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FINE PARTICLE EMISSION PROFILE FOR ROAD DUST IN PITTSBURGH, PENNSYLVANIA

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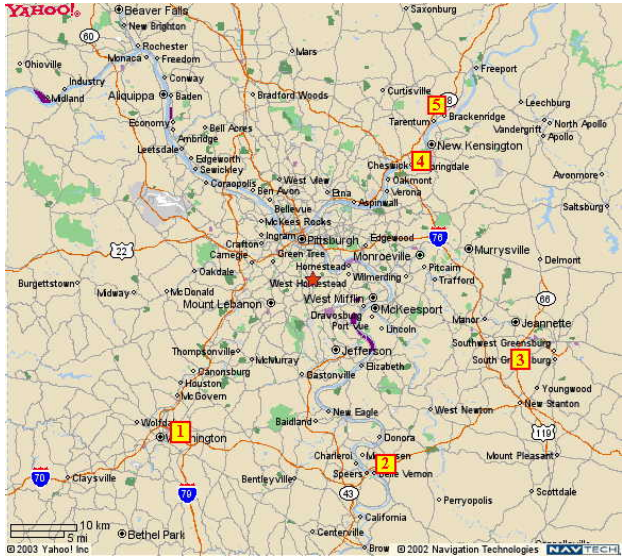
Introduction

Source receptor modeling using the Chemical Mass Balance (CMB) model requires source fingerprints. To better understand the sources of fine particulate matter in Pittsburgh region, $PM_{2.5}$ fingerprints were developed for urban and rural road dust. Samples were analyzed for OC/EC, elemental composition, and organic species. An important contribution of this work is the development of the first road dust finger print with speciated organics information outside of the Los Angeles basin.

Road Dust Collection

Rural Sampling Locations



Urban Sampling Locations

Road dust collection at a rural site.

Road dust samples were collected from 5 rural and 6 urban/suburban sites using a vacuum sampler constructed out of Teflon and stainless steel.

Samples were dried in an oven at 100 °C and then passed through a 37 μm sieve to remove large particles.

The samples were combined to create a composite urban and rural dust sample.

Samples were collected in the summer of 2003.

