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The chemical composition of atmospheric ultrafine particles

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Atmospheric ultrafine particles (with diameter less than 0.1 μm) may be responsible for some of the adverse health effects observed due to air-pollutant exposure. To date, little is known about the chemical composition of ultrafine particles in the atmosphere of cities. Ultrafine particle samples collected by inertial separation on the lower stages of cascade impactors can be analysed to determine a material balance on the chemical composition of such samples. Measurements of ultrafine particle mass concentration made in seven Southern California cities show that ultrafine particle concentrations in the size range 0.056–0.1 μm aerodynamic diameter average 0.55–1.16 $\mu g\,m^{-3}$. The chemical composition of these ultrafine particle samples averages 50% organic compounds, 14% trace metal *oxides*, 8.7% elemental carbon, 8.2% sulphate, 6.8% nitrate, 3.7% ammonium ion (excluding one outlier), 0.6% sodium and 0.5% chloride. The most abundant catalytic metals measured in the ultrafine particles are Fe, Ti, Cr, Zn, with Ce also present. A source emissions inventory constructed for the South Coast Air Basin that surrounds Los Angeles shows a primary ultrafine particle emissions rate of 13 tonnes per day. Those ultrafine particle primary emissions arise principally from mobile and stationary fuel combustion sources and are estimated to consist of 65% organic compounds, 7% elemental carbon, 7% sulphate, 4% trace elements, with very small quantities of sodium, chloride and nitrate. This information should assist the community of inhalation toxicologists in the design of realistic exposure studies involving ultrafine particles.

Keywords: ultrafine particles; atmospheric concentration; chemical composition; emissions rate

1. Introduction

Epidemiological studies suggest that mortality and morbidity rates increase on days with higher than usual airborne particle concentrations (Dockery *et al.* 1993; Pope *et al.* 1995). Statistical associations between increasing particle concentrations and adverse health effects are found for concentration increments as low as 10 $\mu g\,m^{-3}$ at total particle concentrations below 100 $\mu g\,m^{-3}$. In contrast, toxicologists generally find that such low concentrations of chemically inert particles in particle sizes

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larger than about 0.5 μm in particle diameter do not produce serious adverse effects in laboratory inhalation studies (Schlesinger 1995). This suggests that there may be attributes of the airborne particle mixture that are capable of inducing damage to human health, while not contributing greatly to atmospheric particle mass concentrations.

Atmospheric ultrafine particles, defined here as those having diameters smaller than 100 nm (0.1 μm), are present at concentrations of about 10^4 particles per cm^3 of air in the atmosphere of cities. These ultrafine particles dominate atmospheric particle number concentrations, while at the same time making a negligible contribution to particle mass concentrations. One distinct possibility is that the number of inhaled particles is more important in producing the health effects associated with air pollution than is the inhaled particle mass concentration. Alternatively, perhaps a combination of the chemical composition and very small size of atmospheric ultrafine particles is critical in explaining the effect of airborne particles on human health. In order to assist the community of toxicologists in the design of realistic test atmospheres needed to further explore these hypotheses, it is useful to determine the chemical composition of atmospheric ultrafine particles.

At present, very little is known about the chemical composition of atmospheric ultrafine particles. To date, only a single study has been published on ultrafine particle chemical composition in the atmosphere of cities (Hughes *et al*. 1998). The purpose of the present paper is to expand the existing data on urban atmospheric ultrafine particle chemical composition, and to draw comparisons between the measured chemical composition of ultrafine particle emissions from sources and the chemical composition of atmospheric ultrafine particles. Atmospheric measurements made in seven cities in Southern California will be compared with a comprehensive inventory of the chemical composition of ultrafine particle emissions from sources based on a programme of source testing conducted in the South Coast Air Basin that surrounds metropolitan Los Angeles.

