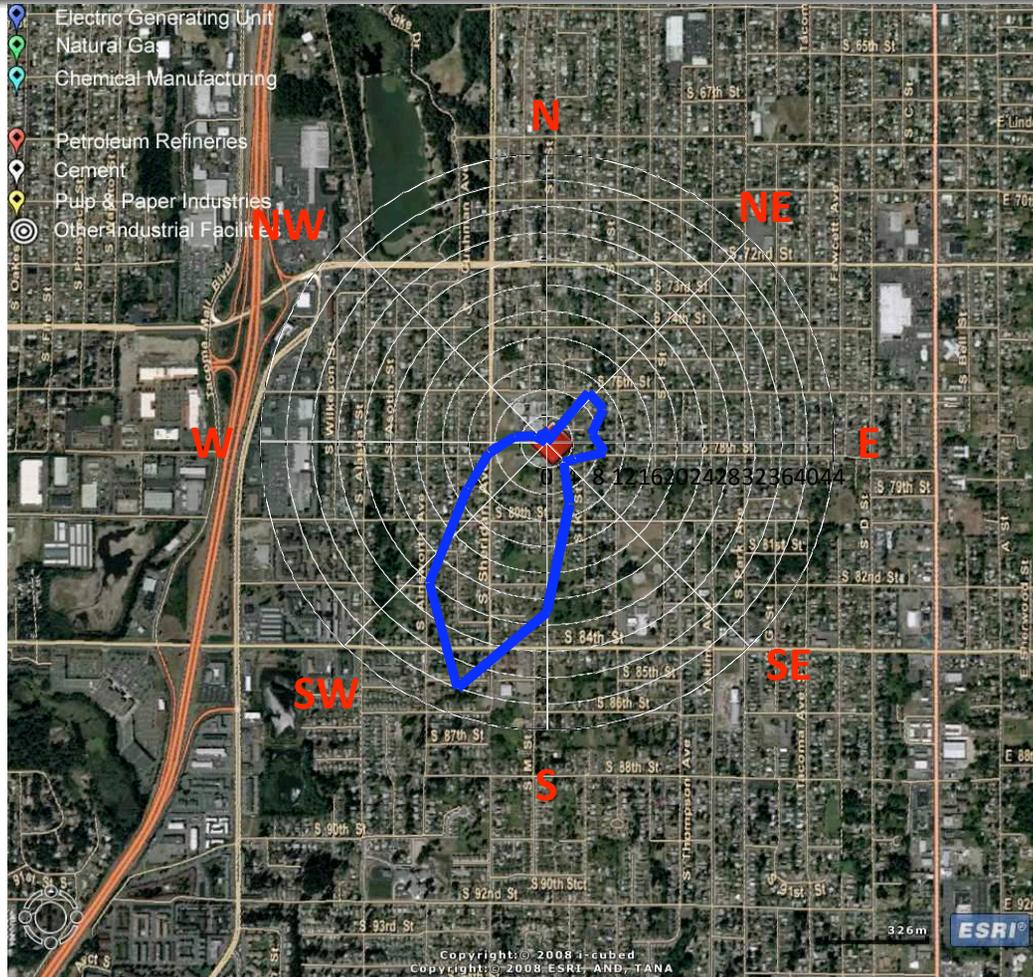
- Carbon fractions (EC_x, OC_x & OP) were not used in modeling because the data were incomplete: EC fractions (EC_x) were not determined prior to 5/12/07.
- Total OC was blank-corrected using the intercept of the uncorrected total OC vs. PM_{2.5} mass plot.
- Started with **73** species + PM_{2.5} mass. Ended up with **24** species + PM_{2.5} mass.
- Meteorological data for Tacoma L Street downloaded from PSCAA's *TrendGraphing* website:
<http://trendgraphing.pscleanair.org/>.

Area Wind Profile

1-hr average wind profile (1/11/06 - 5/7/09)

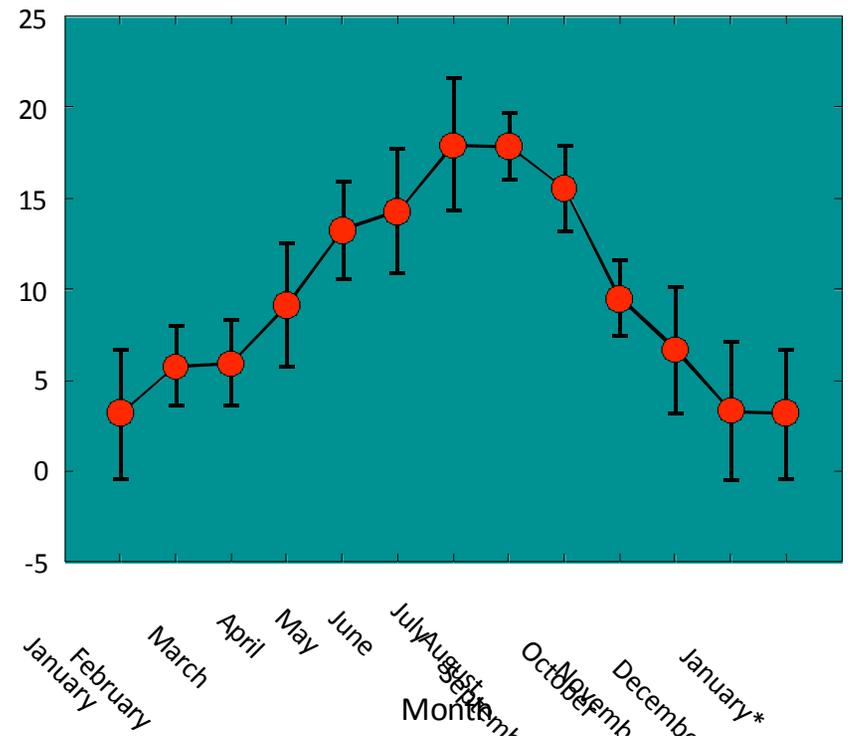
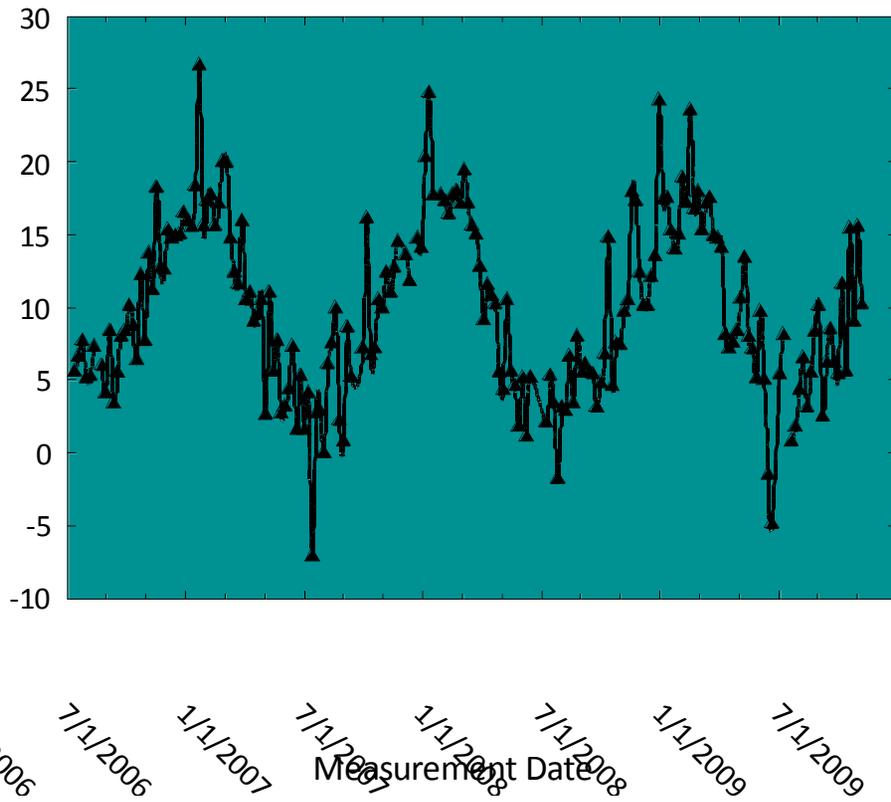
- Most of the wind was 1–2 m/s in speed (2.2 - 4.5 mph).
- Most winds came from the south-southwest.
- There were “hits” from all directions.

