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The Dispersion of Lead from Motor Exhausts [and Discussion]

A. C. Chamberlain, M. J. Heard, P. Little, R. D. Wiffen, R. M. Harrison, W. J. Megaw and J. D. Butler

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The dispersion of lead from motor exhausts

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[Plate 1]

Lead is added to petrol as organic tetraethyl or tetramethyl lead but is emitted as inorganic oxides, sulphides, halides and carbonates. From vehicles cruising at high speed on motorways, the lead is emitted as very small (*ca.* 0.02 μm) discrete particles. In city streets, where there is also a background aerosol, coagulated chain-aggregate particles are found.

The concentration of lead in air downwind of a road can be calculated theoretically, and measured concentrations agree fairly well. Within a few metres of the carriageways of motorways carrying heavy traffic, concentrations as high as 10 μg/m³ are found, but the concentration falls rapidly with distance owing mainly to the upward diffusion of the plume. Measurements of the rate of deposition to surfaces near the M 4 motorway show that an appreciable, but not large, fraction of the lead is deposited within 100 m of the motorway.

Near towns, the contribution from a given highway merges rapidly into the background due to emissions from other roads. The dispersion is countrywide and probably some cross-frontier transfer occurs.

1. Emission from vehicles

Lead is added to petrol as the organic liquids tetraethyl lead and tetramethyl lead. About 75 % of the lead is emitted from the exhaust (references in Huntzicker, Friedlander & Davidson 1975). The lead is in a variety of chemical forms (halides, oxides, carbonates and sulphates). Measurements in London streets (Harrison, Perry & Slater 1974) show that organic lead vapour accounts for 0.1–4.0 % of total lead. Near filling stations the percentage is higher. Most of the organic lead is thought to come from evaporative losses.

The mean particle size (mass median equivalent diameter, m.m.e.d.) of lead in aerosols in urban air has been reported to be 0.2–0.4 μm (Cholak, Schafer & Yeager 1968). These results are derived from measurements with impactors, but as more than half the lead is usually found on the backing filter paper it is necessary to extrapolate the readings to obtain the m.m.e.d. Similar measurements currently being made on the urban aerosol at Chelsea (London) extrapolate to an m.m.e.d. of 0.27 μm but the assumed log-normal distribution has a rather large geometric deviation ($\sigma_g = 7.3$) and it is doubtful if this type of interpretation is meaningful. The interpretation of impactor data is even more doubtful when applied to the motorway aerosol, resulting in an m.m.e.d. below 0.1 μm, but values of σ_g in excess of 50 suggest a complex distribution which is not resolved by the impactor techniques.

Figure 1, plate 1, shows electron micrographs of aerosol collected by thermal precipitator alongside the M 4 near Heston, Middlesex. Three different magnifications are shown. Samples taken upwind of the motorway showed very much fewer particles.

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There are three principal types of particle:

(*a*) round, electron dense particles in the size range 0.01–0.1 μm, some single and some multiple, which decompose in the electron beam in a manner which appears to be characteristic of primary exhaust particles;

(*b*) chain aggregates of less electron dense particles, 0.3–1.0 μm, mostly diesel smoke;

(*c*) larger, often scaly, particles, greater than 1 μm, probably road dust and adventitious material.

Similar particles can be seen in the electron micrographs of Lawther, Commins, Ellison & Biles (1973).

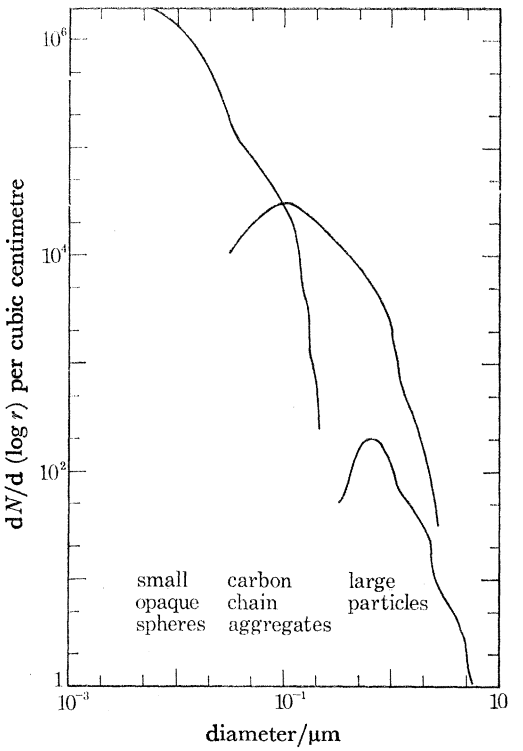

FIGURE 2. Vehicle aerosols: size distributions of three classes of particle; M 4, Heston.

