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New approaches to characterizing urban air particles in central London

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Abstract—Atmospheric particles in central London during July 1996 have been apportioned to sources by two complimentary techniques: (1) morphological characteristics, determined using high-power light microscopy; (2) chemical composition determined by energy dispersive spectroscopy. During the study period, the majority of particles were found to be either biological in origin, or from vehicle-related combustion processes. Trends in the latter group of particles are explored further. Numbers of particles per cubic metre were determined at an hourly resolution over a period of six days, and were found to be significantly correlated with other traffic pollutants such as benzene and 1, 3-butadiene, although there is no relationship with mass of PM10 as measured by a nearby UK Government monitoring station. We suggest in this paper that numbers of particles from car exhausts are more representative of traffic pollution than current estimates which use monitoring by mass.

Keywords: urban air pollution; particulates; London; PM10s; high-power microscopy; energy dispersive spectroscopy.

1 Introduction

On an international scale, the nature of urban air pollution has changed significantly over the last 50 years. In the 1950s and 1960s, the most important environmental health issues stemmed from the occurrence of urban smogs, an atmospheric cocktail characterized by high concentrations of smoke and sulphur dioxide. The most notorious of these events in the United Kingdom (UK) occurred in 1952 in London (Wilkins, 1954). This event provided the stimulus for the UK Clean Air Act of 1956 that aimed to make illegal the burning of coal fuel in urban areas. As a result, but also as a consequence of a national trend in the UK away from domestic coal burning, smoke and sulphur dioxide levels in urban areas have declined markedly since 1960.

However, pollution of a different kind, especially from motor vehicles has increased. The new pollutants include oxides of nitrogen (NO and NO_2), hydrocarbons (e. g. VOCs), carbon monoxide (CO) and fine particulate matter (PM10) (QUARG, 1993). There is international concern for the impact of all these pollutants on human health, singly and in combination, but most recent attention has focused on particulate matter (QUARG, 1996). An extensive epidemiological study of air pollution and human health in six North American cities (Dockery, 1993) demonstrated an especially strong relationship between PM10 mass and human morbidity and mortality, and studies from other cities have subsequently confirmed this finding (Verhoeff, 1996; Katsouyanni, 1997; Woodruff, 1997; Ostro, 1998; Ponka, 1998). These problems are likely to become more widespread and more severe in the future, especially in countries such as China, with rapidly expanding industrial production and motor vehicle ownership.

Despite increasing concern, research into urban air pollution and its effects are still in their infancy, particularly the specific mechanisms directly related to human health problems by particulate pollution, which have yet to be established (Dockery, 1996). Moreover, standard monitoring methods for mass PM10 (that rely on the measurement of variations in total mass) have limitations as they provide little information on particle number, type or source, especially with regard to the finer particles (e. g. those characterised as PM2.5 or smaller). In this paper we

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report on new techniques we are developing to monitor urban air particulates, including those derived from vehicle emissions. We focus on the characterization of particles as deduced from high-power light and electron microscopy (LM and EM) and energy dispersive spectroscopy (EDS), and on temporal variations between traffic-related particle types and other vehicular pollutants in central London. The functional relationships between particulates of biological origin and their environment are discussed in detail elsewhere (Mackay, 1998).

2 Methods

2.1 Monitoring airborne particles using a Burkard spore trap in central London

An adapted Burkard volumetric spore trap was used to collect airborne particles suitable for retrospective individual particle analysis under LM and EM: particles drawn through an orifice impact onto a glycerin/gelatin coated tape, attached to a rotating (2 mm/h) drum. The tape around the drum was 336 mm in length, thus ensuring that a weekly archive of particles was recorded. The trap, situated in Bloomsbury, central London, is classified as a "roadside site" and is surrounded by several major traffic routes (QUARG, 1993): full details can be found in (Battarbee, 1997). The site is also co-located with the automatic urban network (AUN) hydrocarbon monitor in Bloomsbury and 300 m from the AUN site in Russell Square which monitors NO_x, O_3, SO_2 and PM10s. This paper focuses on particles collected over two week long periods: 9th—16th July, 1996 for particle characterization, and 16th—22nd July 1996 for trends in particle number.