Road dust re-suspension and analysis

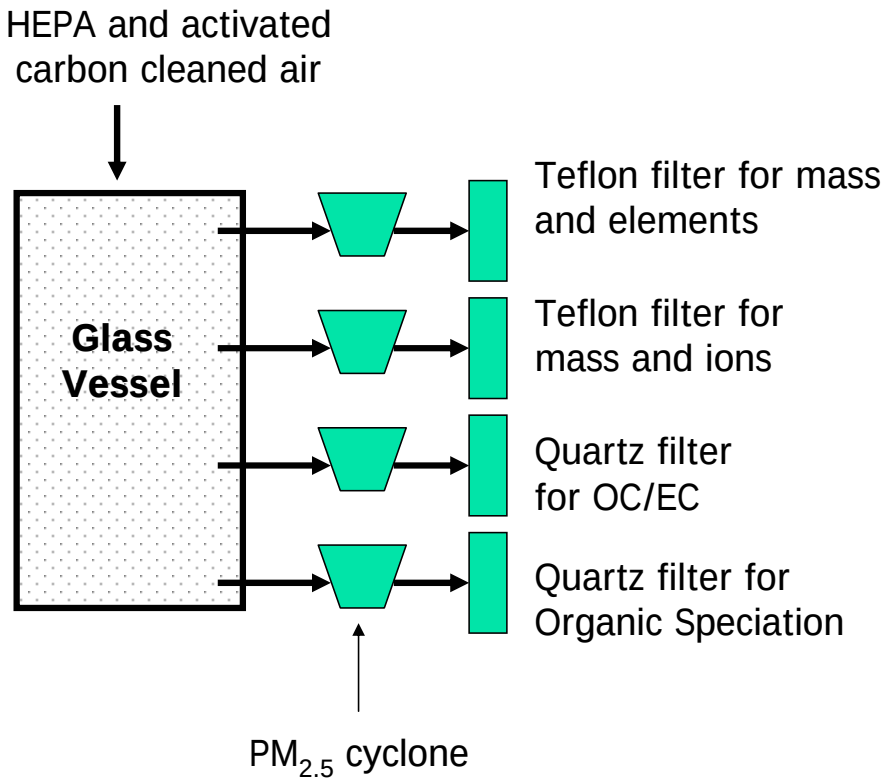


Figure 1. Schematic of Sampling System

To collect $PM_{2.5}$ filter samples, the sieved road dust was re-suspended in a a glass vessel using HEPA and activated carbon cleaned air.

Filter samples were analyzed for:

- $PM_{2.5}$ mass via gravimetric analysis
- OC & EC: Thermal-Optical with Sunset Instrument and NIOSH protocol
- Elemental composition: Acid digestion followed by ICP-MS
- Organic Speciation: Solvent extraction followed by GC-MS

Multiple samples were collected and analyzed for each dust sample to verify measurement repeatability.