Area Wind Profile

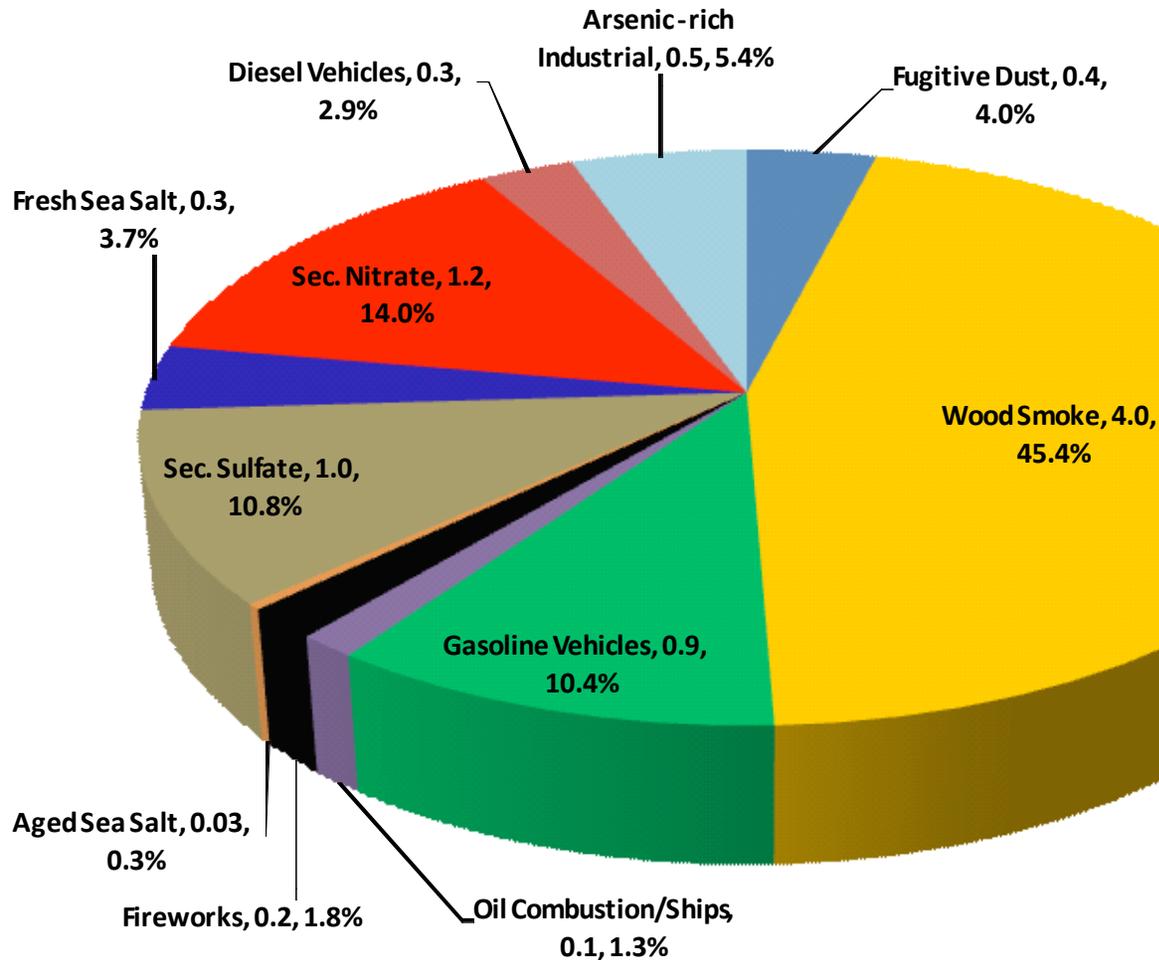


- Same observation; different plot.
- South – Southwest direction is prevalent, even when only wind speeds greater than or equal to 1 m/s are considered.

Tacoma Area Ambient Temperature

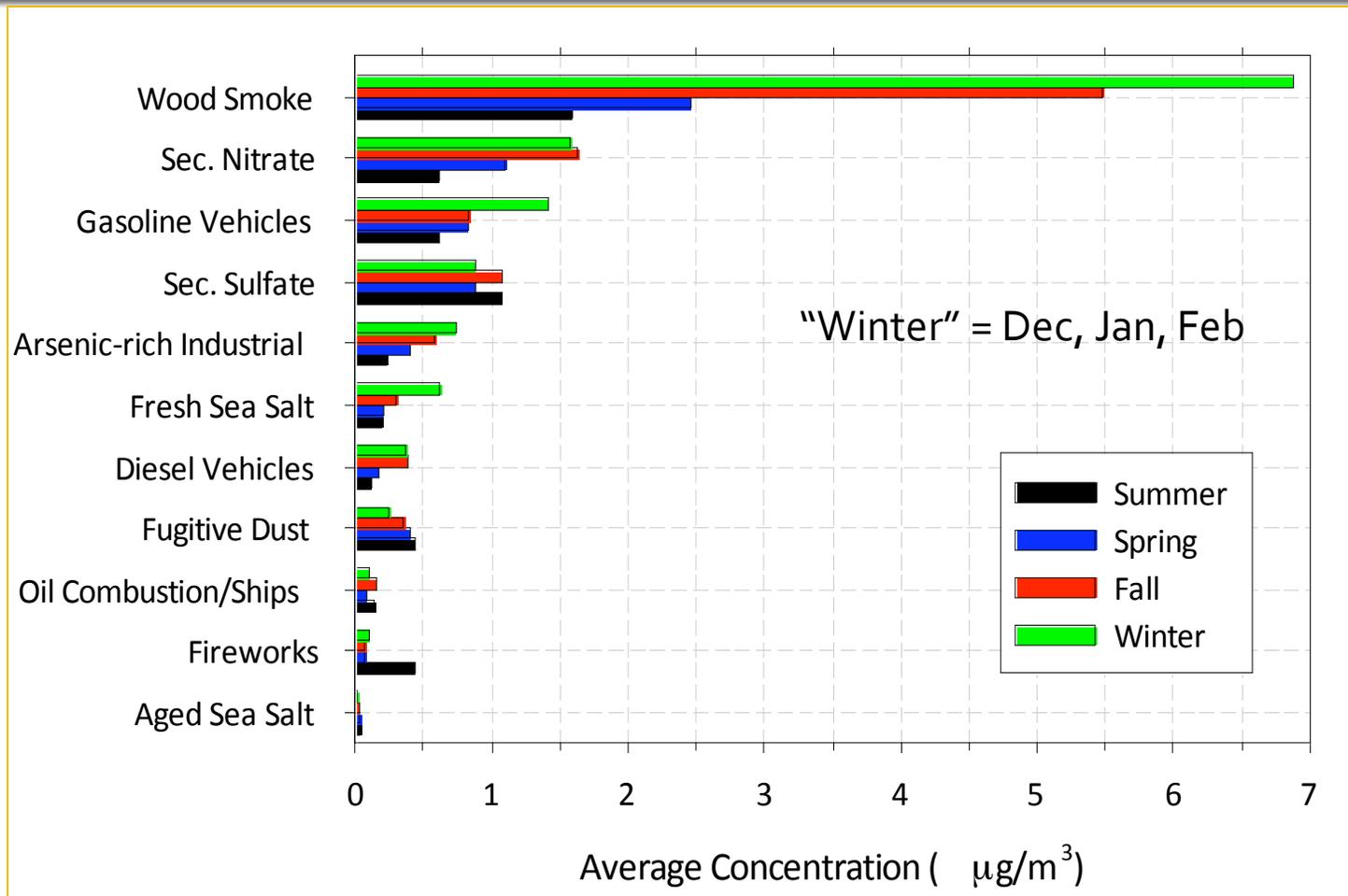


What the data says: Overall

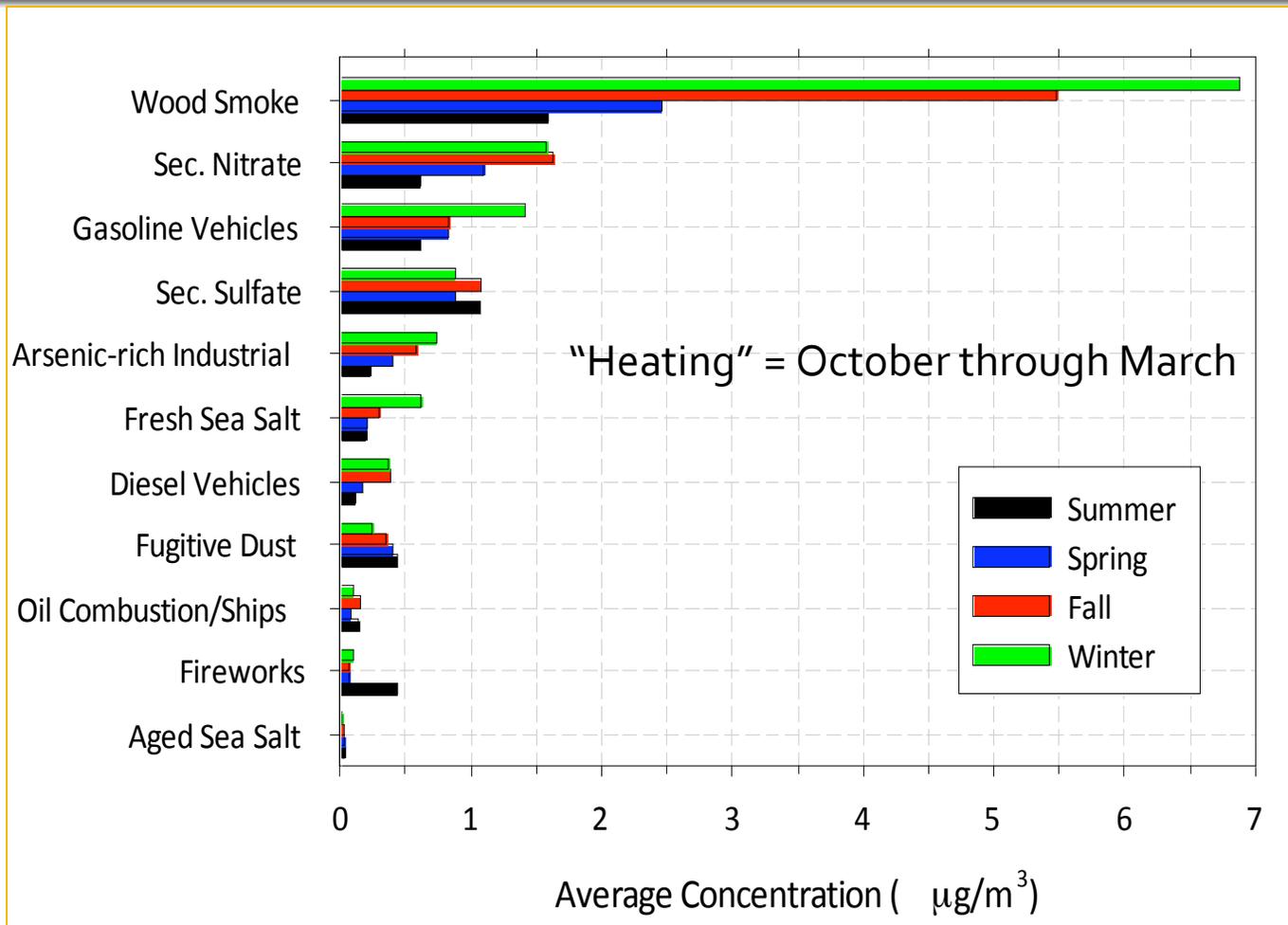


Numerical values in the pie are: resolved source, average concentration in $\mu\text{g}/\text{m}^3$, & percent of total, respectively