Figure 2 shows the particle size spectrum obtained from the electron micrographs. To confirm that the smallest particles contained most of the lead, a diffusion battery (Megaw & Wiffen 1963) was used to estimate the Brownian diffusivity of the lead-bearing particles. In a number of comparisons, the percentage penetration of lead aerosol through the battery gave diffusion mass median diameters of 0.03–0.05 μm corresponding to electron micrograph volume median diameters from 0.04–0.08 μm. The Brownian diffusivity of a particle, unlike its impaction efficiency, does not depend on its density (Fuchs 1964, p. 184). Also, the mass of lead which would be expected to be associated with the small particles agreed in order of magnitude with the measured air concentration. Measurements near a freeway in the U.S.A. with an electrical analyser (Whitby *et al.* 1975) had previously shown that most of the volume distribution of primary exhaust aerosols lies in the nucleus mode (0.01–0.1 μm) with a peak at 0.03 μm. Wind tunnel work with a small engine indicates that the primary exhaust particle is approximately 0.015 μm diameter. The eventual size distribution depends on the rate of

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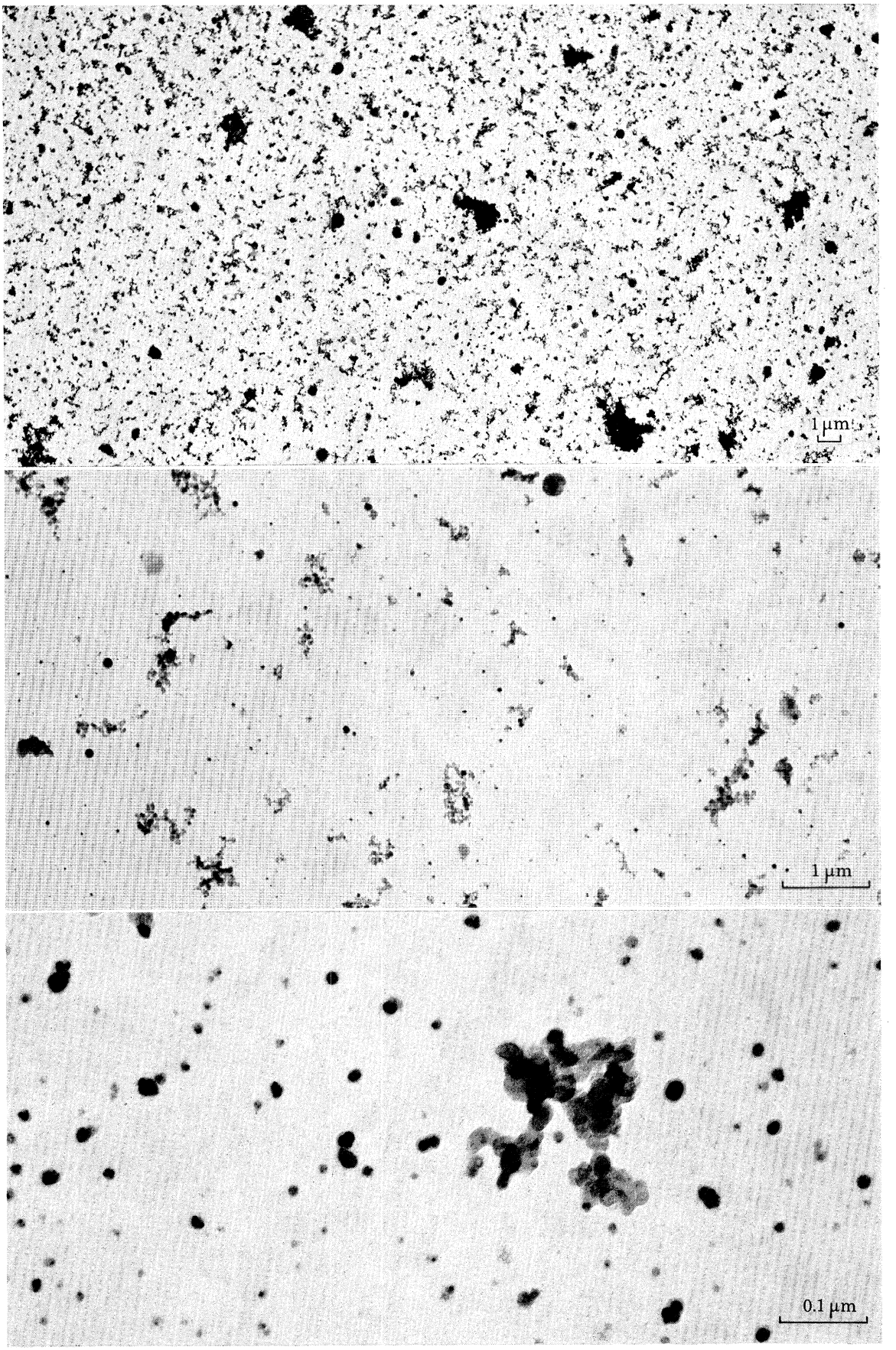

FIGURE 1. Electron micrographs of M 4 aerosol at three magnifications.

(*Facing p.* 578)

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dilution of the exhaust, and the number and size of other aerosol particles with which the lead particles may coagulate. Measurements near the M 40, where the motorway ascends the Chiltern escarpment on a 1 in 20 grade, showed little difference in the size spectrum compared with the M 4, but measurements at the Hogarth roundabout at the end of the M 4 in Chiswick showed a shift in the distribution with more particles in the 0.1–0.5 and 0.5–5 μm ranges. This is attributed mainly to coagulation with the general urban aerosol, but differences in driving modes may also have an effect.