2. Atmospheric ultrafine particle chemical composition

Over the period 1995–1997, field experiments were conducted in Southern California to characterize the size distribution and chemical composition of the airborne particle mixture (Hughes *et al*. 1998, 1999, 2000; Allen *et al*. 2000). Particle number distributions were measured with differential mobility analyser/condensation nucleus counter combinations (TSI models 3071 and 3760), with electrical aerosol analysers (TSI model 3030), and with optical particle counters (Particle Measuring Systems model ASASP-X). Filter-based measurements of particle chemical composition were made in two particle size ranges: fine particles smaller than 2 μm in diameter, and total suspended particulate matter of all sizes. Of most importance to the present study, samples for particle chemical composition determination were collected in six narrow size ranges spanning the interval from 1.8 to 0.56 μm particle aerodynamic diameter using a pair of MOUDI cascade impactors (MSP Corp. model 100). These impactors were preceded by AIHL-design cyclone separators operated at a cut-point of 1.8 μm in order to remove coarse atmospheric particles that may contribute to particle bounce within the impactors (John & Reischl 1980). One impactor of each pair was loaded with Teflon collection substrates (Gelman Teflo, 47 mm in diameter), while the second impactor was loaded with aluminium foil impaction sub-

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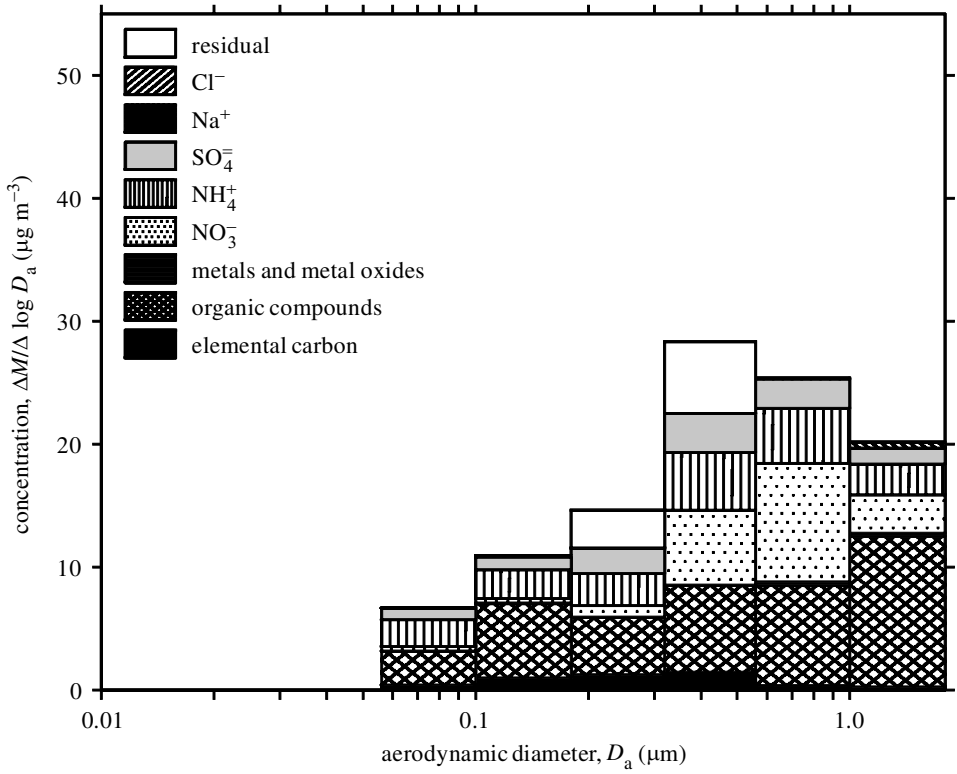

Figure 1. The size distribution and chemical composition of atmospheric particles smaller than 1.8 μm aerodynamic diameter at Riverside, CA, 28 August 1997.

strates (MSP Corp.). The impaction substrates were weighed before and after use in a temperature- and humidity-controlled environment (typically 22 °C and less than 48% relative humidity (RH) but with RH no more than ±3%) using a Mettler model M-55-A mechanical microgram balance. The Teflon impaction substrates were divided in half. One-half was analysed for sulphate, nitrate and chloride by ion chromatography (Mulik *et al.* 1976), using a Dionex model 2020i ion chromatograph, and for ammonium ions by an indophenol colorimetric technique (Bolleter *et al.* 1961), using an Alpchem rapid flow analyser (model RFA-300). Trace-element concentrations were determined from the other half of the Teflon impaction substrates via instrumental neutron activation analysis (Olmez 1989). The concentration and size distribution of organic compounds and black light-absorbing elemental carbon (EC) was determined from samples collected on the aluminium foil impaction substrates by the thermal evolution and combustion procedure of Huntzicker *et al.* (1982), as modified by Birch & Cary (1996) and as adapted to impactor samples by Kleeman *et al.* (1999*a*). In the present work, measurements of organic carbon (OC) concentrations are converted into estimates of organic compound concentrations in the aerosol by scaling measured OC concentrations upward by a factor of 1.4 in order to account for the H, O, S and N in organic compounds typically found in the urban atmosphere.

