DETECTION OF A CONTAMINATING PLUME DURING A ROADWAY TUNNEL SOURCE SAMPLING EXPERIMENT USING A SINGLE PARTICLE MASS SPECTROMETER

Keith J. Bein, Yongjing Zhao, Anthony S. Wexler - University of California Davis
Eric Lipsky, Allen L. Robinson - Carnegie Mellon University
Murray V. Johnston - University of Delaware

Motivation and Hypothesis

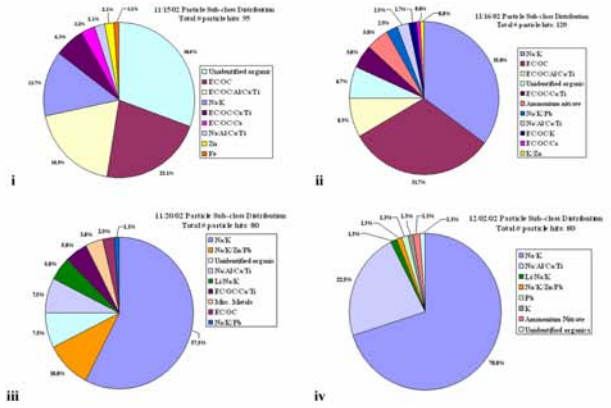
Experiments were performed on five separate days in which the air from an exhaust duct in the ventilation shaft of a roadway tunnel was sampled and characterized by a single particle mass spectrometer (RSMS-2) and an SMPS. Results indicate that particles sampled during the last four experiments are highly correlated, containing very similar chemical compositions. Particles sampled during the first experiment, however, differ significantly from the subsequent experiments; with ~ 92% of the particles sampled containing aliphatic amines. In the current work, we present evidence supporting the hypothesis that the sample collected from the tunnel during the first experiment was highly contaminated by a plume from a nearby coke plant.

Tunnel Sampling

I. Sampling Procedure

- Samples of ambient air where collected from the ventilation shaft of a Pittsburgh tunnel (Squirrel Hill Tunnel) in a large Teflon bag. The Teflon bag was immediately transported to a lab at CMU where the contents were characterized using a single particle mass spectrometer (RSMS-2) and an SMPS.

II. Last Four Experiments

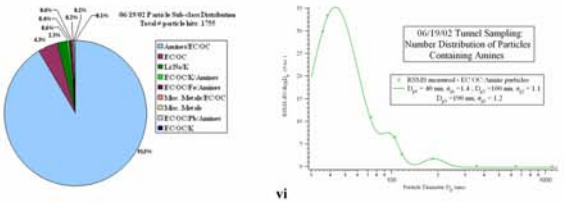


- Figures i. - iv. show the distribution of particles amongst the particle classes identified during four separate tunnel sampling experiments.

- Notice that the particle classes from these four experiments are highly correlated, containing very similar chemical compositions; predominantly combinations of EC/OC, sodium and potassium salts, and road dust.

Tunnel Sampling - continued

III. First Experiment

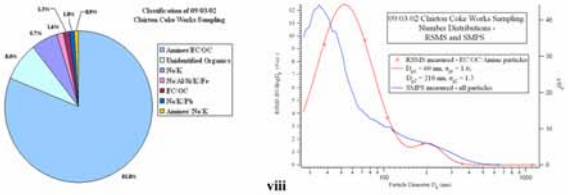


- Figure v. shows the distribution of particles amongst the particle classes identified during the first tunnel sampling experiment (06/19/02). Particle classes from this experiment are significantly different than the subsequent experiments; with ~ 92% of the spectra collected containing signature mass peaks for aliphatic amines. Other source sampling experiments, discussed below, have shown that this group of compounds is a component of the dominant particle class in the emissions of a coke processing plant.

- Depicted in figure vi. is the number distribution of particles containing amines. Notice that these particles are predominantly ultrafine particles, but that a smaller fine mode appears at ~200 nm.

USS Clairton Coke Works Sampling

- The sampling procedure for Clairton Coke Works was similar to that of the tunnel experiments. Emissions from the smoke stack of the plant were collected in a large Teflon bag and brought back to the lab for analysis.