Elemental Composition

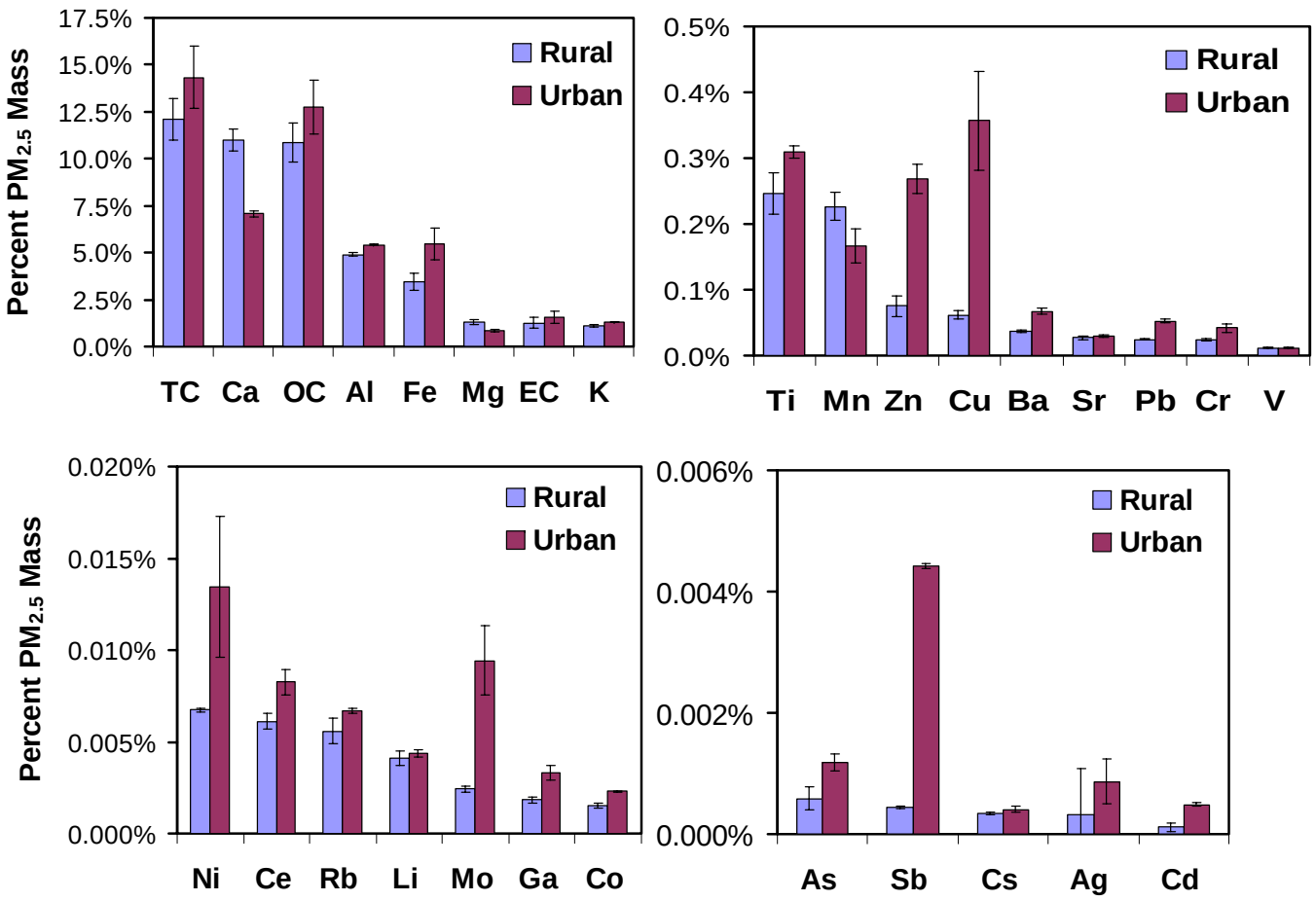


Figure 2. Elemental composition of PM2.5 mass.

Figure 2 shows the elemental composition of the $PM_{2.5}$ mass of the urban and rural road dust samples. The largest constituents of the road dust include organic carbon (OC), calcium, aluminum and iron. Assuming an organic mass to organic carbon ratio of 1.8, the quantified species contribute 43% and 46% of the rural and urban road dust PM2.5 mass, respectively. Major components not analyzed for include silicon and oxygen.

Comparing the urban and rural samples indicates that the urban road dust is enriched in metals associated anthropogenic sources. Notably Fe, Zn, Cu, Pb, Cr, Ni, Mo, Sb. The rural road dust is enriched in elements associated with soil dust. Notably Ca and Mn. The urban road dust is modestly enriched in carbon.

Speciated Organic Composition

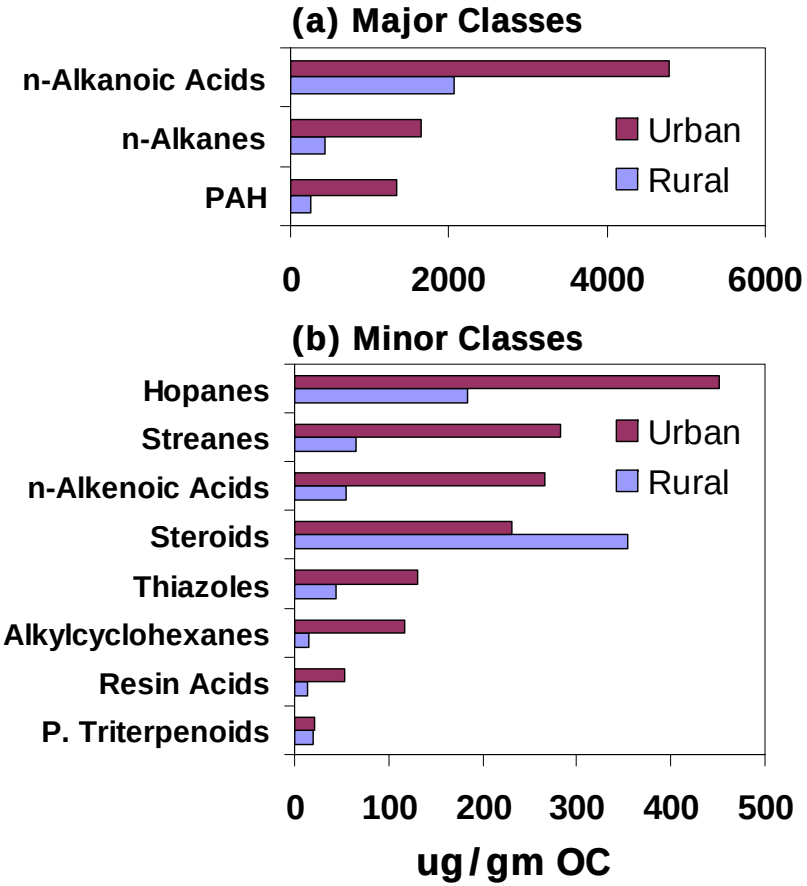


Figure 3. Contribution of major compound classes to OC.