An illustration of the size and chemical composition distribution of chemical substances present in the airborne fine particle mixture in Southern California is shown in figure 1. These data show an accumulation mode aerosol in the particle diameter

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range less than 1.8 μm having a peak in the mass concentration at *ca.* 0.5 μm particle diameter. The fine particle mixture consists largely of elemental and organic carbon, ammonium sulphate and ammonium nitrate. The lower tail of the coarse particle soil dust and sea salt size distribution can often be seen in the larger fine particle size ranges as well.

Ultrafine particles, as presently defined by the community of health scientists, consist of particles smaller than 0.1 μm in diameter. Data on particle chemical composition in this size range are available from the lowest stage of the MOUDI impactor samples, as can be seen at the far left of figure 1. Samples collected for chemical determination over the interval 0.056–0.1 μm particle diameter, while falling in the ultrafine particle size range, are related to the lower tail of the accumulation mode particle size distribution as seen in figure 1. They probably represent the largest mass of the particles in the ultrafine particle size range but may be chemically different from the more numerous particles present at diameters smaller than 10 nm, for example.

Data on ultrafine particle mass concentrations and chemical composition for particles of the size 0.056–0.1 μm aerodynamic diameter at seven Southern California cities and for eight time intervals are shown in figure 2. Each chart represents an average over many samples taken during the time intervals shown.

Average ultrafine particle mass concentrations across all Southern California sites and all seasons studied lie in the fairly narrow range 0.55–1.16 $\mu g\ m^{-3}$. The average ultrafine particle mass concentration is *ca.* 0.8 $\mu g\ m^{-3}$ in the size range 0.056–0.1 μm aerodynamic diameter.

Organic compounds and elemental carbon contribute close to half of the ultrafine particle mass concentration at Pasadena, CA, in the winter months, with noticeable contributions from metal oxides and lesser amounts of sulphates and nitrates, as seen in figure 2*a* (Hughes *et al.* 1998). Samples taken at groups of air monitoring sites that are generally upwind/downwind of each other are illustrated in figure 2*b*, *c*, figure 2*d*, *e* and figure 2*f*–*h*. Fullerton is a city in Orange County, CA, located *ca.* 20 km inland from the Pacific Ocean along air parcel trajectories that often pass over the large industrial and harbour complex at Long Beach, CA, earlier in the day. Ultrafine particle composition at Fullerton is shown in figure 2*b*. Again as at Pasadena, carbonaceous aerosols are the largest contributors to the ultrafine particles at Fullerton, followed by metal oxides, sulphate, ammonium and nitrate ion, in that order. Riverside is located *ca.* 60 km inland from Fullerton and is directly downwind of Fullerton in the summer and early autumn months. Because of the slow wind speeds in Southern California, transport times from Fullerton to Riverside are often a day or longer. Riverside is largely a residential and commercial centre; the samples quantified in figure 2*c* were taken on the campus of the University of California at Riverside, where motor-vehicle traffic is the most obvious source of local particle emissions. Ultrafine particles at Riverside during September–October 1996 are likewise largely carbonaceous, with noticeable metal content and much less sulphate and nitrate aerosol than is associated with accumulation mode particles having diameters of several hundred nm at Riverside.

The ultrafine particle chemical composition in central Los Angeles, shown in figure 2*d*, is dominated by high-density motor-vehicle traffic. Sixty-nine per cent of the ultrafine particle mass concentration in central Los Angeles in August 1997 was carbonaceous, with a higher than usual proportion of black elemental carbon reflecting