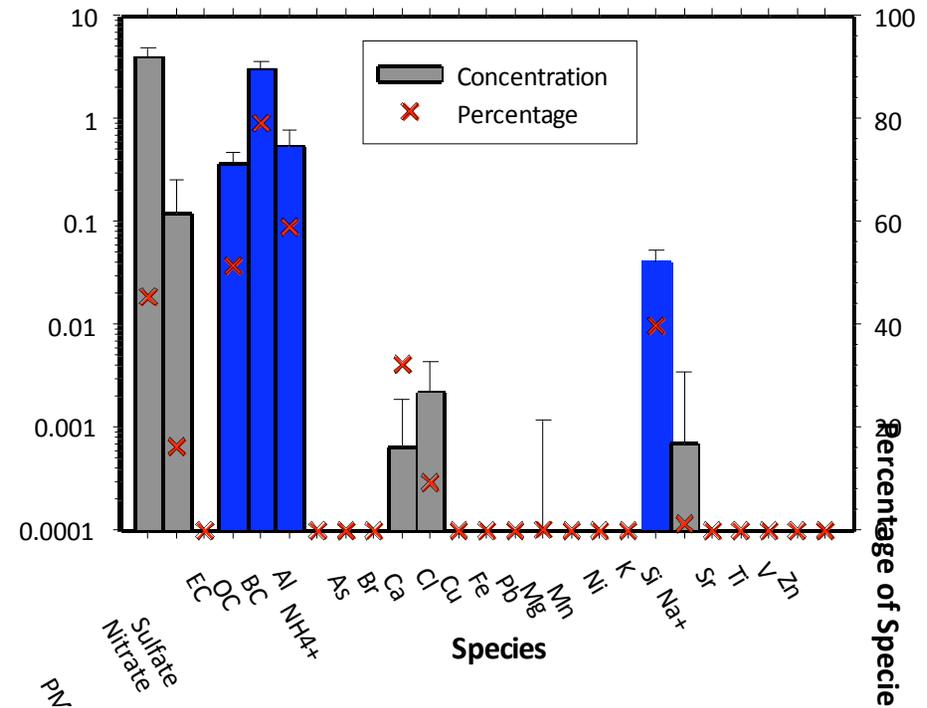
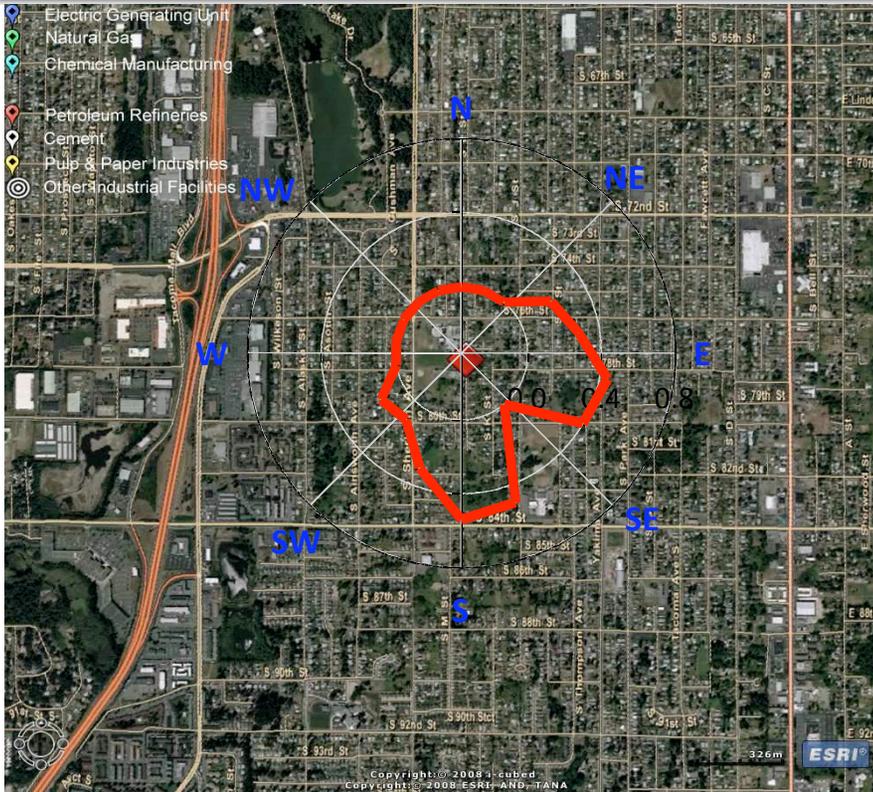
What the data says: By Season



Heating v. Non-heating



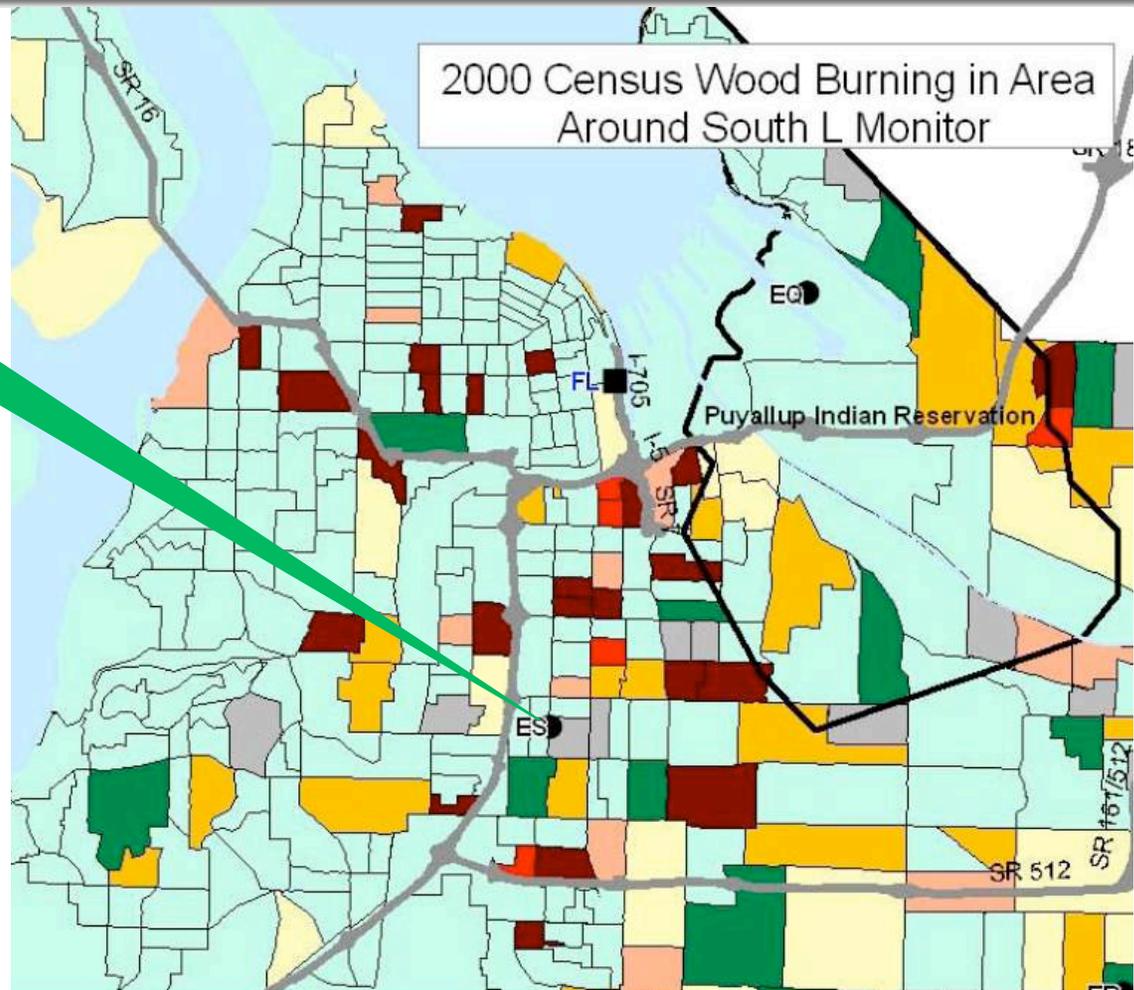
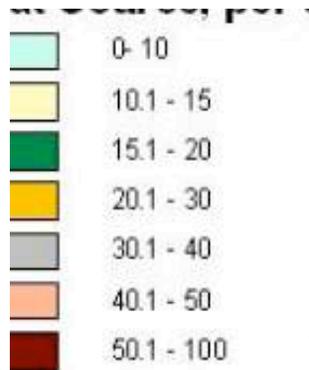
Wood Smoke



Key pollutants are shaded blue. Wood smoke accounts for about 50% of elemental carbon (EC), 80% of organic carbon (OC), and 40% of potassium (K). Compare the CPF (left) with the overall wind profile (shown earlier) and wood stove/fireplace use (next slide).