GC-MS analysis was performed on solvent extracted samples to quantitatively determine contribution of more than 100 individual organic species to the road dust. **Figure 3** shows the contribution of different compound classes to the road dust OC. In total, the identified compounds contribute 0.35% and 0.94% of the OC mass in the rural and urban road dust samples, respectively.

For most of the compound classes, the urban road dust is significantly enriched compared to the rural sample. For example, the contribution of n-alkanes to the urban sample is almost a factor of 4 greater than in the rural sample. The notable exception to this is the enrichment of steroids (cholesterol and beta-sitosterol) in the rural sample.

Alkanes

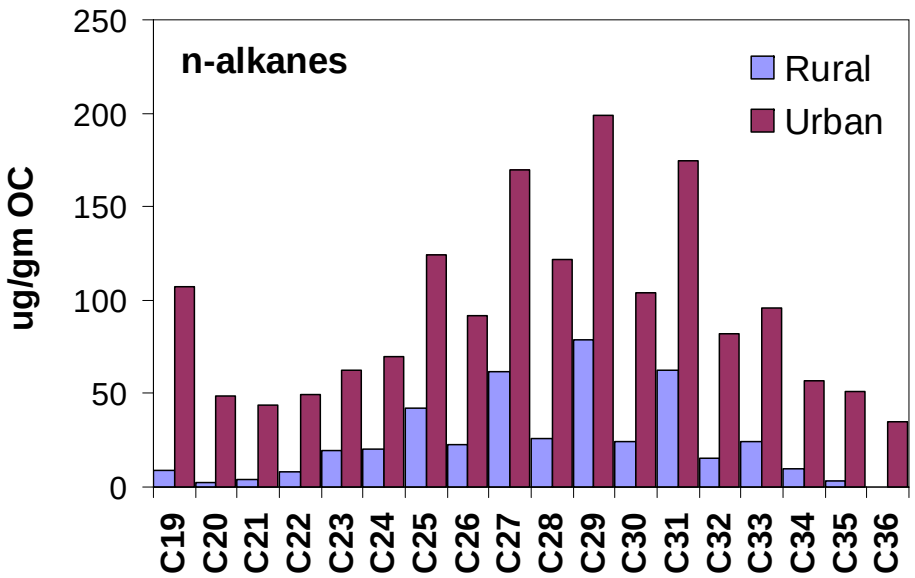


Figure 4. n-alkanes as function of carbon number.

Figures 4 and 5 show the distribution of n-alkanes and n-alkanoic acids as a function of carbon number. These two classes contribute the majority of the identified organic mass. The distribution of these species is similar to that measured in a road dust sample collected in Los Angeles (Rogge et al., 1993).

For the n-alkanes, the urban samples are enriched across the entire range of carbon numbers. The distribution of lower molecular n-alkanes (C-19-C-25) is characteristic for vehicle exhaust. The highest concentrations are observed in higher molecular weight n-alkanes characteristic of vegetative detritus. However, higher even n-alkanes also contribute a significant fraction of mass indicating important non-biological sources to high molecular weight n-alkanes.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T. (1993). "Sources of Fine Organic Aerosol .3. Road Dust, Tire Debris, and Organometallic Brake Lining Dust - Roads As Sources and Sinks." *Environmental Science & Technology* 27(9): 1892-1904.