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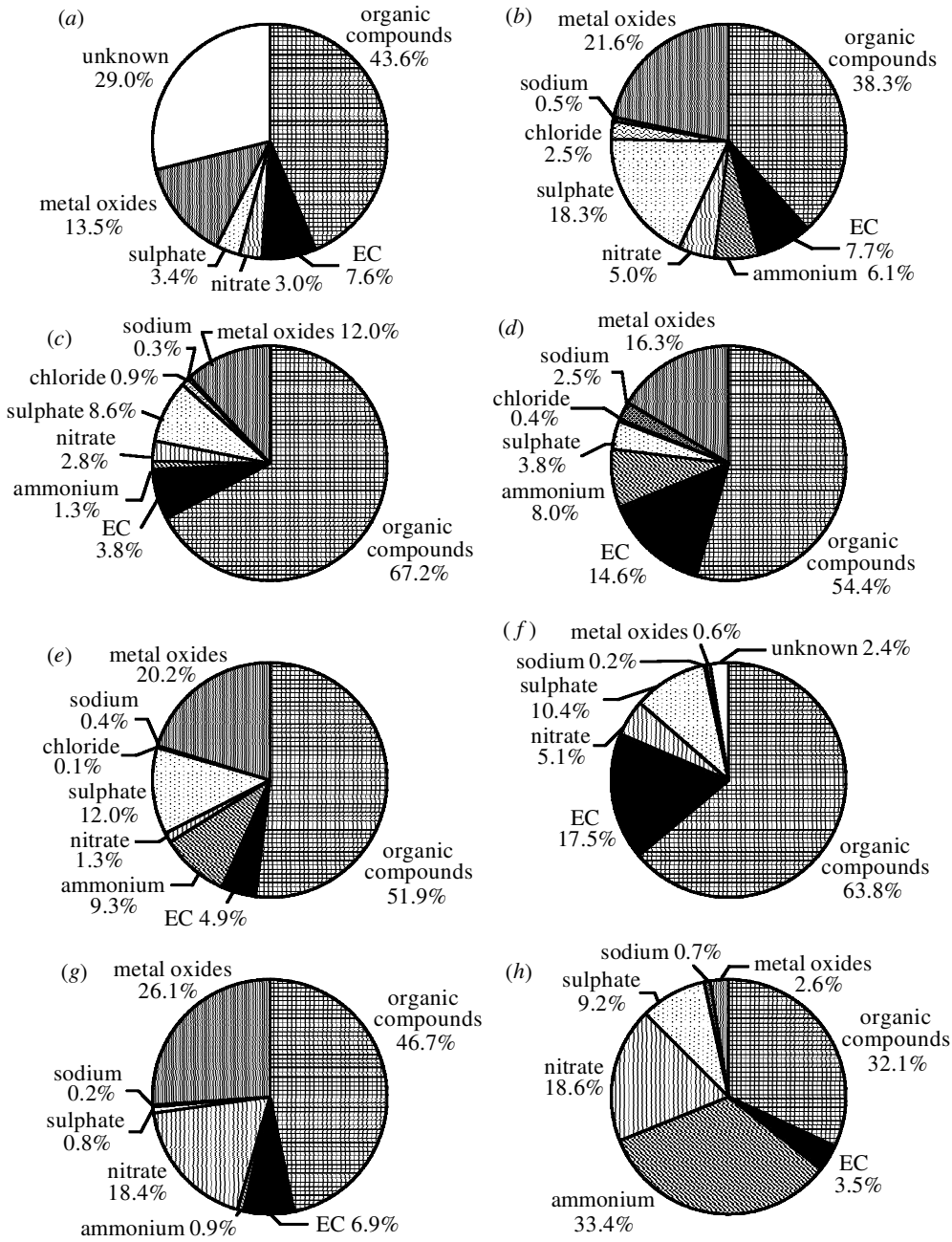

Figure 2. The chemical composition of atmospheric ultrafine particles in the size range 0.056–0.1 μm particle aerodynamic diameter measured at cities in Southern California. (*a*) Pasadena, CA, January–February 1996 (0.82 μg m^{-3}); (*b*) Fullerton, CA, September–October 1996 (0.64 μg m^{-3}); (*c*) Riverside, CA, September–October 1996 (0.63 μg m^{-3}); (*d*) Los Angeles, CA, August 1997 (1.16 μg m^{-3}); (*e*) Azusa, CA, August 1997 (0.80 μg m^{-3}); (*f*) Diamond Bar, CA, September–November 1997 (0.55 μg m^{-3}); (*g*) Mira Loma, CA, September–November 1997 (0.58 μg m^{-3}); (*h*) Riverside, CA, August–November 1997 (0.91 μg m^{-3}).