No. of Homes Using Wood as a Primary Heating Source Per Sq. Mile, in South Tacoma

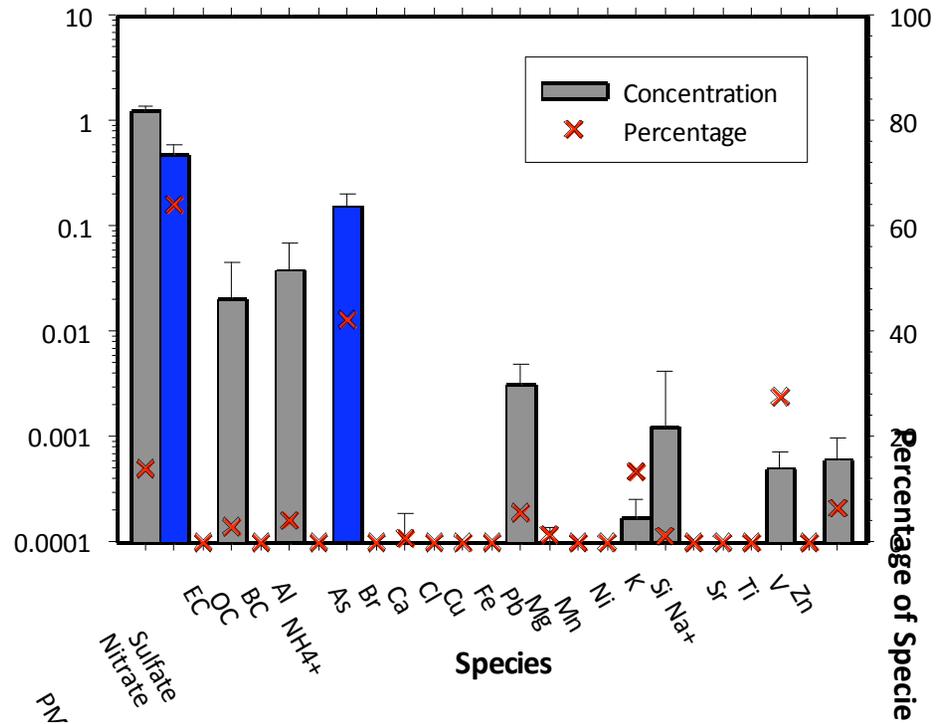
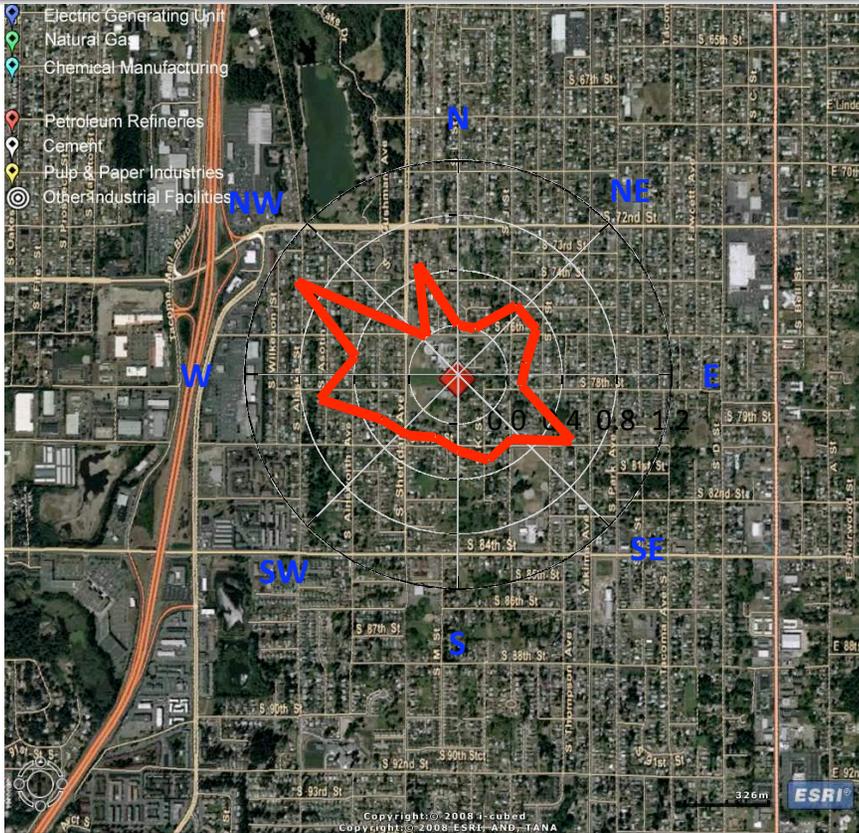
South L St.
PM2.5 Monitor



Wood Smoke

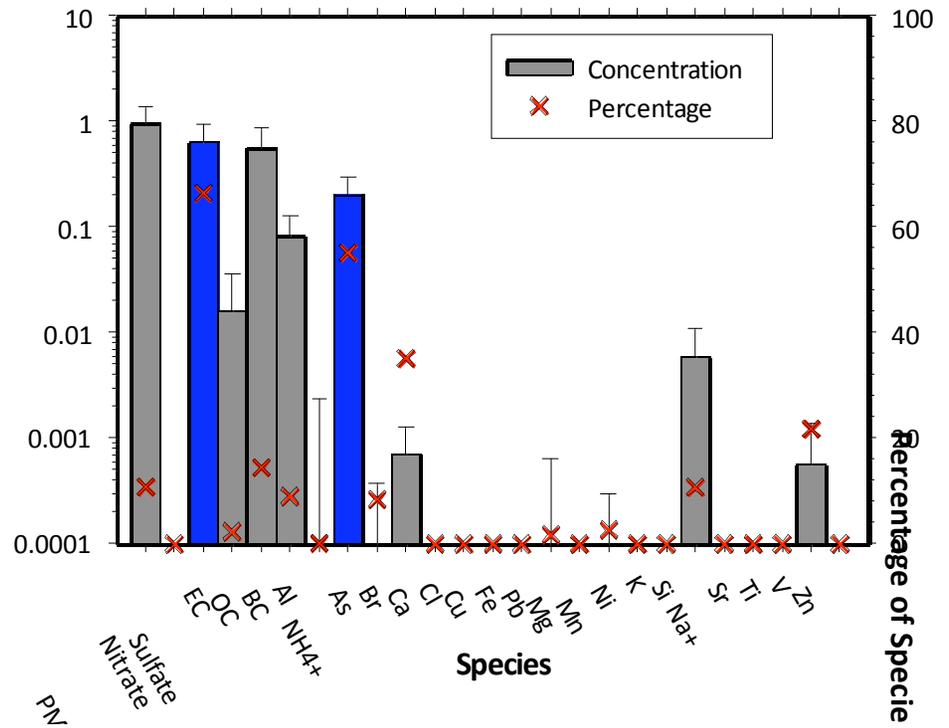
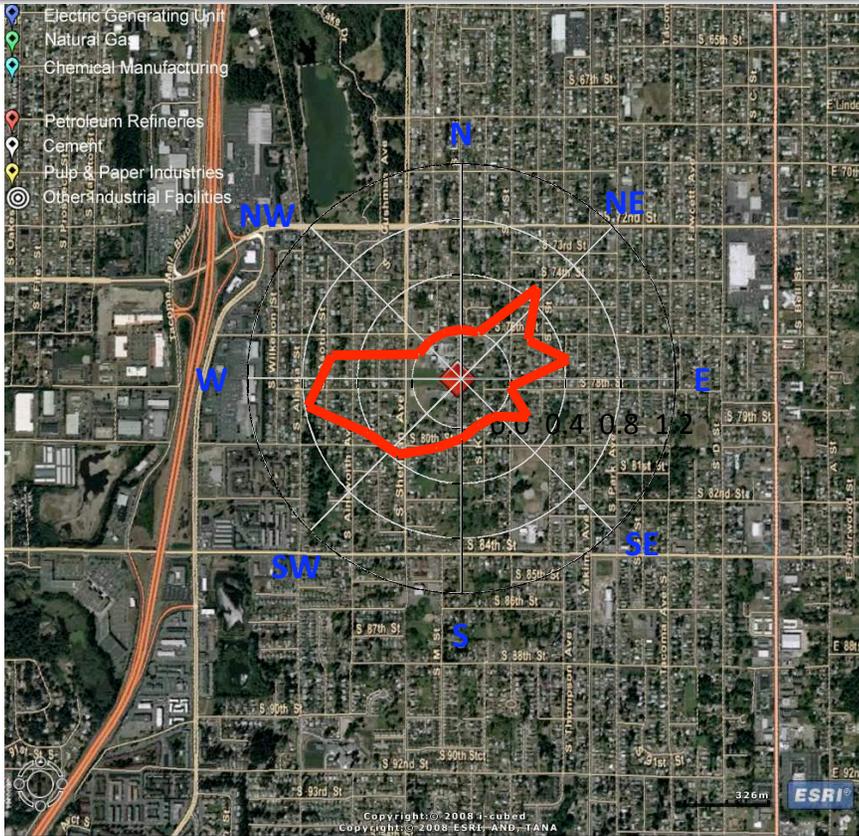
One can see how well the wood smoke time series correlates with the black carbon (BC) and total PM_{2.5} mass series. A close relationship was also observed with total organic carbon

Secondary Nitrate



Key species here are NH_4^+ and NO_3^- . The CPF (left) suggests secondary aerosol produced from locally-generated precursors. It is possible to distinguish this profile from regionally transported particles because the CPF does not show a meaningful relationship with the overall wind profile.