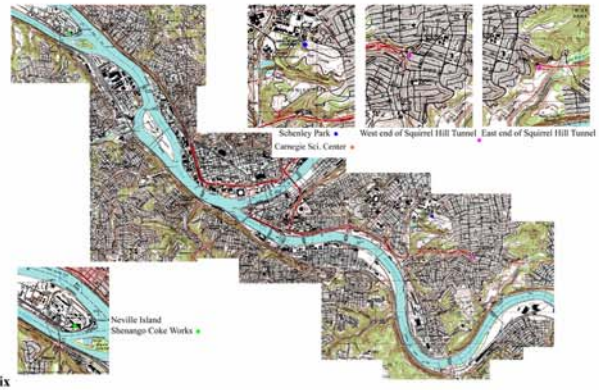


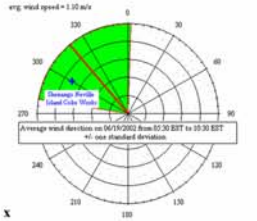
- Figure vii. shows the distribution of particles sampled during the Clairton Coke Works source sampling experiment (09/03/02) amongst the identified particle classes. Notice the overwhelming similarity between these classes and those in figure v, suggesting that the air sampled from the tunnel on 06/19 was largely influenced by emissions from a nearby coke plant.

- Note in both the 06/19 tunnel experiment and the 09/03 Clairton experiment that many particle classes are identical except for the presence or absence of amines, suggesting that amines exist in the gas phase and are partitioned to pre-existing particles through condensation. Although the EC/OC peaks in the spectra of particles from the EC/OC/Amine classes are typically associated with the amines themselves, the possibility that they are actually from primary carbon particles, like combustion particles, should also be considered.

- Plotted in figure viii. is the number distribution of particles containing amines, as measured by RSMS-3, and the total number distribution, as measured by an SMPS. Notice the strong similarity between the distribution of amines in this plot versus that of figure vi., both contain a dominant ultrafine mode in conjunction with a much smaller fine mode. The existence of two modes suggests that amines are present as both primary and secondary components. However, the extent to which they are primary, versus secondary, is not clear and most likely depends on the type of amine (molecular weight, vapor pressure, etc.), as well as ambient and emission conditions. Also notice the good agreement in the size range and shape of the RSMS and SMPS distributions.

Transport





- Figure ix. is a topographical map of the Pittsburgh area and shows the location of Squirrel Hill Tunnel, used for the tunnel experiments, in relation to the nearest coke plant (Shenango Neville Island Coke Works, ~15 km), Schenley Park (Supersites location, 3.6 km) and Carnegie Science Center (~ 9 km). Notice that the four sites are very nearly aligned along the same directional bearing (~300°; measured CW from true North).

- At a distance of 15 km, with an average wind speed of 1 m/s, it would take ~4 hours for an air parcel to travel from Shenango to the tunnel.

- Using wind data from the Schenley Park site, the average wind direction for the five hour period directly preceding the collection of the 06/19 tunnel sample has been plotted in figure x. Note that for the entire period, the wind is blowing from the coke plant towards the tunnel. In addition, from figure ix., notice that the Ohio and Monongahela river channels provide a direct route from source to receptor. Identical analyses were performed for the 11/15, 11/20 and 12/02 experiments using wind data collected at the Carnegie Science Center. The average wind speeds and directions are 1.4 +/- 0.7 m/s and 240 +/- 10° on 11/15, 1.1 +/- 0.4 m/s and 220 +/- 30° on 11/20, and 3.5 +/- 0.7 m/s and 250 +/- 10° on 12/02. Note that the direction of the wind does not correspond to the location of the coke plant, relative to the tunnel, during any of these subsequent experiments. Data for the 11/16 experiment is not available.

Conclusions

- During five separate experiments, particulate matter in the air collected from the ventilation shaft of a roadway tunnel was characterized on the basis of size and composition using a single particle mass spectrometer (RSMS-2) and an SMPS. Results show that particles sampled during the first experiment (06/19/02) were largely composed of aliphatic amines, similar to particles emitted from a coke processing plant rather than those sampled during the other four tunnel experiments, indicating that the sample was heavily contaminated by coke plant emissions. This is supported by the fact that for five hours prior to the collection of the sample, the wind was blowing parallel to a river channel connecting the tunnel and Shenango Neville Island Coke Works, a nearby coke plant.

- Based upon composition and size data, the amines detected during the 06/19 tunnel and 09/03 coke plant experiments appear to be present as both primary and secondary components, although the extent to which they are one or the other is not clear, suggesting that both nucleation and condensation play roles in the partitioning of these compounds into the particle phase.

Acknowledgements

Department of Energy for funding this research