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Table 1. *Average ultrafine particle trace metal concentrations (central Los Angeles, CA, August–September, 1997)*

trace metal	mean concentration (ng m^{-3})	range (ng m^{-3})
groups I and II		
Na	85	(bdl–249)
K	88	(bdl–93)
Cs	0.100	(bdl–0.34)
Ba	19	(bdl–19)
transition metals		
Sc	0.028	(bdl–0.054)
Ti	43	(bdl–43)
V	bbl	
Cr	6.7	(bdl–15)
Mn	bbl	(bbl–0.056)
Fe	186	(bdl–470)
Zn	3.8	(bbl–10)
Mo	0.48	(bdl–0.68)
Cd	0.19	(bbl–0.49)
Au	bdl	
Hg	0.09	(0.038–0.14)
lanthanides		
La	0.021	(bdl–0.021)
Ce	1.2	(bdl–2.3)
Sm	0.012	(bdl–0.019)
Eu	0.20	(bdl–0.37)
Yb	0.26	(bbl–0.50)
Lu	0.014	(0.0011–0.028)
actinides		
Th	bbl	
U	bdl	

bdl denotes 'below detection limits'. bbl denotes 'below blank levels'.

the high concentration of diesel engines in use at that location, not only in highway vehicles but also in railway locomotives and industrial diesel engines. Azusa, CA, is located *ca.* 30 km inland from central Los Angeles and is generally downwind of it in the summer months. As seen in figure 2*e*, 57% of the ultrafine particle mass at Azusa consists of organic compounds plus elemental carbon. Again, significant quantities of metal oxides are present, with noticeable amounts of ammonium and sulphate but little ammonium nitrate, even though aerosol nitrate is quite common in larger particles in the Los Angeles area.

Samples collected at the location of the South Coast Air Quality Management

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District Offices in Diamond Bar, CA, are shown in figure 2*f*. That site is located on a hill immediately adjacent to the intersection of the Pomona and no. 57 freeways. As in central Los Angeles, large quantities of organic compounds and elemental carbon are measured in the ultrafine particles at the Diamond Bar site. Mira Loma is located 10–20 km inland from Diamond Bar and it is immediately downwind from the Chino dairy area. The atmosphere at Mira Loma contains very high ammonia concentrations, well above the odour threshold for ammonia, as well as high concentrations of inorganic nitrate due to nitric acid formation in photochemical smog on the downwind side of the Los Angeles area. As has been seen elsewhere, more than half of the ultrafine particle mass concentration at Mira Loma consists of organic compounds plus elemental carbon, with substantial metal oxides content. At Mira Loma we see our first example of relatively high nitrate aerosol content in ultrafine particles. This could be due to nitric acid reaction with the metal-containing particles seen in figure 2*g*. Alternatively, this could be due to ammonium nitrate formation accompanied by analytical problems with ammonium concentration measurement in the very small samples evaluated here. The ammonium measurement method is less accurate than sulphate and nitrate determination at these very small sample sizes. Clearly, there is both ammonium and nitrate present in the ultrafine particles collected at the Riverside site during approximately the same months, as shown in figure 2*g*. Riverside is 20–30 km downwind of Mira Loma. Overall, the chemical composition of ultrafine particles in Southern California is in the range 32–67% organic compounds, 3.5–17.5% elemental carbon, 1–18% sulphate ion, 0–19% nitrate ion, 0–9% ammonium ion (excluding one extreme outlier at Riverside), 1–26% metal oxides, 0–2% sodium and 0–2% chloride.

The concentrations of catalytic metals in atmospheric particles are of particular interest to the community of toxicologists, because catalytic metals deposited in the lung could catalyse oxidative damage to it. The mean trace element concentration (and range of concentrations) in the ultrafine particles in the size range 0.056–0.1 μm aerodynamic diameter in central Los Angeles is shown in table 1. The acronym 'bdl' in the table indicates that the lowest values were below the detection limits of the neutron activation analysis in some cases. The most abundant transition metals in the ultrafine particles in the central Los Angeles atmosphere were found to be Fe, Ti, Cr and Zn. The catalytic element Ce was also measured at concentrations of *ca.* 1 ng m^{-3}. Additional data on the trace metals content of ultrafine particles in the Pasadena, CA, atmosphere have been published previously by Hughes *et al.* (1998).

