DIESEL ENGINE CONTRIBUTIONS TO ATMOSPHERIC FINE PARTICLE CONCENTRATIONS

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INTRODUCTION

Urban and regional air pollution problems in densely populated areas arise from the combined effects of the emissions from hundreds of different types of air pollution sources. Emissions from stationary fuel combustion sources combine in the atmosphere with the emissions from motor vehicles, including diesel engine exhaust. To these combustion source effluents are added the emissions from widely dispersed small-scale activities in the community such as emissions from food cooking, and the generation of paved road dust as vehicle traffic moves over the streets. As the emissions from these sources mix in the atmosphere and are transported downwind, atmospheric chemical reactions take place. The secondary air pollutants that are formed by atmospheric chemical reactions include secondary particulate sulfates, nitrates and organics that are formed from the low vapor pressure reaction products of directly emitted pollutant gases. This mixture of directly emitted particles and gases, combined with their secondary atmospheric reaction products can adversely affect human health and damage materials. Fine particle air pollutants scatter and absorb light and thus lead to visibility reduction.

In this paper, methods for the characterization of fine particle concentrations in the atmos-phere and fine particle emissions from sour-ces first will be described. Then air quality modeling methods will be discussed that can be used to determine how the various emissions sources present in a city combine to produce the observed airborne particle mix-ture. From these models, the contribution that diesel engine exhaust makes to ambient fine particle concentrations can be determined.

ATMOSPHERIC MONITORING

Fine particle concentrations in the atmosphere can be characterized at community air monitoring stations using the methods described by Gray et al. (1). Fine particle samples collected downstream of cyclone separators are analyzed to determine fine particle mass concentration, organic carbon and elemental carbon (2), ionic species including sulfates, nitrates, chlorides, ammonium ion and sodium, and trace elements by X-ray fluorescence. From these measurements, a material balance can be constructed on the chemical composition of the atmospheric particle mixture that sheds considerable light on the sources that contribute to the atmospheric samples. Of particular importance to the current discussion, the black elemental carbon particle concentrations in cities are often dominated by emissions from diesel engines and thus an ability to account for black carbon particles in the atmosphere is often a key test of various air quality modeling methods that might be applied to study diesel engine exhaust in the atmos-phere. Atmospheric fine particle samples also can be extracted in organic solvents, and from these solvent extracts, the individual organic compounds present in the particles can be determined by gas chromatography/mass spectrometry (3). Among the organic com-pounds that can be quantified are the series of the hopanes and steranes. These are petroleum biomarkers that are present in motor vehicle exhaust that are useful in tracking the quantity of motor vehicle exhaust aerosol in the atmosphere.

MEASUREMENT OF EMISSIONS FROM SOURCES

Use of mathematical models that can reveal

source contributions to atmospheric fine particle concentrations requires that the characteristics of the particle emissions at the most important urban sources be understood. Particulate matter emissions from combustion sources are difficult to measure, in part because organic compounds that form particulate matter at ambient temperature and pressure are often still in the vapor phase at elevated stack temperatures and thus will pass through a particulate matter filter if care is not taken to bring the stack gases to ambient conditions before sampling. The solution to this problem is to employ a dilution source sampling system that cools the source samples by mixing with cooled purified dilution air prior to filtration. Such a source sampling system that can be used to measure the emissions from both stationary and mobile sources has been described by Hildemann et al. (4). This source sampling system has been used to characterize the mass emissions rate and chemical composition of the fine particles released from catalyst and non-catalyst equipped automobiles, heavy duty diesel trucks, oil-fired boilers, natural gas home appliances, meat cooking operations, fireplace combustion of wood, asphalt roofing tar pots, cigarette smoke, paved road dust, plant fragments, tire dust, and brake lining wear dust (5), as well as the particle size distribution of the emissions from many of these sources (6).

Fine particle samples collected during the source testing program of Hildemann et al. (5) have been subjected to solvent extraction and have been analyzed by GC/MS to determine the mass emissions rate of hundreds of or-ganic compounds that are emitted from the source types mentioned above (7-15). Many of these organic compounds are diagnostic for the presence of the emissions from spe-cific sources and can be used to determine source contributions to atmospheric particle concentrations by organic molecular tracer techniques, as will be explained shortly.