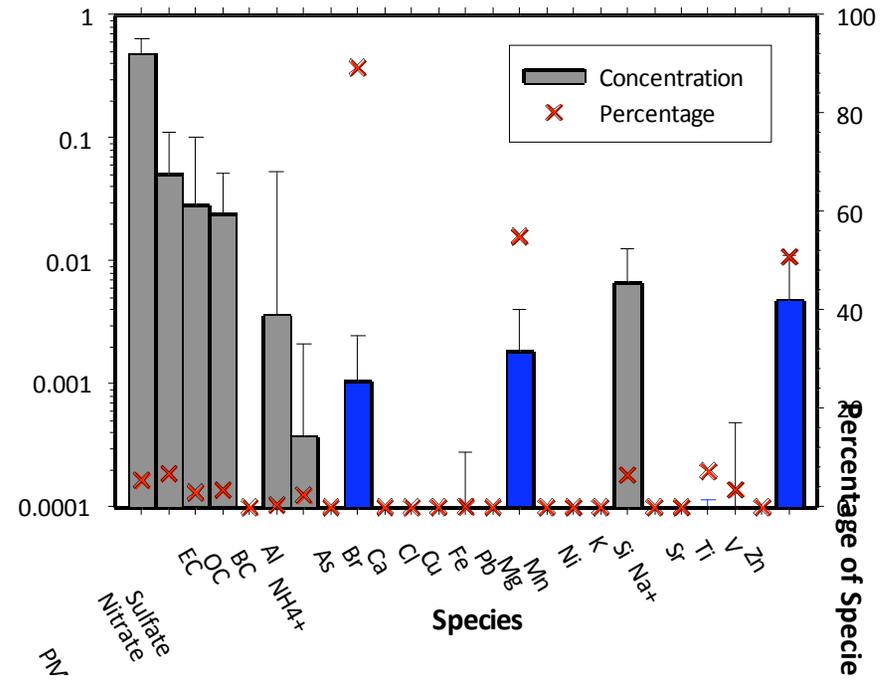
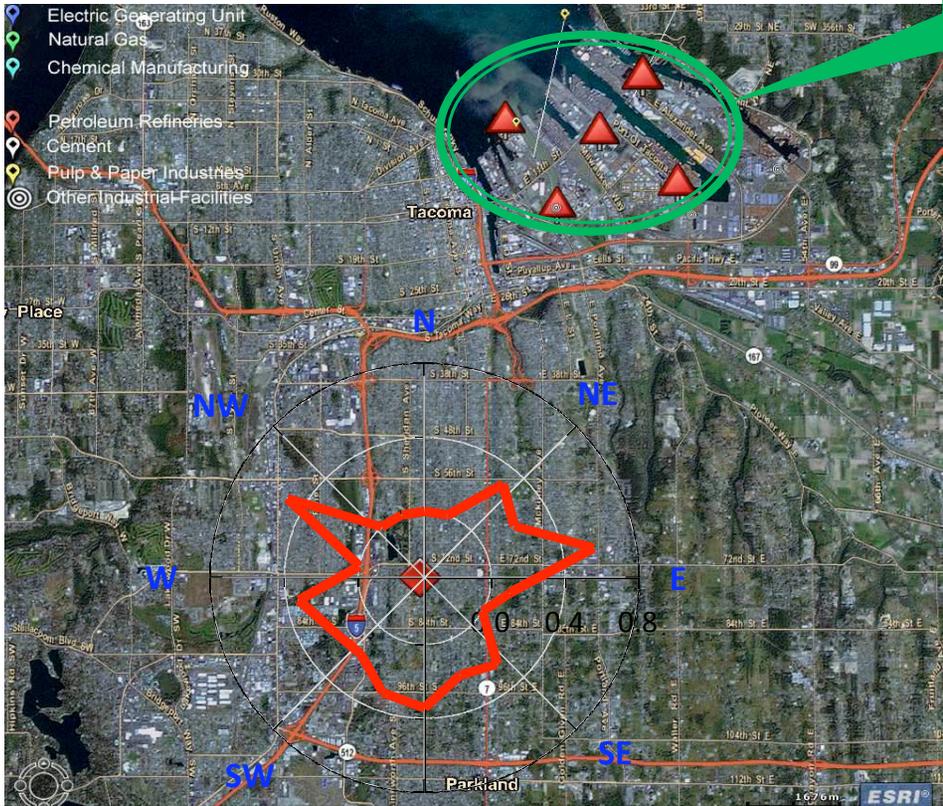
Secondary Sulfate



Key species are NH_4^+ and SO_4^{2-} . Like the secondary nitrate, the most significant contributors to the observed sulfate appear to be local.

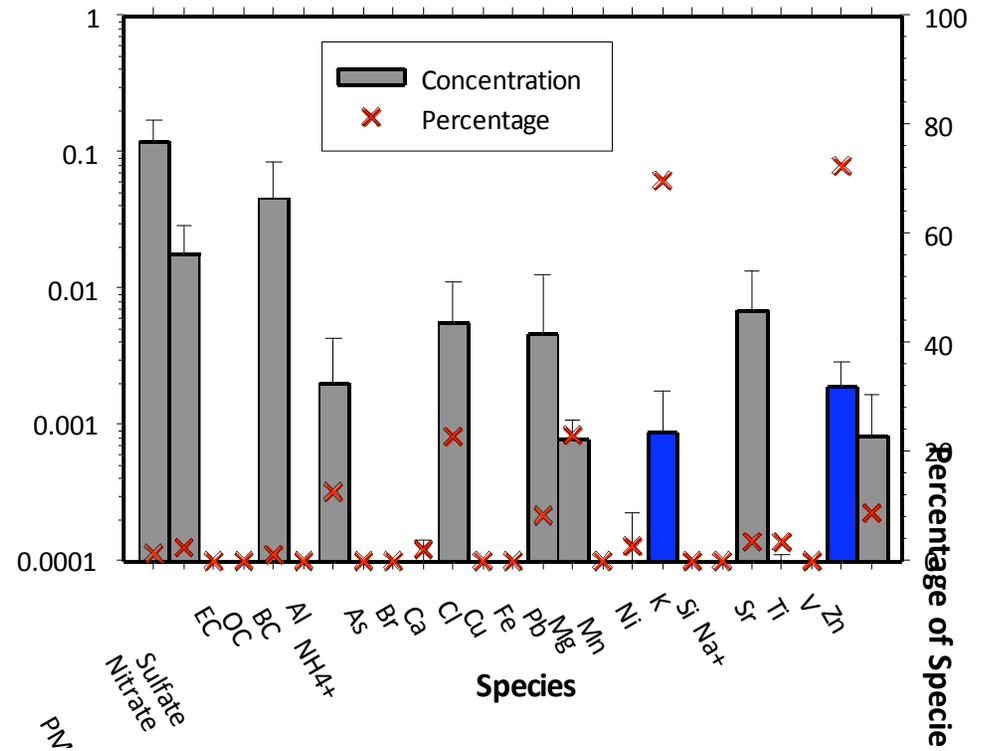
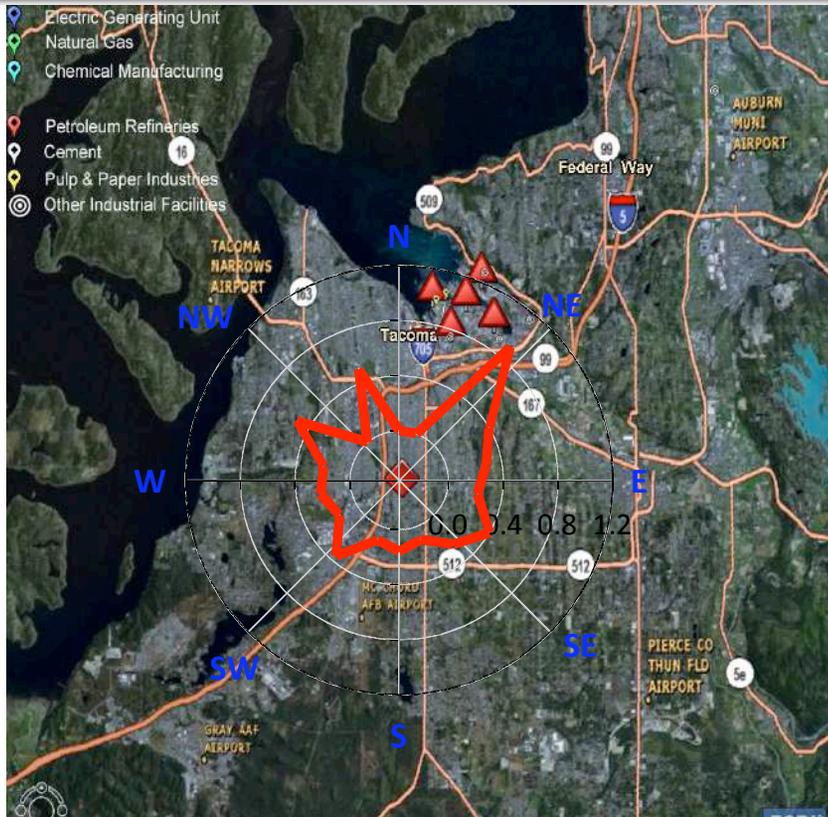
Local Industry/Heavy Metals