3. Emissions of ultrafine particles to the Southern California atmosphere

The size distribution and chemical composition of fine particle emissions from the largest sources in Southern California have been measured by dilution source sampling (Schauer 1998). A pair of MOUDI cascade impactors was operated downstream of the dilution source sampler in order to measure the mass emissions rate, particle size and particle chemical composition by exactly the same methods as previously described for atmospheric particle samples. Sources tested in this way include catalyst-equipped petrol-powered cars and light trucks, non-catalyst petrol-powered cars and light trucks, medium-duty diesel trucks, fireplace combustion of hardwoods and soft wood, meat charbroiling, and cigarette smoke (Kleeman *et al.* 1999*a*, 2000).

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In previous years, the same source sampling system was used to measure the size distribution, mass emissions rate and bulk fine particle chemical composition of the emissions from natural gas combustion, distillate fuel oil combustion, tyre dust, brake lining wear dust, paved road dust, and plant fragments shed as leaves are rubbed together by the wind (Hildemann *et al.* 1991*a*, *b*). Data from these earlier source tests were used to supplement the more recent cascade impactor-based source tests under the approximation that the ultrafine particles counted in the earlier source tests had a chemical composition similar to the bulk fine particle (particle diameter less than 2 μm) samples collected from these sources. Finally, the source test data taken by our research group were combined with data on source activity (e.g. vehicle kilometres travelled, quantities of fuel burned) supplied by the California Air Resources Board as part of their inventory of particle emissions in Southern California. In essence, we took the State of California particulate matter emissions inventory for total suspended particulate matter and for particle mass smaller than 10 μm in diameter, replaced the emissions rate data by our own source measurements when available, and impressed the particle size and chemical composition distribution data from our source tests onto the resulting modified inventory. For the remaining minor sources in the inventory, the State of California emissions rate data, particle size and chemical composition data were retained. Our emissions inventory containing high-resolution size and chemical composition data was originally developed for use in air-quality models that predict the size distribution and chemical composition of the atmospheric particle complex in the presence of transport, chemical reaction in the atmosphere and dry deposition. In previous tests of those models, the model predictions compare quite favourably with measurements of atmospheric particle size and chemical composition (Eldering & Cass 1996; Kleeman *et al.* 1997, 1999*b*), so there is good reason to believe that the emissions inventory is reasonably accurate for fine particles and for PM_{10} (particles smaller than 10 μm aerodynamic diameter). Because that emissions inventory extends into the ultrafine particle size range, it is possible to extract and display the best presently available data on the mass emissions rate and chemical composition of ultrafine particle emissions from sources located within the South Coast Air Basin that surrounds metropolitan Los Angeles.

The primary particle mass emissions within the South Coast Air Basin of California in September 1996 in sizes smaller than 10 μm aerodynamic diameter (PM_{10}) total 380 tonnes per day. These PM_{10} emissions are dominated by close to 320 tonnes per day of mineral dust emissions from travel on paved and unpaved roads, from construction and agricultural activities, and dust raised due to erosion by the wind. For this reason, fugitive dust control has been selected as the usual response by government agencies when faced with meeting air-quality standards for PM_{10}.

New air-quality standards that limit the concentration of atmospheric particles smaller than 2.5 μm aerodynamic diameter ($PM_{2.5}$) have recently been proposed for the United States by the US Environmental Protection Agency. $PM_{2.5}$ emissions in the Los Angeles area total about 122 tonnes per day. Very importantly, from the point of view of the emissions control programme required to comply with a $PM_{2.5}$ air-quality standard, only about half of the primary fine particle emissions are due to fugitive sources, while the other half of the primary $PM_{2.5}$ emissions are directly emitted from stationary and mobile combustion sources. As seen in figure 1, much of the $PM_{2.5}$ in the Southern California atmosphere is also due to aerosol sulphates, nitrates and secondary organic aerosols that are formed by atmospheric chemical reactions.

