

Final Report prepared for the California Air Resources Board
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Executive Summary

Determination of the Elemental Carbon, Organic Compounds, and Source Contributions to Atmospheric Particles During the Southern California Children's Health Study

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An air monitoring network has been operated since 1994 at 13 sites as part of the Southern California Children's Health Study. The Children's Health Study is a large epidemiological investigation of the effects of air pollutant exposure on a population of more than 3600 school children. Data from the air monitoring network are used as part of the process of assessing the pollutant exposure levels in those communities where children being studied live and attend school. The communities studied range from mountainous (Alpine, Lake Arrowhead), to desert (Lancaster) to rural near-coastal areas (Lompoc, Santa Maria), to sites such as Long Beach, Glendora and San Dimas within the Los Angeles County urban area plus Mira Loma and Riverside in the urban plume downwind of the Los Angeles-Long Beach harbor area. These communities were chosen to represent as wide a range of pollutant exposures as possible.

Particulate matter concentration and chemical composition is measured at Children's Health Study monitoring sites using a filter sampler that takes a two week long integrated sample. Initially, the filters collected were designated for fine particle mass concentration determination and for measurement of ionic species including sulfates, nitrates and ammonium ion. Realizing that much of the aerosol in Southern California is carbonaceous, an additional particle sample collected on a prebaked quartz fiber filter suitable for carbon particle analysis was taken during each sampling event. These filters were placed in frozen storage following collection in the hope that they could be analyzed at a later date.

The present report documents the results of the analysis of the archived quartz fiber filters from the Children's Health Study network taken over the period 1994-1998. The quartz fiber filters first were analyzed for organic carbon (OC) and elemental carbon (EC) by thermal evolution and combustion analysis. A separate side-by-side sampling experiment was conducted to assess the particle size cut of the carbon particle leg of the Two-Week sampler. It was found that the carbon particle samples were effectively PM₁₀ samples, and correction factors were generated to estimate fine particle (PM_{2.5}) carbon particle concentrations from the Two-Week sampler data. The results from the EC/OC analysis and side-by-side sampling experiments are presented in Part A of this report. Seasonal composites formed by pooling half of each quartz fiber filter sample also were extracted in organic solvents and subjected to analysis by gas chromatography/mass spectrometry to determine the concentrations of 96 key organic compounds that act as tracers for the particulate matter emitted from specific sources. These organic compound concentrations are displayed and then used within the framework of a chemical mass balance receptor model to calculate the particle concentration increments attributable to gasoline-powered vehicle exhaust, diesel-powered vehicle exhaust, wood smoke, natural gas combustion, tire wear debris and vegetative detritus at each sampling site. At selected sites where enough information was available on paved road dust composition and atmospheric cholesterol concentrations, the atmospheric concentrations of paved road dust and meat smoke also were computed. These results are given in Part B of this report.

Annual average PM₁₀-equivalent elemental (black) carbon particle concentrations range from 0.05 - 1.74 $\mu\text{g m}^{-3}$ over the communities and years studied while annual average particulate organic carbon concentrations are in the range 1.50 - 15.67 $\mu\text{g m}^{-3}$. The coastal sites generally show winter season EC and OC concentration peaks while the mountainous and some inland sites show summer seasonal peaks; both conditions are consistent with seasonal changes in wind direction and mixing depth. The carbon particle data were translated into estimates of PM_{2.5} elemental and organic carbon particle concentrations and then were merged with the Children's Health Study data on fine particle mass and ionic species concentrations. The results of this analysis are depicted in Figure 11 of Part A of the main report. Carbonaceous aerosols account for 32 to 60 percent of the fine particle concentrations between the sites studied. The overall fine particle mass concentrations show a coherent spatial pattern with very low mass concentrations (circa 5-8 $\mu\text{g m}^{-3}$) and aerosol carbon concentrations at the northern and

southern-most monitoring sites, reaching the highest annual average concentration of $35.8 \mu\text{g m}^{-3}$ $\text{PM}_{2.5}$ mass including $14.7 \mu\text{g m}^{-3}$ organic compound mass in 1995 at Mira Loma downwind of the Los Angeles-Long Beach urban complex. Over the period 1994-1998 there is a pronounced downward trend in annual average fine particle mass and carbonaceous aerosol concentrations at the urban sites. The relative chemical composition of the aerosol did not change appreciably during that time. Since all aerosol components are affected about equally, the cause of the downward concentration trend could be due in part to greater atmospheric dilution in the more recent years. Continued improvements in vehicle emissions control technology and use of cleaner fuels also would be expected to contribute to this downward trend in fine particle concentrations.

GC/MS analysis was conducted on seasonal composites of filters taken by the Children's Health Study during the year 1995. The concentrations of 96 organic compounds that act as tracers for particular emissions sources were determined. The concentrations of hopanes and steranes that act as tracers for primary motor vehicle exhaust particles are highest in the winter months at the start of 1995 and lower in the following summer, which is typical of the findings of previous studies. During the winter period at the end of 1995, motor vehicle exhaust tracer concentrations are very low at some of the less populated sites while concentrations are much higher at urban locations like Long Beach and Mira Loma. Concentrations of the wood smoke tracer levoglucosan are much higher in the winter months than in the summer months, as expected. Wood smoke tracer concentrations are higher in Atascadero than at other locations. Using existing data on the organic chemical composition of the emissions from major air pollution sources, the best fit combination of source effluents needed to reproduce the distribution of atmospheric organic compounds was computed. On this basis, the contributions of gasoline powered motor vehicle exhaust, diesel powered motor vehicle exhaust, wood smoke, vegetative detritus, natural gas combustion aerosol, and tire wear debris to both PM_{10} equivalent organic compound concentrations and PM_{10} mass concentrations were computed. At a few selected sites it was also possible to quantify the amount of meat smoke and paved road dust in the atmosphere. Diesel exhaust aerosol mass concentrations at the most heavily urbanized sites typically lie in the range $1.7\text{-}5.6 \mu\text{g m}^{-3}$, falling to as little as $0.3 \mu\text{g m}^{-3}$ at the least affected rural site (Lompoc) in certain seasons. Gasoline-powered motor vehicle exhaust aerosol mass concentrations are typically smaller than the diesel engine contributions, although a few counter examples can be found. The gasoline engine exhaust particle concentrations show greater seasonality than is the case for diesel engine particles. This is believed to be due in part to the effect of cold start conditions on the gasoline-powered vehicle fleet in the winter months. Wood smoke concentrations are highest at Atascadero, averaging up to $5.5 \mu\text{g m}^{-3}$ during the winter period at the end of 1995 at that site. In those cases where paved road dust concentrations can be estimated, indications are that the road dust contribution to PM_{10} concentrations is very large, on the order of $20\text{-}55 \mu\text{g m}^{-3}$ at urban sites in the Los Angeles metropolitan area. The road dust concentration estimates could be refined to produce more accurate values if other filters from the Children's Health Study were analyzed for their trace elements content such that soil mineral concentrations were revealed directly. Meat smoke concentrations are comparable to wood smoke concentrations at those monitoring sites where meat smoke concentrations can be quantified.