Main "Industrial" Area



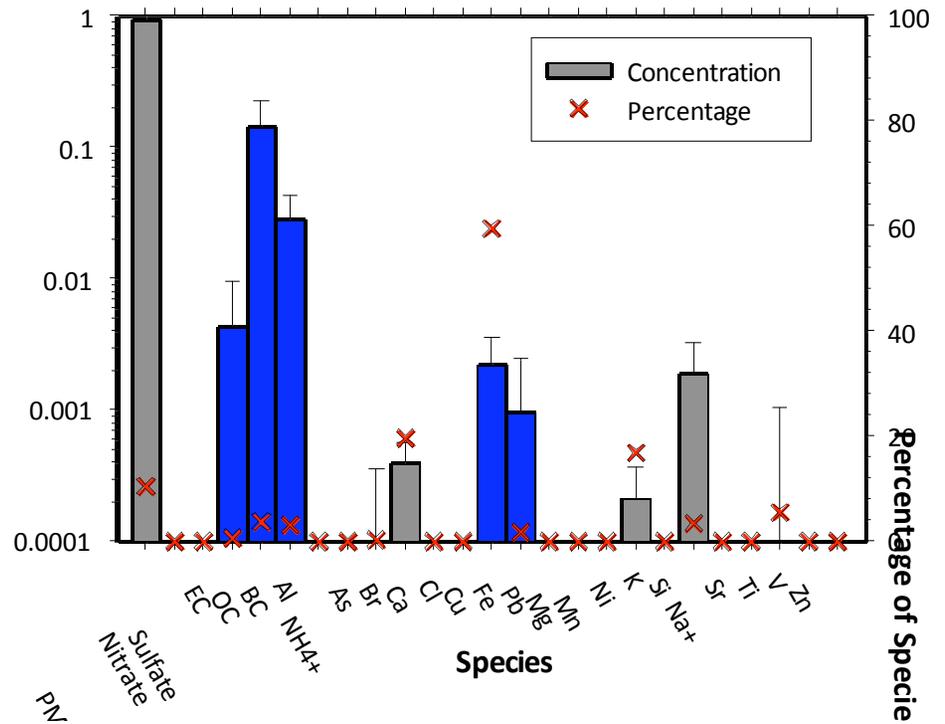
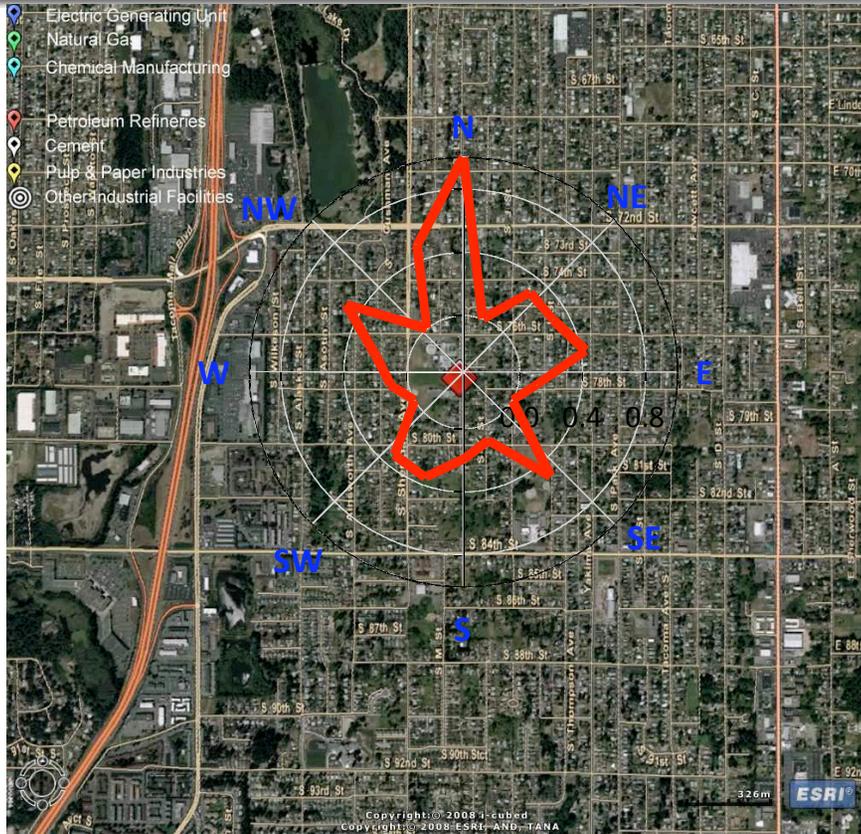
Accounts for as much as 90% of the arsenic (As), 50% of zinc (Zn), and about 50% of lead (Pb). The contributions appear to be a mixture of crustal-laden remnants of the now-defunct ASARCO smelter and local industrial emissions.

Oil Combustion/Ships



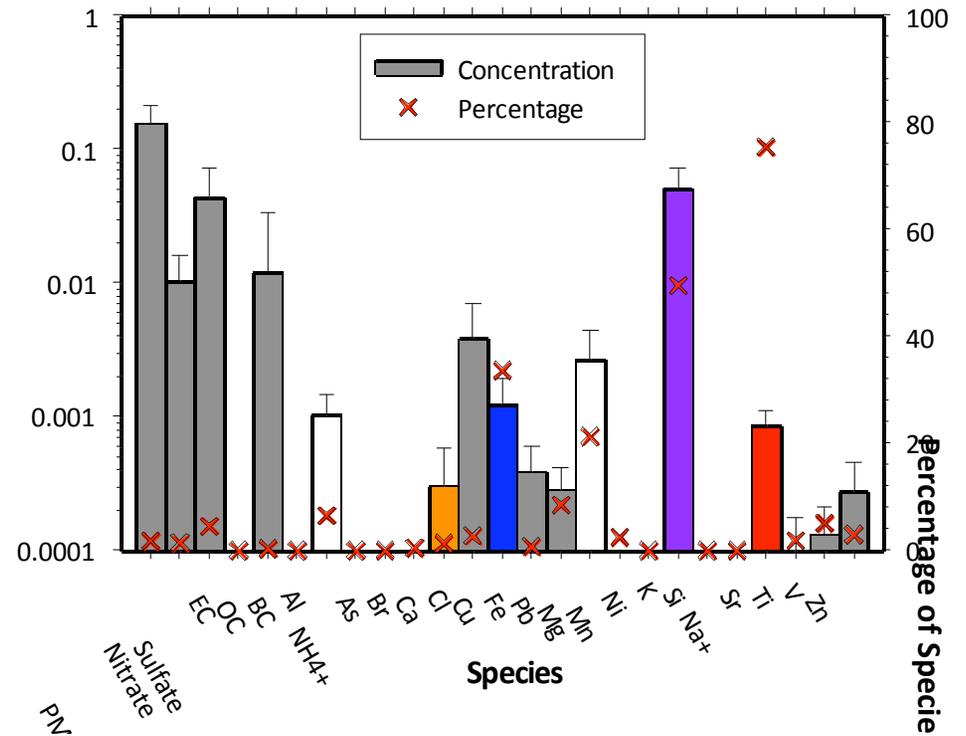
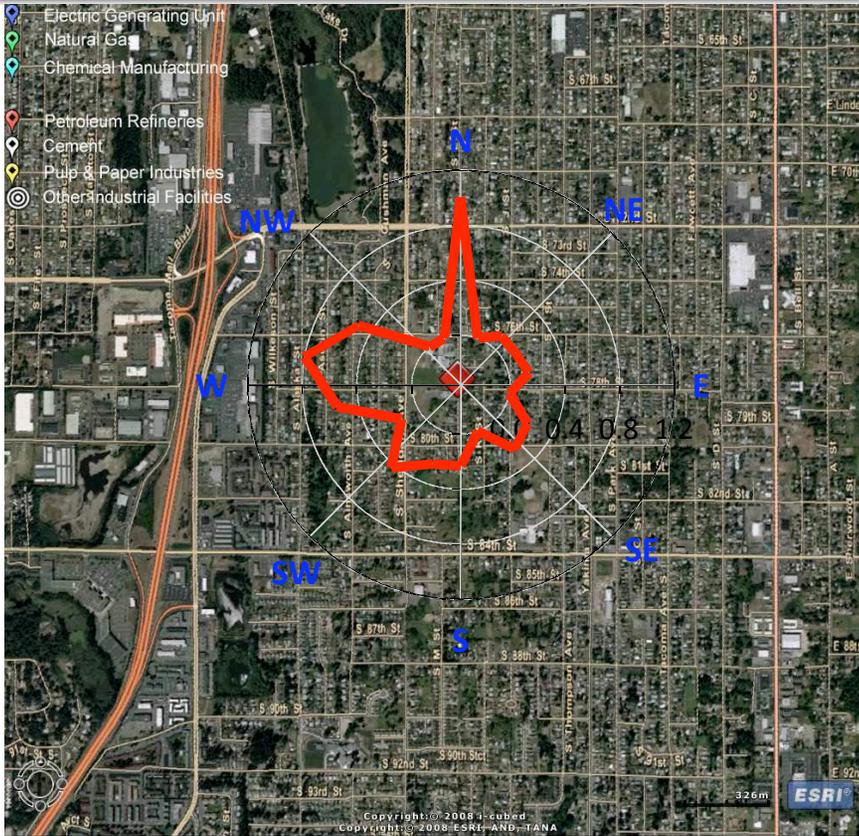
Accounts for about 70% of nickel (Ni) and 70% of vanadium (V), markers for oil combustion. While the CPF suggests contributions from multiple directions (probably as a result of residual oil combustion sources as well as wind “maneuvers”), it is easy to notice the apparent influence of port emissions.