2.2 Morphological analysis of individual particles using light microscopy

Particle counting and identification were undertaken using light microscopy at 1500 x magnification. A continuous and representative subsection of the tape was counted using an eye piece with adjustable cross-hairs such that only particles occurring within a 40 μm wide band were counted. Brightfield illumination was used so that particle colour could be recorded. Geometric particle sizes (down to 0.5 μm) were measured on a graticule attached to the eye pieces.

Several distinct morphological parameters were used to classify each particle, i. e. particle size, colour, surface texture and shape. Optical characteristics, such as whether the particle was opaque, transparent or translucent, it's symmetry and whether it formed part of an aggregation or not, were also recorded. Reference publications used to identify particle types, including a full bibliography, can be found in Long (Long, 1998). Cluster analyses, based on k-medoid partition methods (Kaufman, 1990) were performed on the data to determine underlying structures in the dataset, and to group particles according to morphological characteristics. Particle sizes were excluded from the analyses as morphological types alone could be attributed to a source, independent of size, which tended to obscure trends in the analyses (Long, 1998).

2.3 Elemental composition determined by energy dispersive spectroscopy (EDS)

The JEOL 733 Superprobe at Imperial College London was used for the semi-quantitative analysis of elemental composition of individual particles collected on the translucent tapes. This is an automated system which gives the relative *X*-ray counts of the selected 21 elements: Na, Mg, Al, Si, P, S, Cl, Ca, K, Ca, Ti, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb (Rose, 1996). New particle groups were determined by cluster analysis based on the relative chemical composition of particles analyzed.

3 Results

3.1 Morphological characteristics of particle groups

Seven distinct groups, based on the morphological characteristics of particles identified

between 9th—16th July 1996, have been derived from cluster analyses. These seven groups are biological particulates (e.g. spores), soot particles (vehicles), unclassified, soil dust/minerals (translucent), carbonace particles, rubber and inorganic fly-ashes; their relative frequency are 35.4%, 21.0%, 13.8%, 9.3%, 7.4%, 7.1% and 6.0% respectively. Particle types have been identified as far as possible, some particles are more easily recognized than others, e.g. carbonaceous particles have a porous surface, whereas others can only be identified through a set of characteristics, e.g. inorganic fly-ash spheres. Relative compositions of particle morphology appear to be linked to four major sources and activities in and around London: traffic (soot particles and rubber); combustion by-products (carbonaceous particles and inorganic fly-ashes); wind erosion of surface particles (e.g. soil dust); and biological particles (e.g. spores).

3.2 Chemical characteristics determined by EDS and cluster analysis

A total of 15736 particles from the 9th—16th July, 1996 were analyzed by EDS, and only the principal elements of the "average" chemical compositions of particles in each category are shown (Table 1). Several of these clusters share similar properties, such as having a large proportion of Ca (e.g. Clusters 3 and 9), or having Si as their dominant element (e.g. Nos. 5 and 7), and when compared to reference samples, these nine categories may be summarized into six, each with a different, suggested source (Table 2). Based on these analyses alone, the majority of particles would appear to be industrial related or derived from fossil fuel combustion. These are likely to be over-estimates, as will be discussed below. Unsurprisingly, for an inland city, sea-salts form the least common particle type.

Table 1 Size and main elemental concentrations of particles in each cluster group (9th—16th July, 1996)

Cluster	Total, %	Main elements and their relative contents, %
1	23.0	Fe(62.6), S(8.1), Si(6.3), Ca(5.6)
2	17.4	S(27.3), Ca(18.1), Si(8.7), Ti(5.9), Al(5.3)
3	12.0	Ca(42.0), S(36.3), Si(5.2)
4	10.3	Si(32.2), Al(13.0), S(12.0), Ca(11.8), Fe(9.3)
5	9.9	Si(53.2), Al(14.7), Ca(6.6), K(5.6), Fe(4.7)
6	8.8	Cl(56.1), Ti(10.7), Na(9.2)
7	8.7	Si(82.3), Al(5.6)
8	8.3	Si(41.9), Al(27.9), Fe(7.2), K(6.7)
9	1.7	Ca(71.2)

Table 2 Suggested sources of particle groups based on their chemistries EDS

Group type	Corresponding cluster	Suggested source
Fe-rich particles	Cluster 1	Industrial
S-rich particles	Cluster 2	Fossil-fuel combustion/secondary particles
Ca dominated particles	Clusters 3 and 9	Gypsum
Si-rich particles	Clusters 4 and 8	Surface dusts
Si-dominated (i.e. > 50%)	Clusters 5 and 7	Cement factory
Cl-Na-Ti rich particles	Cluster 6	Sea-salts