As the particle size is small, the dispersion of exhaust lead can be considered in terms of the well established theory of diffusion of gases and smokes. Dispersion is determined by wind and turbulence, since the sedimentation velocity of the particles is smaller compared with turbulent air velocities. Deposition on roadside verges, which is considered later, is secondary to dispersion in determining the air concentration downwind of highways. The emission of lead from cars on a roadway can be calculated from the flow of traffic, lead content of petrol, petrol consumption and percentage emission of lead. Where traffic flow is given this will be petrol-driven vehicles per hour unless otherwise stated. Assuming 1000 vehicles per hour, 0.49 g Pb l^{-1} in petrol, fuel consumption 0.24 l km^{-1} (30 miles per gallon) and 75 % emission, the source strength q is 10 μg s^{-1} per metre length of roadway. This result can also be derived from measurements at Warren Spring Laboratory of the emissions from a car driven in traffic (Hogbin & Bevan 1976), if the average velocity is taken as 60 miles per hour (*ca.* 97 km h^{-1}).

2. Lead in air near roads

Cars travelling on a lane of a motorway create a line source of lead in air, and if the wind is perpendicular to the motorway the concentration χ near ground level downwind can be calculated using established formulae (Pasquill 1974). If cars travel equally spaced on all lanes,

$$\chi_{(x)} = (2/\pi)^{\frac{1}{2}} \frac{q}{uw} \int_{x}^{x+w} \frac{\mathrm{d}x}{\sigma_z(x)}, \tag{1}$$

where q is the source strength of Pb (in micrograms per metre per second), u the wind speed in metres per second, w the width in metres of motorway between edge beams, taken as 25 m (edge beam separates carriageway from hard shoulder), x the distance in metres of point of measurement from edge beam, and $\sigma_z(x)$ the standard deviation in metres of vertical spread of plume ($= ax^s$, where a, s are parameters depending on atmospheric stability; Pasquill, 1974, tab. 6, IX).

In figure 3, χ is plotted for stability categories B (unstable), D (neutral) and E (stable). A wind speed of 2 m s^{-1} has been assumed. This is close to the harmonic mean wind speed at height 1 m at inland stations in southern England. Figure 3 shows that atmospheric stability in the range of categories B–E accounts for a 1:3 range in calculated χ. The most extreme stable categories F and G are thought unlikely to apply since the vehicle motion and heat of exhausts creates initial dispersion. Allowing also for variations in wind speed, a variation by a factor of ten at least can be expected. There are also further variables difficult to allow for:

(*a*) Roughness of terrain: calculations of figure 3 assume roughness length $z_0 = 0.1$ m. In towns z_0 may be about 1 m, which will increase dispersion and reduce χ by about 50 %, but in very enclosed urban situations, with a canyon effect, χ may be increased.

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(*b*) Angle of wind to motorway: Calder (1973) has shown that the angle, θ, makes little difference unless it exceeds 60° to the perpendicular, i.e. wind nearly parallel to road. Then χ is increased and at $\theta = 75°$ the increase is about 50 % relative to $\theta = 0°$.

(*c*) Elevation of motorway: if the roadway is elevated by say 10 m, then mixing while the plume descends to ground level, including the effect of eddies caused by the roadway structure will result in a minimum σ_z of about 5 m. This means that χ at ground level will be a maximum when x is about 100 m, and will not show the rapid increase for small x of figure 3. Conversely, in a cutting, particularly under stable conditions, dispersion will be poor.

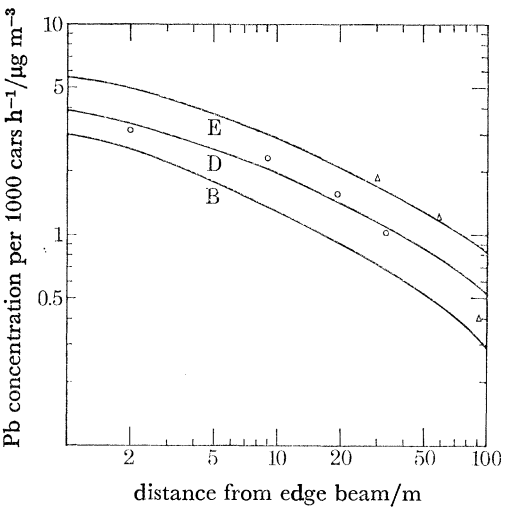

FIGURE 3. Lead in air plotted against distance from motorway. Lines are labelled with Pasquill stability categories. Measurements: ○, Little & Wiffen (1977); △, Bevan *et al.* (1974).

The points in figure 3 are derived from measurements by Bevan, Colwill & Hogbin (1974) and by Little & Wiffen (1978) of lead in air alongside the M 4 motorway at Heston, Middlesex. This is the busiest length of motorway in the U.K., with about 4000 vehicles per hour during much of the day. Bevan *et al.* measured Pb in the central reservation of the M 4 continuously on weekdays from 30 August to 27 October 1972, and showed that the concentration correlated closely with traffic volume. They also ran samplers for several days at each of four distances (30, 60, 90 and 120 m from the edge beam) and compared the results with simultaneous samplers from the central reservation. From the ratios so derived, the mean χ (central) (15.1 μg/m³), and the mean traffic flow (3800 vehicles per hour), the points in figure 3 are derived. Little & Wiffen sampled at 2, 9, 19 and 34 m from the edge beam for about 10 h on each of 3 days, and also did traffic counts. The values of χ normalized to 1000 vehicles per hour so derived are also shown in figure 3. The stability categories for these runs were B (twice) and C/D. For the runs performed by Bevan *et al.*, no estimate of stability is available. At the time of their work the maximum lead content of petrol was 0.84 g/l, whereas at the time of Little & Wiffen's work it was 0.50 g/l, and if allowance is made for this difference the two sets of results agree well. On 1 January 1978 the maximum was further reduced to 0.45 g/l. The agreement of the experimental points in figure 3 with theory, both in absolute magnitude and in variation of χ with x, give confidence that dispersion of exhaust lead is similar to that of other smokes.