Alkanoic Acids

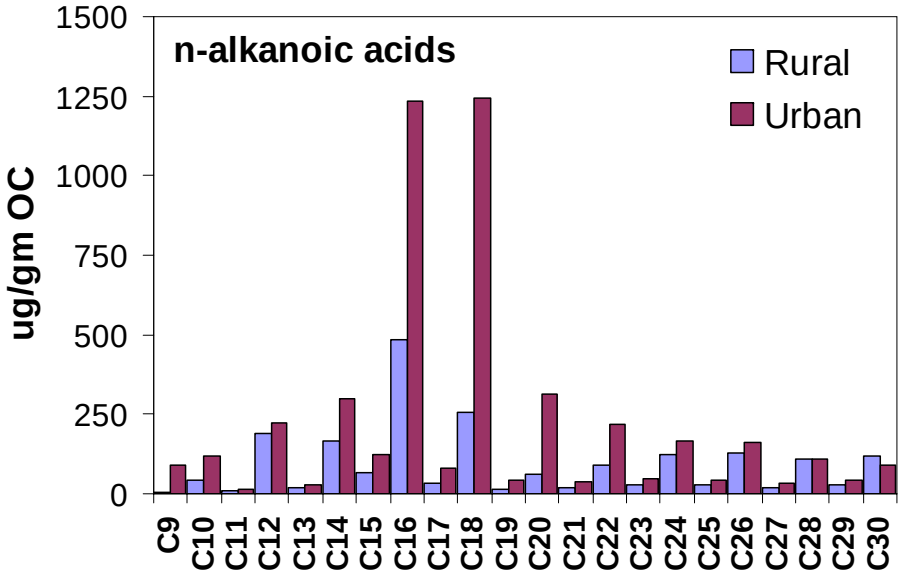


Figure 5. n-alkanes as function of carbon number.

Figure 5 shows the distribution of n-alkanoic acids with carbon number. For the n-alkanoic acids, stearic and palmitic acids are the dominant homologues in both the urban and rural sample and a strong even-to-odd distribution is prevalent. This pattern in high molecular weight n-alkanoic acids is a characteristic of vegetative detritus. Unlike the n-alkanes, the urban samples are only enriched at certain carbon numbers, notably C-16, C-18 and C-20. Little enrichment in the urban sample is observed in the higher molecular weight n-alkanoic acids.