MODELING THE EFFECT OF EMISSIONS SOURCES ON AMBIENT AIR QUALITY

Two approaches can be employed to compute the contribution that specific emissions sources make to the atmospheric fine particle burden. In the source-oriented modeling approach, an atmospheric transport model is used to track pollutant emissions through a simulation of atmospheric fluid motion (and possibly chemical reaction) as the pollutants are transported from their sources to community air monitoring sites. To use this method, a grid system is first laid down over the urban area of interest. The spatial and temporal distribution of fine particle emissions from each of the major emissions sources to be studied is inventoried within each of these grid cells. Then these particle emissions are released into a simulation of atmospheric transport and dilution that is driven by historically measured meteorological data. Pollutant concentrations predicted to result from this atmospheric transport process are then compared to ambient measurements made at community air monitoring stations. Examples of diesel engine contributions to atmospheric carbon particle concentrations in the 1980's in the Los Ange-les area have been computed by Gray and Cass (16). Related transport models also have been developed that can predict the source contributions to the individual organic com-pounds present in the atmospheric particles (17) and that can predict the evolution of the size distribution of the chemical composition of the atmospheric fine particle complex (18,19).

In the second modeling approach, particulate organic compounds that act as tracers for the presence of the effluent from particular sources are used to determine the relative importance of the many sources that contribute to an atmospheric fine particle sample. Source profiles, first, are constructed that describe the relative distribution of organic compounds plus silicon, aluminum and elemental carbon in the direct particle emissions from the urban sources tested by Hildemann et al. (5) and Rogge et al. (7-15). Then, the best

linear combination of those source profiles required to reconstruct the distribution of organic compounds measured in atmospheric particle samples is determined by least squares regression techniques (20). From this analysis, the absolute magnitude of up to nine different source types that contribute to the atmospheric fine particle burden can be dis-tinguished, apart from the sulfates, nitrates and ammonium ion that are present in the particle samples due to gas-to-particle con-version processes in the atmosphere (20). An example of such an organic chemical tracer analysis of source contributions to the fine particle concentrations in the Los Angeles area in the early 1980's is given in Figure 1 from the study by Schauer et al. (20). Figure 1 shows that diesel engine emissions were among the most important fine particle sources in Los Angeles at that time. In more recent years as new fuels and engine technologies have been introduced into the vehicle fleet, elemental carbon concentrations in the Los Angeles atmosphere have declined to about half of the concentrations measured during the 1982 period represented in Figure 1, suggesting that diesel engine contributions to ambient fine particle concentrations probably have declined significantly over the last 15 years (21).

REFERENCES

1. Gray, H.A., Cass, G.R. (1986) Characteristics of Atmospheric Organic and Elemen-tal Carbon Particle Concentrations in Los Angeles. Environmental Science and Technology, 20,1567-1582.

2. Birch, M.E., and Cary, R.A., (1996) Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust, Aerosol Science and Technology, 25, 221-241.

3. Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., and Simoneit, B.R.T. (1993) Quantification of Urban Organic Aerosols at a Molecular Level: Identification, Abundance and Seasonal Variation, Atmospheric Environment 27, 1309 1330.

4. Hildemann, L.M., Cass, G.R., and Markowski, G.R., (1989) A Dilution Stack Sampler for Collection of Organic Aerosol Emissions: Design, Characterization and Field Tests, Aerosol Science and Technology, 10, 193-204.

5. Hildemann, L.M., Markowski, G.R., and Cass, G.R. (1991) Chemical Composition of Emissions from Urban Sources of Fine Organic Aerosol, Environmental Science and Technology, 25, 744-759.

6. Hildemann, L.M., Markowski, G.R., and Cass, G.R. (1991) Submicrometer Aerosol Mass Distributions of Emissions from Boilers, Fireplaces, Automobiles, Diesel Trucks, and Meat-Cooking Operations, Aerosol Science and Technology, 14,138-152.

7. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1991) Sources of Fine Organic Aerosol. 1. Charbroilers and Meat Cooking Operations. Environmental Science and Technology 25,1112-1125.

8. Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T. (1993) Sources of Fine Organic Aerosol. 2. Noncatalyst and Catalyst-equipped Automobiles and Heavy Duty Diesel Trucks. Environmental Science and Technology 27, 636-651.

9. 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 and Technology 27, 1892-1904.

10. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1993) Sources of Fine Organic Aerosol. 4 Particulate Abrasion Products from Surfaces of Urban Plants. Environmental Science and Technology 27, 2700-2711.

11. Rogge, W.F., Hildemann, L.M., Mazurek,

M.A., Cass, G.R., and Simoneit, B.R.T. (1993) Sources of Fine Organic Aerosol. 5. Natural Gas Home Appliances. Environmental Science and Technology 27, 2736-2744.

12. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1994) Sources of Fine Organic Aerosol. 6. Cigarette Smoke in the Urban Atmosphere. Environmental Science and Technology 28,1375-1388.

13. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1997) Sources of Fine Organic Aerosol. 7. Hot Asphalt RoofingTarpot Fumes. Environmental Science and Technology 31, 2726-2730.

14. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1997) Sources of Fine Organic Aerosol. 8. Boilers Burning No. 2 Distillate Fuel Oil. Environmental Science and Technology 31, 2731-2737.

15. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1997) Sources of Fine Organic Aerosol. 9. Pine , Oak, and Synthetic Log Combustion in Residential Fireplaces. Environmental Science and Technology, in press.

16 Gray, H.A., and Cass, G.R. (1997) Source Contributions to Atmospheric Fine Carbon Particle Concentrations, accepted for publication in Atmospheric Environment

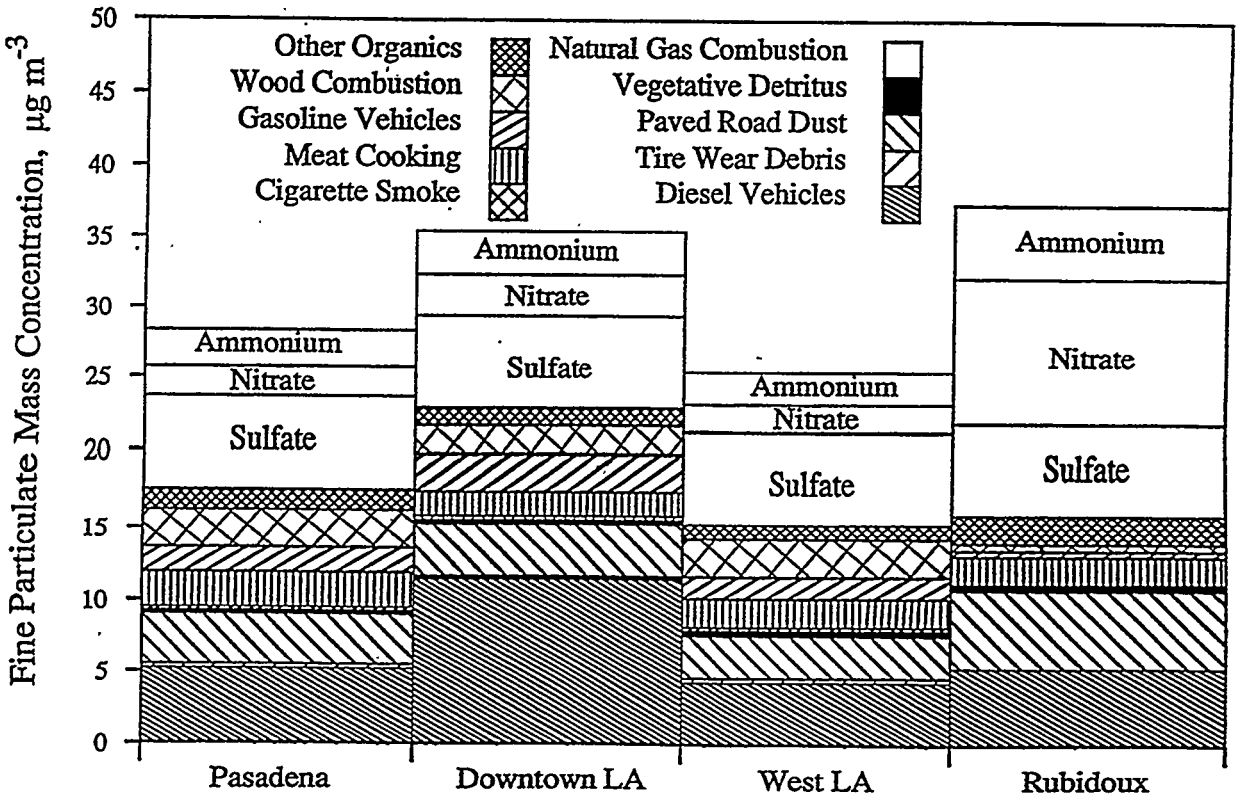
17 Rogge, W. F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1996) Mathematical Modeling of Atmospheric Fine Particle-associated Primary Organic Com-pound Concentrations. Journal of Geophysi-cal Research Atmospheres 101 (D1 4), 19379-19394.

18. Eldering, A., and Cass, G.R. (1996) A Source-Oriented Model for Air Pollutant Effects on Visibility, Journal of Geophysical Research -Atmospheres, 101,19,343-19,369.

19. Kleeman, M.J., Cass, G.R., and Eldering, A. (1997) Modeling the Airborne Particle Complex as a Source-Oriented External Mixture, Journal of *Geophysical Research-Atmospheres, 102, 21,355-21,372.*

20. Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and B.R.T. Simoneit (1996) Source Apportionment of Air-borne Particulate Matter Using Organic Com-pounds as Tracers, *Atmospheric Environ-ment, 30, 3837-3855.*

21. Christoforou, C.S., Salmon, L.G., Hannigan, M.P., Solomon, P. A., and Cass, G.R. (1997) Trends in Fine Particle Concentration and Chemical Composition in Southern California, submitted to *Journal of the Air and Waste Management Association.*



Source apportionment of fine mass concentrations — annual average.

Figure 1.