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TABLE 1. MEASUREMENTS OF LEAD IN AIR NEAR MOTORWAYS AND OTHER STREETS

location	site type†	sampling periods	petrol vehicles per hour	lead in air/μg m^{-3} measured	lead in air/μg m^{-3} background (estimated)	χ / μg m^{-3} per 10^3 vehicles h^{-1}	reference
M 4, central reservation	O	24 h	3800	15.1	0.4	3.9	Bevan *et al.* (1974)
M 4, 2 m from edge beam	O	daytime	3600	8.9	0.4	2.4	Little & Wiffen (1978)
M 40, 2 m from edge beam level	O	daytime	970	3.3	0.2	3.2	
1/20 grade in cutting	C	daytime	950	10.3	0.2	10.6	
1/20 grade on embankment	O	daytime	990	6.4	0.2	6.2	
London							
Fleet Street, central constricted	C	daytime	1200	3.2	0.8	2.0	Waller *et al.* (1965)
Exhibition Rd, S.W.7 kerbside	O	daytime	1300	3.2	0.5	2.0	Harrison *et al.* (1974)
Seymour Place, W.1	C	daytime	424	4.0	1.0	7.1	
Talgarth Rd, W.14	O	daytime	3880	8.8	0.5	2.2	
Upper Berkeley St, W.1	C	daytime	420	4.3	1.0	7.9	
Lancaster, A 6	C	24 h	830	3.5	0.5	3.6	Harrison (1977)

† O, open site; C, constricted site

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The reduction of χ with increasing x is independent of loss by deposition, which is considered below. In an urban area, where the background lead in air from the whole network of roads is likely to be 0.5–1.0 μg m^{-3}, the effect of one particular highway becomes difficult to distinguish beyond about 100 m from the carriageway. In table 1, other roadside measurements of lead in air are compared with those from the M 4. The M 40 samples were taken where the motorway ascends the Chilton escarpment on a 1 in 20 grade partly on embankment and partly in cutting. The χ values normalized to 1000 vehicles per hour show the effects of increased petrol consumption uphill and of the confinement of the cutting. The particle size spectrum was little different from that near the M 4. Other measurements of lead in air are also compared in table 1. At open sites with freely moving traffic, the normalized χ is about 2 μg m^{-3}, but in narrow city streets, with slow moving traffic, it is higher.

3. Lead in air from areal sources

The mean concentration of lead in air over a city or district will now be considered in terms of the mean source strength per unit area. The concentration C near ground at the centre of a circular area radius x_2 in which the source strength is Q μg m^{-2} s^{-1} is

$$C = \int_{x_1}^{x_2} \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{Q}{u} \frac{\mathrm{d}x}{\sigma_z(x)};$$

$$C/Q = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{(x_2^{1-s} - x_1^{1-s})}{ua(1-s)}, \qquad (2)$$

where appropriate values of u, a and s are to be taken according to the meteorological conditions.

The lower limit of integration x_1, is taken as 50 m, as the measurements to be compared, unlike those of table 1, are made typically at sites not immediately adjacent to roads.

Table 2. Areal emissions of lead and concentrations in air

region	area / km^2	equiv. diam. / km	emission of Pb: (t/a)	emission of Pb: $Q/(10^{-2}$ μg m^{-2} s$^{-1})$	mean Pb in air, C / μg m^{-3}	C/Q / s m^{-1}
Birmingham C.B.	2.1×10^2	16	125	1.9	0.75	39
Inner London	2.3×10^2	17	270	3.8	0.8	22
Los Angeles County	4.4×10^3	75	6400	4.6	2.4	52
U.K.	1.7×10^5	465	9000	1.7	0.14	82

References

Emissions: U.K., Stubbs (1972); Inner London, Ball & Hume (1977); Birmingham, M. L. Williams (personal communication); Los Angeles, Huntzicker *et al.* (1975).

Concentrations: U.K., Cawse (1974, 1975), Cambray *et al.* (1975); London, Ball & Hume (1977), Lawther *et al.* (1973); Birmingham, Archer & Barratt (1976); Los Angeles, Huntzicker *et al.* (1975).

In table 2, literature values of C and Q for Inner London, the U.K. and Los Angeles are given. A statistical analysis of Pasquill stability categories according to time of day, from observations over 10 years at London, Birmingham and Bristol, was supplied by the Meteorological Office and used to calculate C/Q on an annual mean as a function of the diameter of the area considered. The diurnal frequency of stability categories was weighted by the diurnal variation of traffic flow. This is important because the most stable categories E and F, for

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which dispersion is poor and C/Q large, occur mainly at night when traffic is lighter than by day. Table 3 shows that the weighted frequencies of categories E and F are about half the unweighted.

TABLE 3. FREQUENCY OF STABILITY CATEGORIES

category	A	B	C	D	E	F
wind speed (m s^{-1}) at height 10 m	1.0	1.4	3.5	5.6	2.8	1.4
% frequency as observed	0.8	6.0	15.4	61.0	7.2	9.7
as weighted by diurnal variations of traffic density	1.3	8.1	22.1	60.4	3.9	4.3

Figure 4 shows good agreement between calculated and measured values of C/Q. No allowance has been made for contributions to C from emissions outside the areas considered nor for deposition.