3.3 High resolution, temporal trends in total traffic-derived particulates

Fig.1—2 show each temporal trends in total traffic related particulates counted at hourly intervals over a period of 6 days: Tuesday 16th July 1996-Monday 22nd July 1996. In Fig.1, total numbers of traffic-derived particulates per m^3 are plotted against concentration of particles, as measured by a tapered element oscillating microbalance (TEOM) at the AUN Russel Square site (secondary y axis). Numbers of PM10 exhibit a diurnal trend, with highest numbers occurring during peak rush-hour times in London: c.06:00—09:00 in the morning, 12:00—14:00 in the afternoon, and then again 17:00—19:00 in the early evening. Numbers of particles counted in this

study only fall to low levels for a short period between the hours 03:00—05:00. In general, there appears to be at least a four-fold increase in numbers of vehicle related particles between light traffic times and rush hour times. Numbers of particles decrease to their lowest levels towards the end of this study period, coinciding with the weekend, although the relationship between these numbers and prevailing weather conditions is currently being explored further. Concentration of particulates appears to show little diurnal variation. Further, there is little overall correlation between particle mass concentration and particle number counted (Table 3), especially towards the end of the study period, where large mass concentration increases are not recorded in estimated particle number.

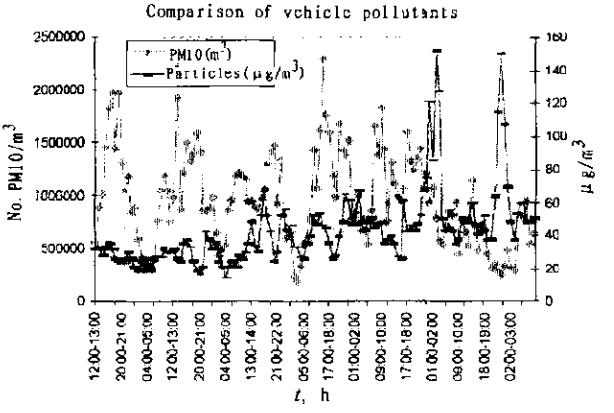

Fig. 1 Temporal plot of total traffic-derived particulates counted (expressed per m^3) during one week in July (hours), plotted against concentration of particulate matter ($\mu g/m^3$) as measured by the TEOM monitor at the AUN Site at Russel Square in central London. Particulate weight is non-specific for all particles, whether they are vehicular in origin or not

Table 3 Pearson's product-moment correlation matrix between benzene, 1, 3-butadiene, particle concentration and particle number. At $p = 0.01$, significant relationships are indicated by an asterix

	Benzene, ppb	1, 3-butadiene, ppb	Particles, $\mu g/m^3$	PM10s
Benzene, ppb	1.00			
1, 3-butadiene, ppb	0.80*	1.00		
Particles, $\mu g/m^3$	0.20	0.08	1.00	
PM10, number/m^3	0.34*	0.39*	−0.15	1.00

Fig. 2 also shows changes in numbers of traffic related particles, but plotted against benzene (ppb) on the secondary axis. Overall, there appears to be a better and more statistically significant correlation between the two pollutants than between mass concentrations and benzene (Table 3). Correlations between benzene, particle concentration and particle number were also calculated against another hydrocarbon derived from vehicles, 1, 3-butadiene. Once again, particle numbers are significantly correlated with this species, whereas particle concentration shows no significant correlation.

4 Discussion

4.1 Particle characterization

It has been estimated in central London that particles derived from traffic account for over 80% of all particulates monitored (QUARG, 1996; Mackay, 1998), whereas the proportion estimated in this study is approximately 20%, similar to the proportion estimated by SEIPH (SEIPH, 1996). The majority of particles identified during this study were biological in origin,