Polycyclic Aromatic Hydrocarbons

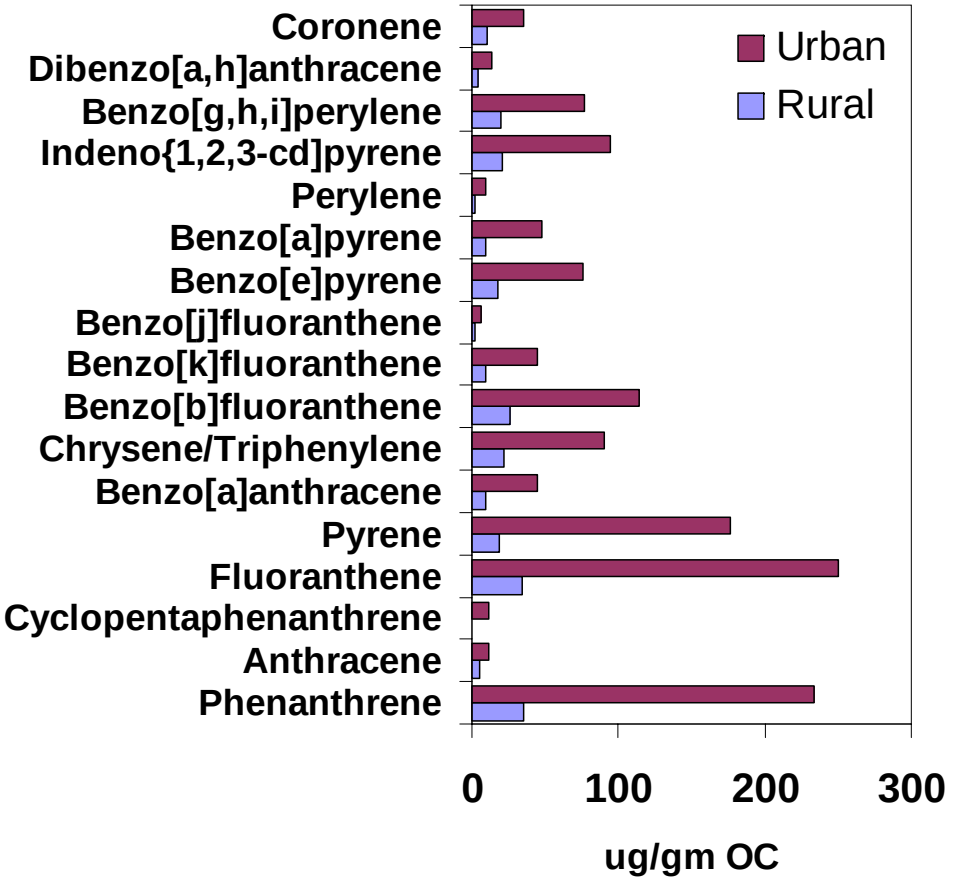


Figure 6. Road dust polycyclic aromatic hydrocarbons (PAH).

Figure 6 compares polycyclic aromatic hydrocarbon concentrations in the urban and rural road dust samples. PAHs are emitted by a number of combustion sources including gasoline powered vehicles, natural gas and wood combustion. Coke production is thought to be the dominant source of PAH in the Pittsburgh metropolitan area.

The urban road dust sample is significantly enriched in PAH relative to the rural sample. This enrichment underscores the influence of anthropogenic activities on road dust composition in urban environments. For higher molecular weight PAH (C-18 or larger), the ratio of urban to rural PAH is 4.1 ± 0.5.