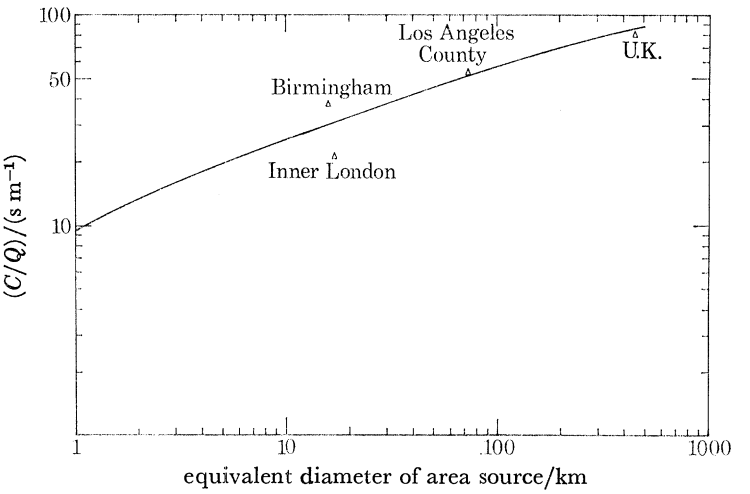

FIGURE 4. Lead in air from area source. The line is calculated from equation (2) with the use of table 3.

Owing to the shorter daylight, categories E and F are more frequent in winter than in summer. Calculations were done for the seasons separately, and gave the ratio of C/Q in winter:summer to be about 1.2:1. Measurements of C have given winter:summer ratios of 1.6 in rural areas (Cawse 1974) and about 2 in cities (Ball & Hume 1977; Day, Evans & Robson 1977). It is not known why the observed seasonal variation is larger than calculated. The seasonal variation of C provides a possible method of estimating the contribution of lead in air to lead in blood for the population, by seeing if the latter shows seasonal variations.

For comparison with the results for lead, table 4 shows estimates of C/Q for the mean rural concentrations of SO_2 and NO_x in the U.K. C/Q for SO_2 is lower than C/Q for Pb, probably because SO_2 is deposited more rapidly on the ground surface, and also converted to SO_4^{2-} by photochemical and other routes. C/Q values of 34 and 84 s m^{-1} for SO_2 in Los Angeles and New York respectively can be deduced from a table of emissions and concentrations given by Hidy, Mueller & Tang (1977).

Figure 4 can be used to estimate the contributions to lead in an urban area from cars on a motorway through it. The total source strength of 1 km of motorway with 1000 vehicles per hour is 10000 μg s^{-1}, and this contributes 0.01 μg m^{-2} s^{-1} to Q for the area of 1 km^2 comprising

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a strip 500 m wide on either side of the motorway. From figure 4 this will contribute about 0.1 μg m^{-3} to the mean lead in air over this area. This is unlikely to be detected statistically against an urban background typically in the range 0.5–1.0 μg m^{-3}. For example, Archer & Barratt (1976) estimate that 9.5 kg of lead are discharged weekly from cars within a radius of 0.25 miles of the M 6 interchange at Gravelly Hill in Birmingham. This gives $Q = 0.03$ μg m^{-2} s^{-1} and $C \approx 0.3$ μg m^{-3} as the contribution of the local traffic. Measurements (Archer & Barratt 1976; C.U.E.P. 1975) in 1973–4 gave $C = 1.5$ μg m^{-3} in the centre of the Salford Circus roundabout near the centre of the interchange and $C = 1.0$, 0.7 and 0.9 μg m^{-3} near houses on the periphery of the interchange. The mean C in Birmingham generally was 0.75 μg m^{-3} (Archer & Barratt 1976). Lead levels in roadside dust near the Gravelly Hill interchange did not differ significantly from those in the city generally.

TABLE 4. COMPARISON OF NORMALIZED CONCENTRATIONS OF POLLUTANTS

pollutant	emissions in U.K. t a^{-1}	emissions in U.K. μg m^{-2} s^{-1}	mean conc. μg m^{-3}	C/Q s m^{-1}	reference
Pb	9000	1.7×10^{-3}	0.14	80	
smoke	2.3×10^{6}	0.43	57	133	Meetham (1950)
SO_2	6×10^{6}	1.1	36	33	Garland (1977)
NO_x (measured at NO)	1.4×10^{6}	0.26	10.6†	41	Derwent & Stewart (1973)

† Mean concentration at Harwell, 1973–5 (Cox, Derwent & Sandalls 1976). Levels for SO_2 and Pb at Harwell are close to U.K. non-urban averages.