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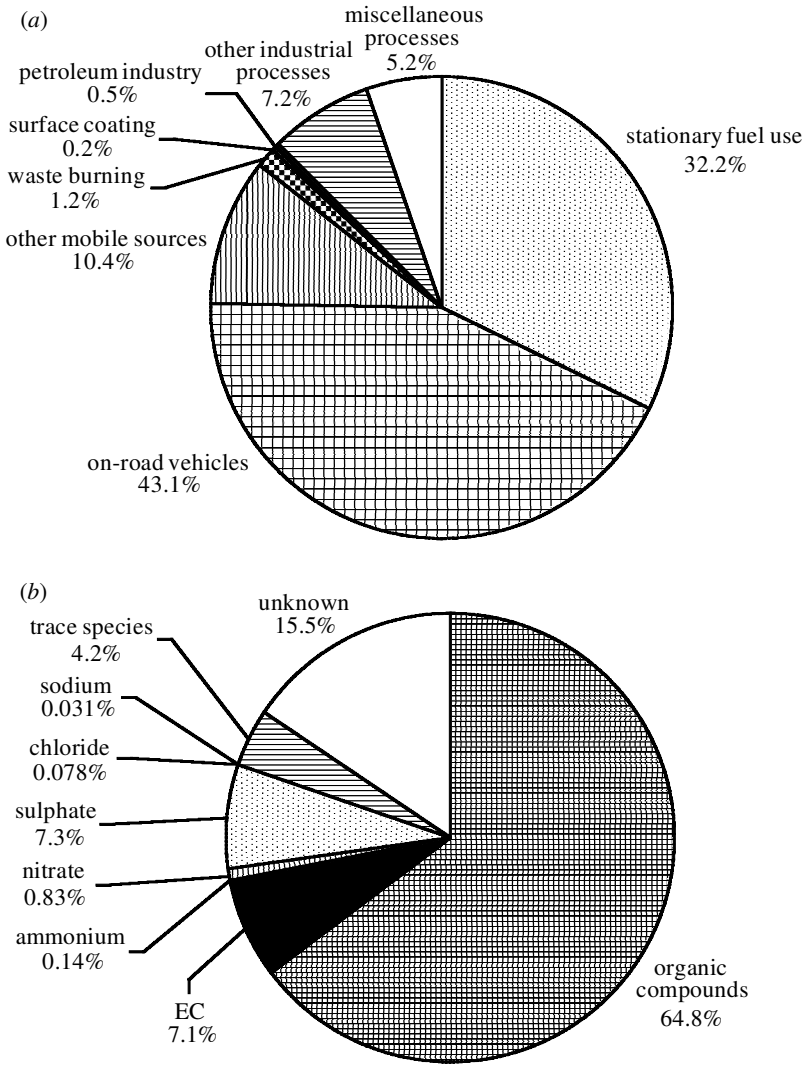

Figure 3. Ultrafine particle emissions in California's South Coast Air Basin (1996) that surrounds Los Angeles: (*a*) source contributions to primary ultrafine particle emissions; (*b*) chemical composition of primary ultrafine particle emissions. Total $PM_{0.1}$ emissions are 13.25 tonnes per day.

The emissions inventory for ultrafine particles ($PM_{0.1}$) constructed for the Los Angeles area indicates a mass emissions rate of 13 tonnes per day in particle sizes smaller than 0.1 μm aerodynamic diameter. This emissions rate is approximately consistent with the measured 0.8 $\mu g\, m^{-3}$ ambient ultrafine particle concentration, indicating that most of the ultrafine particle mass in the Southern California atmosphere could well be due to primary particle emissions from sources. As shown in figure 3*a*, the largest sources are on-road motor vehicles (43%), stationary source fuel combustion (32%), non-highway mobile sources (10%, particularly diesel engines used in off-road vehicles and in mobile equipment such as refrigeration units), and other

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industrial processes (7%, of which the most significant is commercial food preparation, e.g. meat charbroiling). Of course, if one lives very close to a heavily travelled street, far more than 43% of the ultrafine particles would be from motor-vehicle traffic, as those emissions occur at ground level in the immediate vicinity of the person affected.

The chemical composition of the primary ultrafine particle emissions in the Los Angeles area is indicated in figure 3*b*. The composition is 65% organic compounds, 7% elemental carbon, 7% sulphate, 4% trace elements, with very small quantities of sodium, chloride and nitrate. It may be important to note that the fuels used in the Los Angeles area are generally limited to very low sulphur content. If the trace elements were converted to the molecular mass of their common oxides, much of the unknown mass shown in figure 3*b* would be explained. These emissions data are quite similar to the chemical composition of the atmospheric samples described earlier. The average over the pie charts in figure 2 shows a mean ambient ultrafine particle chemical composition that is 50% organic compounds, 14% trace metal *oxides*, 8.7% elemental carbon, 8.2% sulphate, 0.6% sodium and 0.5% chloride. Ammonium and nitrate are significantly higher in the atmospheric samples than in the source emissions inventory, indicating that some ammonium nitrate formation is occurring on the atmospheric ultrafine particles studied here.