Molecular markers for motor vehicles

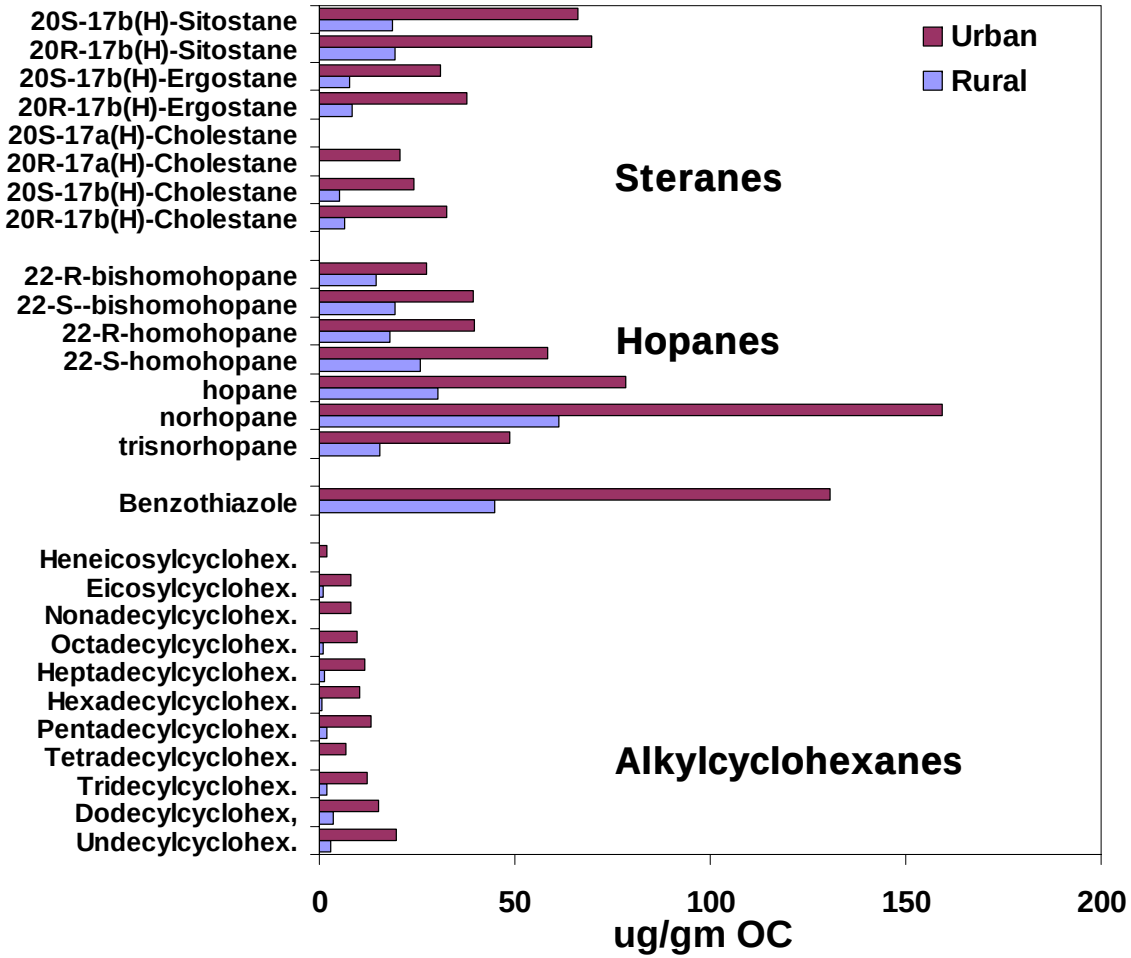


Figure 7. Road dust motor vehicle markers.

Figure 7 compares motor vehicle marker concentrations in urban and rural road dust. Hopanes and steranes are commonly used as markers for diesel and gasoline motor vehicles. Benzothiazole is a marker for tire wear aerosol. Alkylcyclohexanes have been identified in vehicle exhaust.

All of these markers are substantially enriched in the urban road dust sample consistent with the much higher vehicular traffic on urban roads. It is interesting to compare the enrichment of these molecular markers to elemental carbon (EC). Motor vehicles and diesel vehicles in particular are the dominant source of EC in urban environments. The urban to rural ratio of EC in road dust is 1.25 (**Figure 2**) versus 2.4 for hopanes and 4.3 for steranes.

Steroids

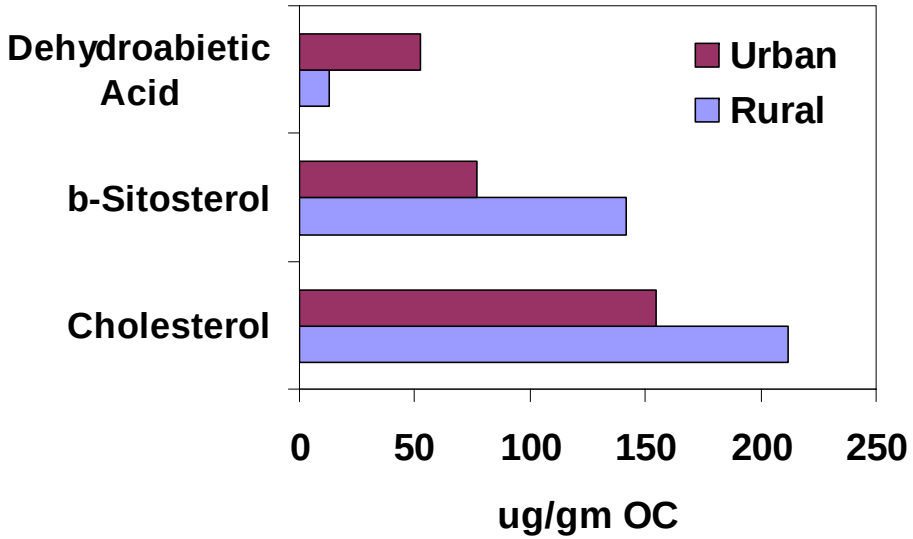


Figure 8. Road dust steroids and resin acids.

Figure 8 compares urban and rural road dust steroid and dehydroabietic acid levels. Dehydroabietic acid is a tracer of soft wood combustion and cholesterol is a marker for meat cooking emissions. Beta-sitosterol is a plant derived sterol, also known as a phytostero. Beta-sitosterol is measured in soft-wood smoke and is also found in plant abrasion products.

The two steroids are the only quantified compounds that were enriched in the rural road dust relative to the urban wood dust. We interpret this as the rural road dust being enriched in material of biological origin.