4. DEPOSITION OF LEAD

Little & Wiffen (1978) measured the deposition of lead beside the M 4 motorway by exposing shallow trays of grass, 10 cm high, placed on the central reservation and at several distances upwind and downwind of the motorway. An exposure period of 3 h was enough to measure deposition. Wind speed and traffic density were also measured. The results, normalized to 1000 vehicles per hour, are shown in figure 5, together with results of Huntzicker *et al.* (1975 and private communication) obtained near a freeway in Los Angeles. The ratio of the rate of deposition (μg cm^{-2} s^{-1}) to the air concentration (μg cm^{-3}) is the velocity of deposition (v_g). This was found by Little & Wiffen to decrease from 1.0 cm s^{-1} at 2 m from the edge beam to 0.24 cm s^{-1} at 34 m. The higher v_g very near to the motorway was probably due mainly to the turbulence caused by nearby vehicles passing at speed. Little & Wiffen estimated from their deposition measurements that about 9 % of the lead emitted from vehicles on the motorway was deposited within 100 m. Huntzicker *et al.* found 6 % deposited within 150 m. There is a possibility of additional deposition of large particles derived from the surface of exhaust systems, on the roadway surface itself, particularly where cars accelerate rapidly. Cawse (1974, 1975), and Cambray, Jefferies & Topping (1975) measured both the air concentrations and the deposition of lead at a number of rural and coastal sites in the U.K. The total (wet and dry) deposition collecting in funnels was measured and also the dry deposition to horizontal filter pads, sheltered from rain. These pads collected on average about 40 % as much as the open funnels. The velocity of deposition to the filter pads averaged 0.4 cm s^{-1}, compared with a velocity of deposition of 0.24 cm s^{-1} to grass 34 m from the M 4.

By using the results of Cawse, it is possible to estimate the budget of emission and deposition of lead from vehicles in the U.K. (table 5). Of 8000 tonnes per year (t/a) which escapes the

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immediate vicinity of roads, about half is deposited over the U.K. and the remainder blown to sea. Meetham (1950) estimated that 2.3×10^6 t/a of carbonaceous material was emitted yearly in the U.K. of which 1–1.5 Mt/a were blown to sea and the rest deposited. Very similar results to those of table 5 can be obtained if the ratio of Pb (1973) to smoke (1950) in air and in deposited matter is taken on the ratio (3.5×10^{-3}) of the emissions. The current ratios of Pb to total particulates in the atmosphere is about 5×10^{-3} in rural districts (Cawse 1974) and 8×10^{-3} in London (Ball & Hume 1977).

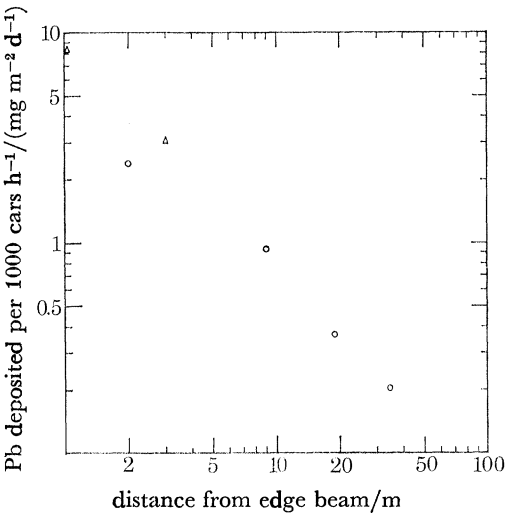

FIGURE 5. Rate of deposition of lead near motorways. Data: ○, Little & Wiffen (1977); △, Huntzicker *et al.* (1975).

TABLE 5. EMISSION AND DEPOSITION OF LEAD IN THE U.K.

Emission

emission from motor vehicles (1973) (Stubbs 1972)	9000 t/a
deposited near to roads (Little & Wiffen 1978)	900 t/a
dispersed over countryside	8000 t/a

Deposition

	total area / km²	rate of deposition / mg m⁻² a⁻¹	deposition / t a⁻¹
cities and industrial areas	5600	70	460
rest of U.K.	164000	24	3940
total deposited			4400
blown to sea			3600

5. LEAD IN HERBAGE

As well as measuring the rate of deposition of lead to freshly prepared trays of grass grown in the laboratory, Little & Wiffen (1978) and Little (personal communication) measured the lead content of grass growing on the verges and in the fields adjoining the M 4. This was done in August 1976, when grass was parched after a hot dry spell, and again in May 1977, when it was growing rapidly in a wet spring. The results (table 6) show about a sixfold difference in concentration between the two samplings. Davies & Holmes (1972), found a two- to threefold difference in concentration in samples taken near roads in Birmingham in dry and wet weather. There are two reasons for this. Much of the lead on leaves is a surface deposit removable by washing and also during rapid growth the accumulated deposit is diluted by increasing mass of herbage.

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The results near the M 4, the A 491 and A 456, and the Lausanne–Geneva highway (Bovay 1970), given in table 6, all show a rapid fall-off with distance from the road. Bovay comments that it is difficult to detect the effect of emissions from a road beyond 50 m.

From table 6 it appears that the lead content of herbage at 1 m from a road carrying 1000 vehicles per hour is about 50 parts/10^6 dry matter in normal growing conditions. The corresponding rate of fallout of lead (figure 5) is about 3 mg m^{-2} d^{-1}. However, figure 5 refers to occasions when the wind is blowing from the road towards the sampling position, and the result must be divided by 2 for comparison with the data for herbage. It follows that the normalized specific concentration (Chamberlain 1970), defined as the ratio of concentration in herbage to rate of fallout, is about 35 m^2 d kg^{-1}. This compares with 24 m^2 d kg^{-1} found by Roberts *et al.* (1974) in Toronto by comparing the lead concentrations in grass with the rate of fallout of lead near a smelter.