4. Conclusions

The average ultrafine particle mass concentration in the atmospheres of seven cities in Southern California in particles with aerodynamic diameter between 0.056 and 0.1 μm is in the range 0.55–1.16 $\mu g\,m^{-3}$. The chemical composition of these ultrafine particles is, typically, 32–67% organic compounds, 3.5–17.5% elemental carbon, 1–18% sulphate ion, 0–19% nitrate ion, 0–9% ammonium ion (excluding one extreme outlier at Riverside), 1–26% metal oxides, 0–2% sodium and 0–2% chloride. When averaged over all monitoring sites, average ambient ultrafine particle mass concentrations are *ca.* 0.8 $\mu g\,m^{-3}$, and the average chemical composition is 50% organic compounds, 14% trace metal *oxides*, 8.7% elemental carbon, 8.2% sulphate, 6.8% nitrate, 3.7% ammonium ion (excluding one outlier), 0.6% sodium and 0.5% chloride. The most abundant catalytic metals measured in the ultrafine particles were Fe, Ti, Cr, Zn, with Ce also present. A source emissions inventory constructed for particles smaller than 0.1 μm in diameter for California's South Coast Air Basin that surrounds Los Angeles identified primary ultrafine particle emissions equal to 13 tonnes per day, largely from motor-vehicle exhaust and from stationary-source fuel-combustion sources. The average chemical composition of the ultrafine particle emissions studied in Southern California consisted of 65% organic compounds, 7% elemental carbon, 7% sulphate, 4% trace elements, with very small quantities of sodium, chloride and nitrate. The mass emissions rate is sufficient to explain the 0.8 $\mu g\,m^{-3}$ ambient ultrafine particle concentration measured in the Los Angeles area, and the chemical composition distribution in the emissions is generally similar to measured ambient ultrafine particle concentrations once the trace metals in the emissions are converted to the mass of their common oxides. The ambient ultrafine particles in the Southern California atmosphere in the size range 0.056–0.1 μm in diameter may be explained by primary particle emissions plus secondary aerosol nitrate formation at some places and times. This information should assist the com-

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munity of laboratory toxicologists in the construction of realistic test atmospheres for particle-inhalation studies, and focuses attention on primary particles from combustion sources in the event that emissions controls for ultrafine particles are eventually needed.

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Discussion

C. F. Clement (*Wantage, Oxon, UK*). I would like to draw attention to the need to identify the primary particles corresponding to the chemical compositions shown. Some of the constituents, e.g. sulphates, could well arise from condensation on existing particles. In particular, the percentage of metal constituents seemed to vary considerably with location. It is not easy to form ultrafine metal aerosols; has the origin of the observed metals been identified?

G. R. Cass. A partial assessment of the trace metals sources has been conducted. The ultrafine particle emissions inventory used to construct figure 3 contains emissions estimates for over 30 trace elements emitted from 62 different types of emissions sources. Source chemical composition profiles showing the major chemical species are available for these sources but data on the minor species are absent in many cases. Petroleum refining, metallurgical industry fumes, engines and some sources processing mineral matter are indicated as sources of a significant fraction of the ultrafine particle iron, for example. Further source testing is needed to refine and extend the database.

R. Agius (*University of Edinburgh, UK*). You have shown that organic compounds comprise a substantial component of atmospheric ultrafine particles (up to 70%). Could you please shed some light on the chemical species in this important component?

G. R. Cass. We have not yet performed a detailed analysis of the individual organic compounds present in the ultrafine particles. We have, however, examined fine particle emissions ($d_p < 2\,\mu m$) from the most important sources of ultrafine organic aerosol, which include natural gas combustion, food cooking, woodsmoke, and motor vehicle exhaust. If the ultrafine particles resemble the fine particles from these sources chemically, then we would expect to find PAH, oxy-PAH, meat fat components, levoglucosan and related sugar derivatives, resin acids, substituted phenolic compounds, and heavy petroleum hydrocarbons (e.g. unburned motor oil).

M. S. Bingley (*Cobham, UK*). Could the high concentration of iron in your atmospheric particle analysis be due to bore wear in automobile engines?

G. R. Cass. Engine wear has not yet been established as the major source of the iron.

D. Costa (*US EPA, NC, USA*). Do we have information on composition of indoor ultrafine particulate matter and to what extent do outdoor ultrafines penetrate indoors?

G. R. Cass. We have not yet studied ultrafine particles in indoor air.