Comparison with Los Angeles Road Dust

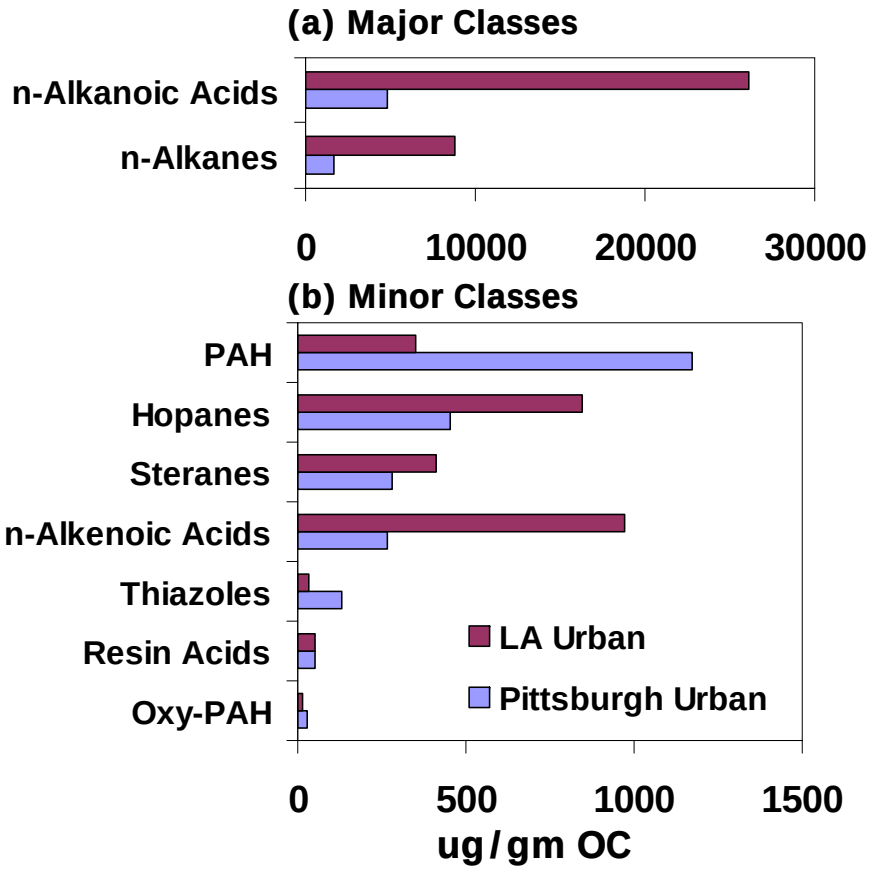


Figure 9. Pittsburgh and LA road dust.

Rogge et al. (1993) measured the organic molecular composition of a road dust sample collected in Los Angeles. OC contributes approximately 13% of the $PM_{2.5}$ mass in both the Pittsburgh and LA road dust samples. EC levels in the two samples are also comparable (~ 1% of $PM_{2.5}$ mass). **Figure 9** compares the contribution of major organic classes to the OC in the of the Pittsburgh urban sample and the Los Angeles sample. The distribution of compounds within these classes is generally similar between the two samples.

Los Angeles road dust is enriched in most of the compound classes compared to Pittsburgh. For example, alkanoic acids and n-alkanes are more than a factor of 5 higher in the LA samples. Hopanes and steranes are enriched by a factor of ~ 1.5 in the LA samples suggesting a large contribution of vehicular emissions to road dust in LA. PAH and thiazoles are the only two compounds classes that are elevated in Pittsburgh road dust compared to LA. The enrichment of PAH is likely due to differences in the industrial sources between Pittsburgh and LA. A much larger fraction of the OC in LA road dust was identified on a compound by compounds basis compared to Pittsburgh (5% in LA versus 0.9% in Pittsburgh).

Conclusions

- Significant differences were observed in the composition of urban and rural road dust
  - Urban – elevated in vehicular markers and metals associated with anthropogenic sources
  - Rural – elevated in markers for biological material
- In sum, the identified organic species contributed less than 1% of the OC mass

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