TABLE 6. LEAD IN HERBAGE NEAR ROADS

road	cars per hour	date	10^6[Pb] in dry matter†	reference
M 4	3600	Aug. 76	876 (4), 580 (9), 428 (19), 227 (34), 122 (54)	Little & Wiffen (1978)
M 4	3600	May 77	174 (4), 108 (9), 30 (19), 26 (34), 23 (54)	Little (personal communication)
Lausanne/ Geneva	875	Aug. 69	67 (1), 42 (4), 15 (10), 19 (12), 10 (24)	Bovay (1970)
A 491 (Birmingham)	800	July/Aug.	42 (1), 19 (25), 10 (50)	Davies & Holmes (1972)
A 456 (Birmingham)	700	July/Aug.	37 (1), 28 (75), 15 (50)	

† The numbers in parentheses are the distances in metres from the kerb at which the measurement was taken.

From the results of Cawse (1974), the rate of fallout of lead in country districts of the U.K. is about 0.07 mg m^{-2} d^{-1}. Applying the same factor of 35 m^2 d kg^{-1}, this suggests that a lead concentration of about 3 parts/10^6 dry matter in herbage in country districts could be attributed to fallout. Lead in herbage harvested each year at Rothamsted since 1920 has been measured by Williams (1974). The concentrations range from 5 to 20 parts/10^6 dry matter with no significant increase over the years. There has been a significant accumulation in top soil, but sampling variations between plots gave a range of increments of 3–20 kg ha^{-1} in 50 years. This can be compared with an annual fallout of 24 mg m^{-2} (0.24 kg ha^{-1}) assumed for country districts in table 5.

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Discussion

R. M. Harrison (*Department of Environmental Sciences, University of Lancaster, Lancaster LA1 4YQ, U.K.*). I wish to comment upon two points arising from Dr Chamberlain's most interesting paper.

First, the question of the chemical form of the inorganic lead aerosol is important, as this may influence the efficiency with which inhaled lead is absorbed into the bloodstream. Although studies of lead in fresh vehicle exhaust have shown it to consist primarily of lead halides, little is known of the chemical form of the lead present in urban air. Our own recent studies of urban lead aerosols collected in Lancaster and Preston have shown the presence of some lead halide (PbBrCl), but the major portion of the lead has aged in the polluted urban atmosphere to form sulphates ($(NH_4)_2SO_4.PbSO_4$ and $PbSO_4$).

My second point refers to the particle size distributions reported by Dr Chamberlain. It must be borne in mind that particle size distributions determined by means of impactors are expressed in terms of aerodynamically equivalent spherical particles of unit density. These may be numerically very different from the distribution of sizes of the same particles when determined by other techniques, such as electron microscopy, as a result of non-spherical geometry, and probably more importantly, a density in the case of lead compounds of approximately 6 g cm^{-3}.

W. J. Megaw (*Department of Physics, York University, 4700 Keele Street, Downsview, Ontario, M3J 1P3, Canada*). I should like to ask if there is any evidence that any of the lead emitted by automobile exhausts is in droplet form when sampled. This is of some importance where particle size distributions are calculated from chemical analysis of impactor stages because a 1 μm

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droplet which has grown on a 0.1 μm particle will be collected and assessed as though it were a larger particle than 0.1 μm. Dr Chamberlain has suggested that the lead is emitted as inorganic oxides, sulphides, halides and carbonates and all of these compounds are only very slightly soluble in water (PbO, 0.0017 g/100 ml; $PbSO_4$, 0.004; PbF_2, 0.064; $PbBr_2$, 0.4; $PbCl_2$, 1.0; PbI, 0.04; $PbCO_3$, 0.0001). In spite of the high humidity in the vehicle's exhaust system one would not therefore expect that many of the lead particles would have grown into droplets before being sampled.

On the other hand, Cawse (1977, personal communication) reports that quite a high proportion (40 % in West Glamorgan, 82 % in Oxfordshire and 97 % in the Shetlands) of the lead deposited in the United Kingdom is soluble in water and he suggests that the relatively low value for West Glamorgan may be due to local resuspension of insoluble mine tailings. It may be that the lead levels are so low and the quantities of water used for solution are so large that the compounds mentioned would be classed as soluble. The other possible explanation is that the lead particles emitted by vehicles may undergo chemical change in the atmosphere and I would ask if there is any evidence for this. I would suggest that it is of some importance to determine whether appreciable quantities of lead iodide are emitted or produced subsequently as this is an effective ice nucleator and may contribute to man-made climatic change.

A. C. Chamberlain. It is correct that particle size distributions determined by impaction are in terms of mass median equivalent diameters. The density and shape of the particle affect the calibration. There is some evidence of a shift to higher m.m.e.d. values for lead in London in foggy weather, which might be caused by droplet formation on the larger particles or by more coagulation in stable atmospheric conditions.

It is unlikely that droplets would form on the primary particles of about 0.02 μm diameter. In any case, small droplets dry out in the thermal precipitator used to sample for the electron microscope. Density does not affect the particle size deduced from the diffusion box.

When exhaust aerosols are aged, halides are converted to oxides, carbonates and sulphates (Ter Haar & Bayard 1971). Bromine is lost from the particles more rapidly than chlorine (Winchester, Zoller, Duce & Benson 1967). Iodide is not emitted, and on thermodynamic grounds it is unlikely to be formed.

