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URBAN MODELING OF ORGANIC AEROSOL SOURCE EMISSIONS

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ABSTRACT

A mathematical model was used to predict the characteristics of fine organic aerosol that would be present in the Los Angeles atmosphere if direct organic aerosol source emissions were transported without chemical reaction. The model was successful at tracking both the seasonal variations observed in ambient samples of organic aerosol, and the distribution of the urban organic material present as a function of gas chromatographic elution time. Using the model, the major sources of urban organic aerosol were identified for this urban area. Differences between ambient measurements and model predictions were used to assess the degree of secondary organic aerosol formation.

Approach

Approximately one-third of the fine particulate matter present in the atmospheres of urban areas like Los Angeles consists of organic material, and many organic compounds present in ambient air have been found to be carcinogenic or mutagenic. Little was known at the outset of this research about the contributions of emissions from specific sources to the concentrations of organic aerosol found in the ambient air of urban areas.

Using a literature-based estimate of carbonaceous aerosol emissions in the Los Angeles area (Gray, 1986), the major sources of fine organic aerosol were tentatively identified, and source types were selected for sampling that accounted for close to 80% of the organic aerosol emissions (see Table 1). Dilution sampling techniques were developed (Hildemann *et al.*, 1989) and then used to sample sources that included a distillate oil-fired industrial-scale boiler, a home fireplace, natural gas home appliances, a commercial charbroiler, cigarette smoke, a roofing tar pot, and a fleet of gasoline- and diesel-powered vehicles. Grab sampling techniques were used to characterize tire wear debris, paved road dust, and brake lining debris (Hildemann, 1989).

High-resolution gas chromatographic analyses were performed on each source sample collected, using an extraction protocol specifically developed for filter samples containing only a few milligrams of aerosol mass (Mazurek *et al.*, 1987). Both the neutral and acidic organic compounds present were separately quantified. Using a simple computational approach, a quantitative, 50-parameter characterization of the elutable fine organic aerosol emitted from each source type was constructed (Hildemann, 1989). Then, the quantitative characteristics identified for each source type were used in conjunction with an atmospheric transport model (Cass, 1981; Gray, 1986) to predict the organic aerosol characteristics that would prevail in the ambient air *if* the primary organic aerosol emissions were transported without chemical reaction.

Table 1. Sources of Organic Aerosol Emissions Selected for Testing

Source Type	% of Total Fine Organic Aerosol Emissions in Los Angeles Basin*
Paved road dust	18.6
Charcoal broilers	15.9
Noncatalyst gasoline vehicles	13.5
Diesel vehicles	7.6
Brake lining	5.4
Cigarettes	4.9
Fireplaces	4.6
Roofing tar pots	2.7
Natural gas combustion	2.5
Tire wear	2.4
Catalyst-equipped gasoline vehicles	1.2
Distillate oil stationary sources	0.2
TOTAL SOURCES SAMPLED	79.5

* Estimated based on data in Gray, 1986.

Results

The predictions of fine organic aerosol characteristics expected in the urban atmosphere based on the model were compared with gas chromatographic analyses of actual ambient samples collected at three different sites in the Los Angeles area over a one year period, on a month-by-month basis. The model was found to track both the seasonal variations observed in the ambient organic aerosol samples and the distribution of the organic compounds as a function of gas chromatographic elution time. Emissions from vehicles and fireplaces were identified as significant sources of solvent-extractable organic aerosol.

Model predictions of the amounts and elution profiles of neutral organic material present at the ambient monitoring sites agreed well with actual measurements. This suggests that most of the neutral organic particulate matter present in the urban atmosphere originates directly from primary aerosol source emissions.

In contrast, the model significantly underpredicted the amount of acidic organic material present in ambient fine particulate matter. Thus, acidic organic aerosol present in the Los Angeles Basin cannot be explained by direct organic aerosol emissions from urban area sources, which suggests that much of this ambient acidic organic fraction results from subsequent chemical transformations in the atmosphere. The amount of secondary organic aerosol present was estimated based on the difference between predicted and measured concentrations of fine ambient acidic organic aerosol. Using this approach, secondary organic aerosol was calculated to contribute no more than 25–30% of the total mass of fine organic particulate matter present in Los Angeles.

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