Gasoline Vehicles



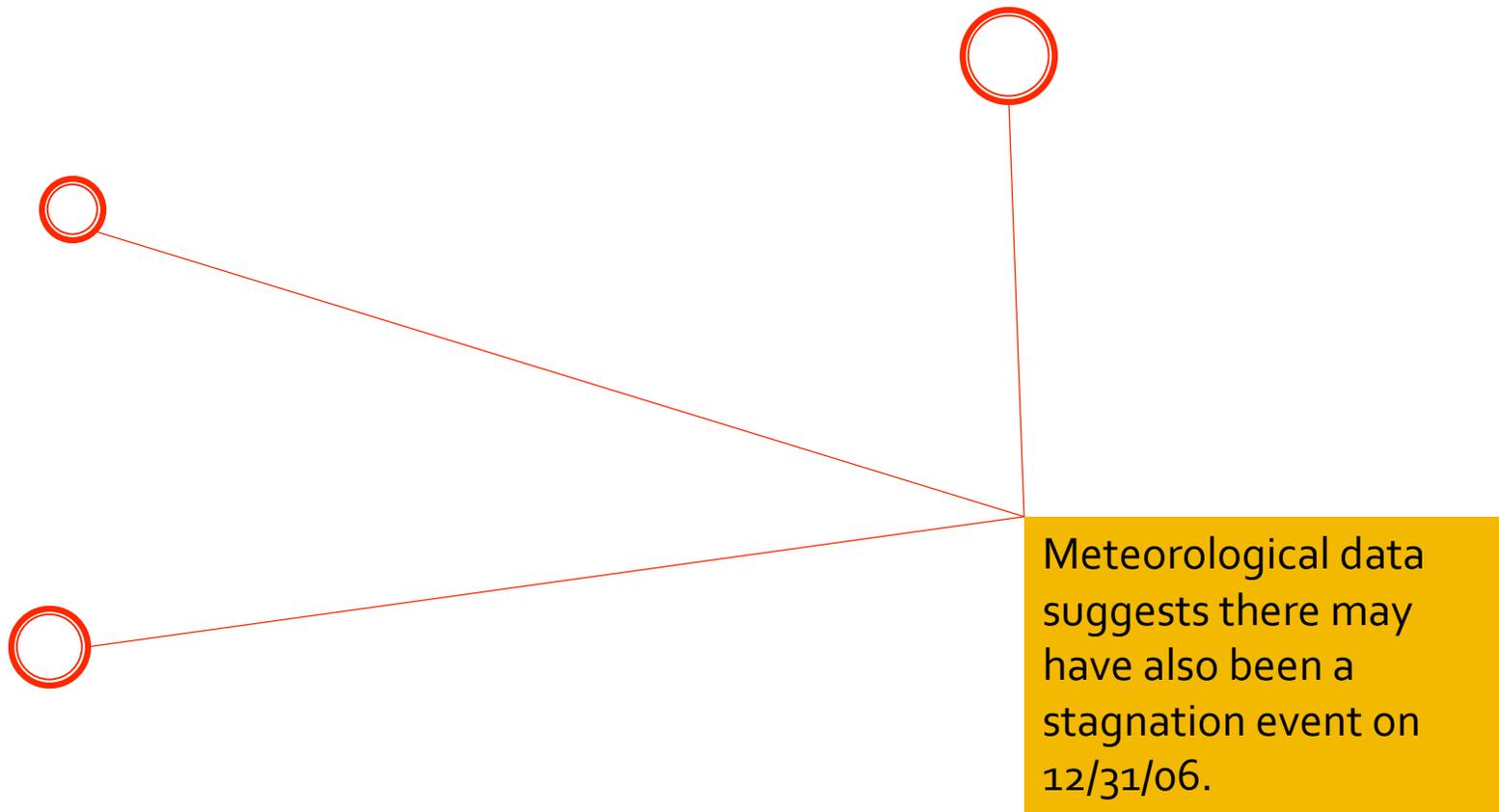
The concentration of organic carbon (OC) is expected to be higher than the elemental carbon (EC) concentration in emissions from gasoline-fired vehicles.

Fireworks

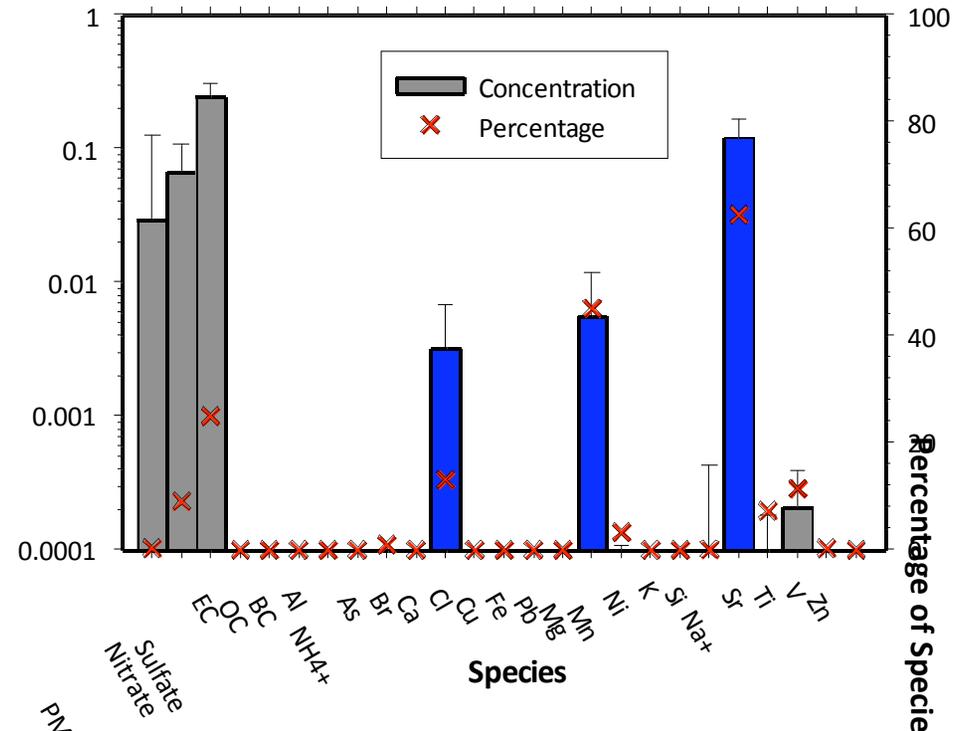
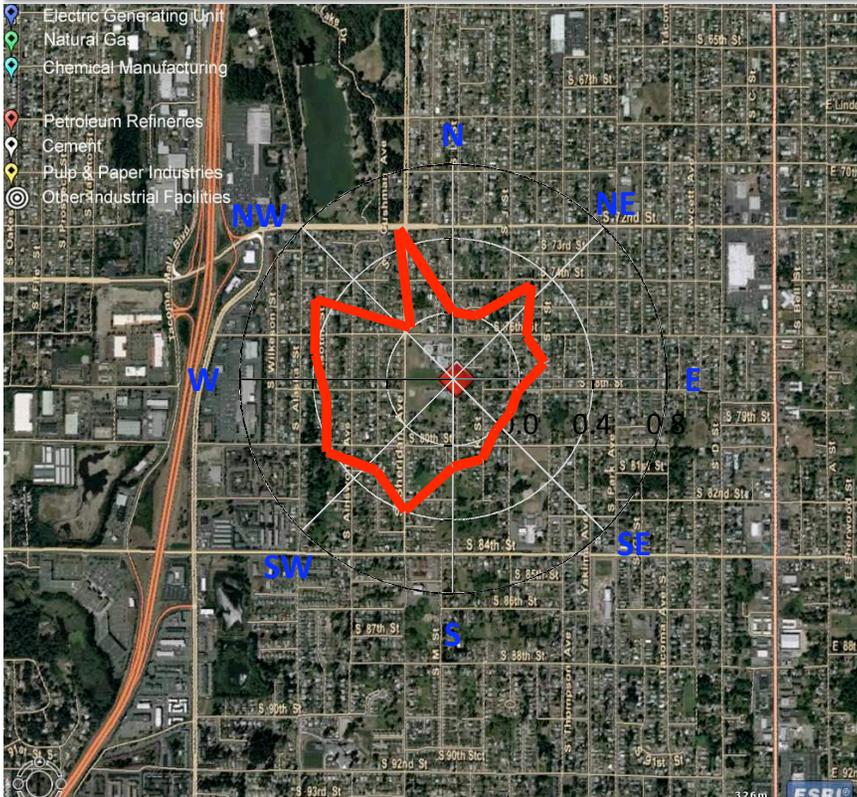


Key species are strontium (Sr) and potassium (K). Now, let's take a look at the time series...

Definitely celebration time! (Fireworks)