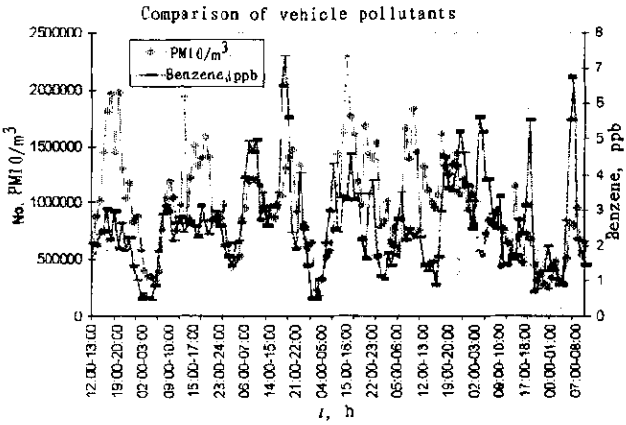

Fig.2 Temporal plot of total traffic-derived particulates counted (expressed per m^3) during one week in July (hours), plotted against concentration of benzene (ppb) as measured by a hydrocarbon monitor at the AUN Site in central London. Benzene is derived from vehicular combustion

reflecting the time of year of the sampling period and therefore accounting for the overall lower proportion of traffic related particles. In contrast, Mackay and Rose (Mackay, 1998) estimated biological particle numbers to be less than 1% during a winter period in 1996.

Light microscopy and EDS analyses are largely complementary with regard to source apportionment of particles. The two most common particle types identified, soot and biological particles, can be easily distinguished by LM, whereas these latter particles cannot be detected by EDS because EDS cannot recognise elements lighter than Na, including C and O, which are abundant in both these particle types. EDS, however, can readily identify other particle types that are more difficult to identify optically such as gypsum and sea salts. EDS is also useful in determining local sources of pollution, such as the particles apportioned to a nearby cement factory, illustrating the usefulness of the method for environmental planning and regulation of industry in urban areas. Finally, the relative proportions of particles identified by the two methods are somewhat different. This is probably because C and O are not represented by EDS analyses, leading to an over-representation of other elements. For example, because the C in soot particles is not detected by EDS, other elements measured, e. g. Fe, will automatically appear to have a higher composition, wrongly placing many of these particles in the "Industrial" group.

4.2 Temporal trends in traffic related particulates

Total particle numbers associated with traffic estimated in this study, have a wide range, varying from under 500000 particles m^{-3} in the early hours of the morning, rising to c. 2 million particles m^{-3} when traffic flows are heaviest and continuous (Department of Transport, 1989). Measurements by TEOM expressed as mass measurement (g/m^3) do not however show the same trends; even the two peaks towards the end of the study period occur when traffic flow is lightest, and so are unlikely to be related to particles sources from vehicle combustion. The PM10 component measured by the TEOM is an amalgamation of all particle types (including traffic related particles, construction activity, surface dust and secondary particles) and are strongly influenced by larger, heavier species. When numbers of vehicle-related particles, as counted in this study, are compared with benzene (which is derived almost exclusively from traffic combustion) very similar trends and a significant correlation can be shown, whereas there is no such correlation between PM10 mass and benzene, and even less correlation with 1, 3-butadiene, also derived from

vehicles. Recent studies have now begun to suggest that particulates in the smaller size ranges, i. e. those in the PM2.5 fraction, pose the greatest threat to human health, as they can penetrate deeper into the respiratory tract, and have a higher surface area to volume ratio, enabling these species to effectively hold onto greater amounts of other pollutants (Salvaggio, 1994). Mackay and Rose (Mackay, 1998) have demonstrated that over 90% of the particle fraction derived from vehicles can consist of particles less than PM2.5 in diameter. These smaller particles have little weight, and therefore current reported measurements using TEOM PM10 instrumentation are likely to grossly under estimate the more likely proportions of vehicle-related particles in the urban aerosol. This may be one reason why there is little correlation between concentration of PM10 by TEOM and the other pollutants, benzene and 1,3-butadiene. These results indicate the need for a fuller deployment of TEOM PM2.5 monitors as part of the AUN. A more comprehensive study of particle type and size, in relation to other traffic pollutants and meteorological conditions is currently in preparation.

4.3 Future developments

Although good results can be achieved with our current systems, improvements in our methodologies are still necessary, especially with regard to developing: (1) digital analytical techniques to speed up microscopic analyses of the tapes collected and to assist in source apportionment, and (2) additional chemical analyses, such as EDS that can monitor elements lighter than Na, i. e. C and O and imaging *X*-ray photo-electron spectroscopy (IXPS), which measures the surface chemistries of particles.

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