As the fallout of lead in country districts is about 24 mg m^{-2} a^{-1}, and rainfall typically 500–1000 l m^{-2} a^{-1}, the concentration of lead in water would only be about 20–50 μg l^{-1} if all the lead fell in rain, and this is low compared with the solubilities of the lead compounds.

The uptake of lead aerosols from the lung, in unpublished human experiments with the use of ^{203}Pb, has been found to be little different whether the subject inhaled fresh automobile exhaust, exhaust aged in sunlight, or aerosols of lead oxide or nitrate.

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J. D. Butler (*Department of Chemistry, University of Aston, Birmingham, U.K.*). In our investigation of airborne particulate lead concentrations at the M6–A38(M) Midlands motorway interchange mentioned by Dr Chamberlain, we have observed that the difference between the daytime and night-time concentrations decrease with distance from the junction. This is not

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unexpected, of course, since the traffic during the day is heavier than at night. However, when expressed in the form of a percentage of night concentration/day concentration extending over many months, the result can be used to measure the effect of traffic on air quality in the vicinity of the source.

Comparison of kerbside night/day concentrations with those at 45, 510 and 580 m gives values of 50, 61, 98 and 100 %, respectively. In other words, the day and night values cannot be distinguished beyond about 580 m because they have blended into the general urban background value of around 0.8 μg Pb m^{-3}. This is the distance, therefore, over which the interchange exerts its principal influence on air quality.

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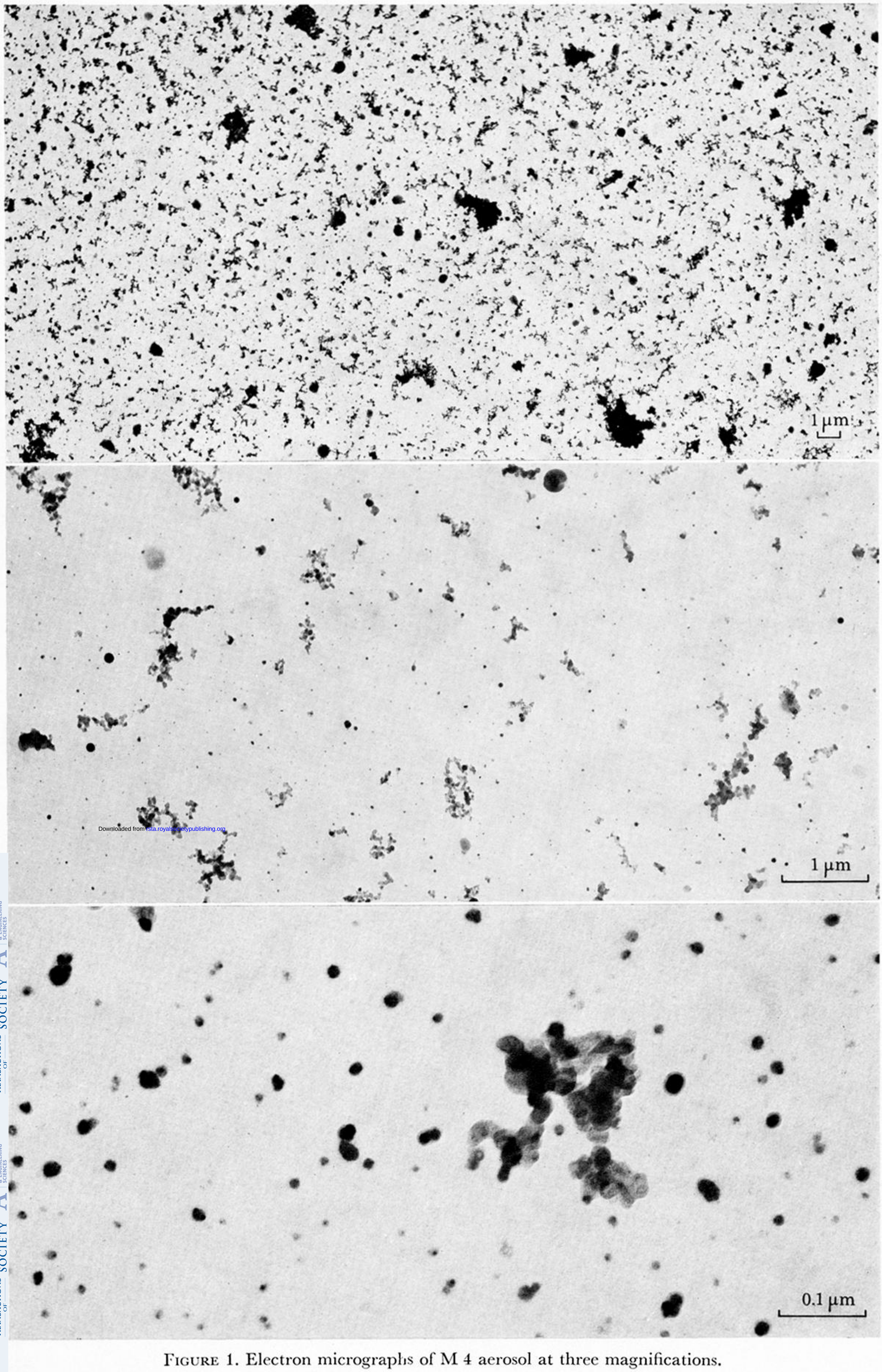

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FIGURE 1. Electron micrographs of M 4 aerosol at three magnifications.