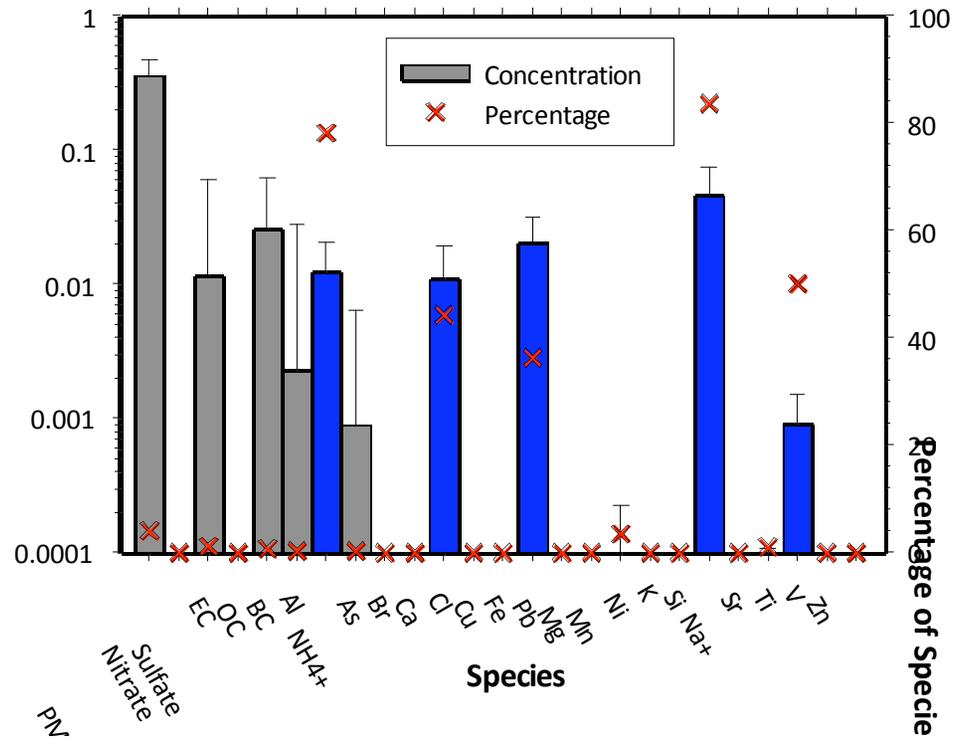
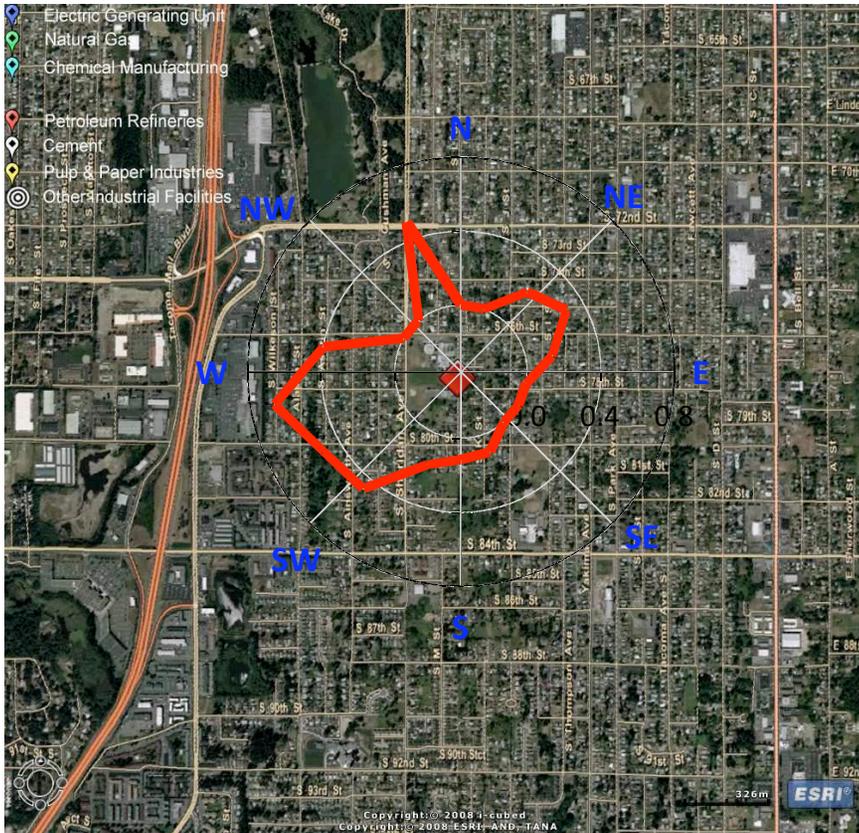


Aged (Processed) Sea Salt



Aged sea salt can be distinguished from fresh sea salt (previous slide) because there is an abundance of sodium (Na^+) and magnesium (Mg), but with no chloride (Cl^-) or other halogens. The sea salt Cl^- has been substituted by NO_3^- through atmos. reaction with nitric acid (HNO_3).

Fugitive Dust



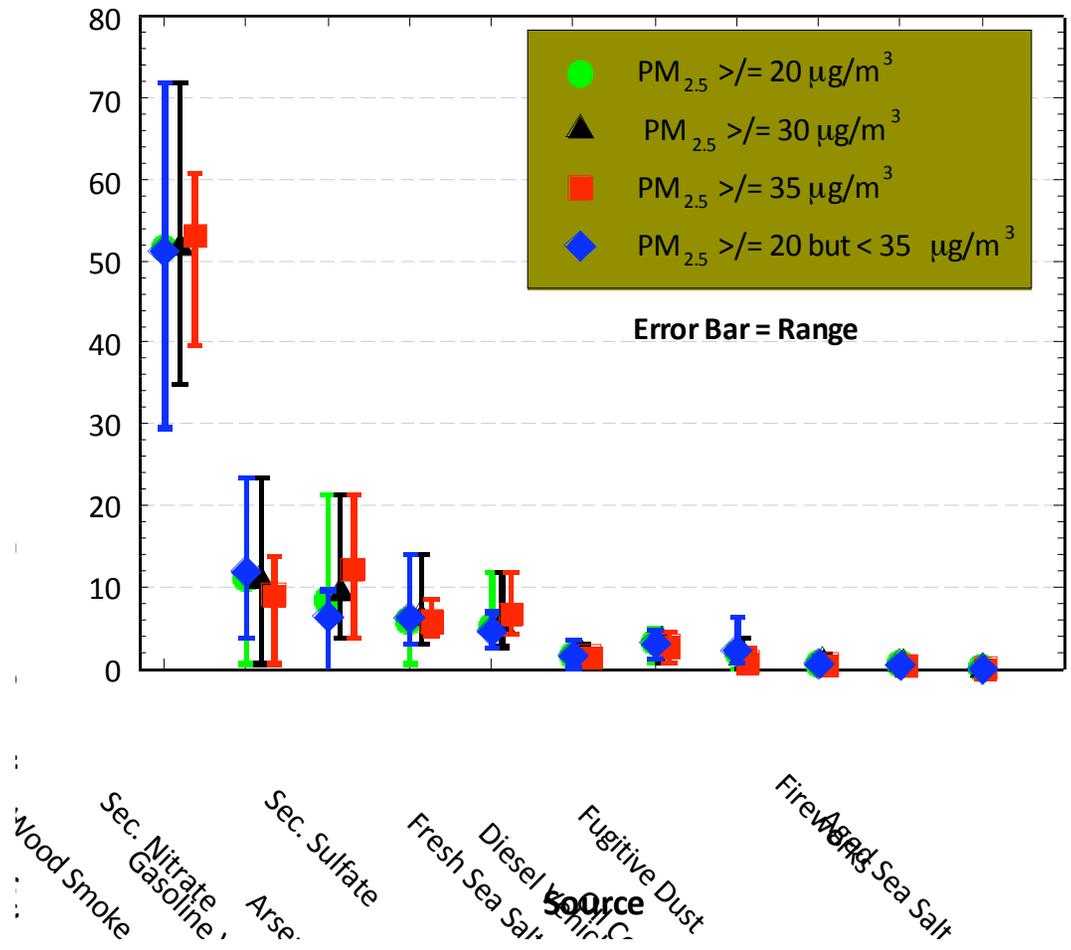
Recognized by the abundance of crustal elements. Re-suspended dust appears to be a significant contributor to these emissions. There is also a rock quarry in this direction.

Contributions by Year

Sample Year	2006	2007	2008	2009*
Measured PM _{2.5} Mass ($\mu\text{g}/\text{m}^3$)	9.4	10.8	8.3	10.4
Average Concentrations ($\mu\text{g}/\text{m}^3$) (Percentage of Measured Mass)				
Wood Smoke	4.8 (51%)	4.4 (41%)	3.0 (37%)	3.7 (35%)
Secondary Aerosol	2.0 (21%)	2.5 (23%)	2.1 (25%)	2.4 (23%)
Motor Vehicles	0.9 (9%)	1.2 (11%)	1.0 (11%)	2.7 (26%)
Industry	0.6 (6%)	0.6 (5%)	0.3 (4%)	0.5 (5%)
Other Identified Sources	1.1 (12%)	0.8 (8%)	1.1 (13%)	0.7 (7%)

*Only the first 5 months of data were available for 2009.

Percent Contributions on Elevated PM_{2.5} Days



Contributions on Elevated PM_{2.5} Days ($\geq 30 \mu\text{g}/\text{m}^3$)

Sample Date	Measured PM _{2.5} Mass ($\mu\text{g}/\text{m}^3$)	Wood Smoke	Secondary Aerosol	Motor Vehicles	Industry	Other Identified Sources
11/1/2006	33.0	72%	8%	10%	7%	4%
12/7/2006	32.6	51%	13%	12%	7%	5%
12/19/2006	32.7	63%	12%	9%	5%	3%
12/31/2006	54.3	53%	5%	16%	12%	4%
1/12/2007	44.9	59%	17%	6%	4%	2%
1/30/2007	39.1	61%	20%	12%	6%	4%
10/27/2007	34.5	52%	21%	9%	6%	3%
11/8/2007	33.2	35%	37%	11%	3%	6%
2/18/2008	32.8	37%	23%	12%	3%	9%
1/19/2009	38.3	40%	18%	26%	5%	3%
2/18/2009	31.1	46%	15%	16%	3%	5%

Summary

PMF results show that:

-  Most important source is wood smoke, contributing at least one half (50%) of the measured PM_{2.5} mass during the heating season. “Wood smoke” may include contributions from wood stoves, outdoor burning & other home heating devices.
-  On average, wood smoke accounts for at least 50% of the ambient PM_{2.5} concentration when the measured ambient PM_{2.5} concentration exceeds 30 µg/m³.
-  Important wood smoke sources appear to be located to the south /southeast of the sampling site.

Summary

PMF results also show that:

4. Secondary aerosol accounts for about 25% of the measured mass. Further analysis suggests locally-generated aerosol from multiple local NO_x and SO₂ sources.
5. Significant contributions from arsenic, lead, & zinc-rich emissions. These emissions could be a combination of background emissions from the now-defunct ASARCO smelter and active major industries located within the Port of Tacoma.
6. Stagnation events exacerbated impacts from local PM_{2.5} sources on certain days (e.g., 12/31/06).
7. Annual wood smoke contributions appear to have been decreasing since 2006. Not so much for other sources. A multi-prong control strategy may be needed.

Questions?

David Ogulei, Ph.D., P.E.

Science & Engineering Section
Washington State Department of Ecology

Call: (509) 454-7899 or (360) 407-6803

E-mail: David.Ogulei@ecy.wa.gov