This report was commissioned to provide advice to the DETR, Welsh Office, Scottish Office and the Department of Environment for Northern Ireland on the source apportionment of airborne particles in the UK. Airborne particulate matter remains a cause of concern primarily because of adverse effects on health, but is also associated with other deleterious effects such as soiling of buildings and loss of visibility.

There has been much progress in understanding airborne particulate matter in the UK atmosphere since the publication of the Third Report of the Quality of Urban Air Review Group in 1996. Emission inventories have been refined and source estimates improved, but the major advances have been in the use of numerical models for source apportionment and estimation of future concentrations, and in receptor modelling techniques based upon use of ambient air quality data to apportion the mass of particulate matter to its various sources. The report confirms a major finding of the Third Report of QUARG that PM_{10} may be regarded as having three predominant source types, namely primary fine particles, secondary aerosol and coarse particles. The fine particle fraction ($PM_{2.5}$) is composed predominantly of secondary particles, including both inorganic salts and organic compounds, and primary combustion-generated particles, mainly from road traffic and in some areas from coal burning and industry. The coarse particles in the range from 2.5 to 10 µm comprise predominantly suspended soils and dusts together with some seasalt, biological particles and particles from construction work. The fine particle component contains both local emissions and a regional component, the two varying substantially from day to day in relative amounts.

6.1 SAMPLING METHODOLOGY

A key area in which understanding has improved since the Third Report of QUARG is in the effect of sampling technique upon the measured concentrations of PM_{10}. It is now clear that the TEOM samplers used in the national networks collect a lower mass of particles than some other PM_{10} samplers, such as gravimetric Hi-Vols and Partisols, which do not preheat the airstream prior to filtration. Preliminary work comparing the mass of PM_{10} collected by different samplers indicate that TEOMs are under-estimating particle mass by around 20% relative to these other techniques due to the evaporation of water and semi-volatile components. Since there is considerable uncertainty in this factor, analysis in this report has used a factor of 30% as a conservative approach.

Work on source apportionment must carefully define the technique used to determine total particle mass. This does not present a major problem in the UK since both monitoring and development of air quality standards have so far been based on the same TEOM instruments. There is therefore a consistency between the monitoring method and the current air quality standard, and hence any under-estimation of PM_{10} by the TEOM relative to other sampling methods does not imply a relaxation in the protection of public health. Notwithstanding these improvements in understanding, there remain some major questions yet to be answered concerning the actual primary and secondary components detected by the TEOM $PM_{2.5}$ and PM_{10} instruments in the UK networks.

6.2 EMISSIONS INVENTORIES

Source inventories for PM_{10} emissions in the UK are available from the National Atmospheric Emissions Inventory for the entire country, from the London Research Centre for several specific UK conurbations and from TNO for the whole of Europe disaggregated by country. Exhaust emissions of PM_{10} from UK road transport peaked in 1990 and had declined by 24% by 1996. Similarly, estimated urban emissions from this source peaked in 1991 and declined by 22% by 1996. Road traffic also makes a contribution from tyre dust and brake wear, but this is relatively modest. Nationally, road traffic contributes 25% of primary PM_{10} emissions with

other major contributions from combustion in energy production and transformation (mainly power stations) (18%), commercial, institutional and residential combustion (17%), and non-combustion processes (industrial processes – mining and quarrying and construction) (28%). Almost all the particle mass emitted from vehicle exhausts is in the <2.5 µm range; for stationary combustion sources, around 50-60% of the primary PM_{10} emitted is believed to be in the <2.5 µm range, whereas the PM_{10} emitted from mining, quarrying and construction comprises mainly coarser particles. These coarse particle sources tend to be more localised. We present for the first time national UK emissions inventories for the smaller size fractions of particulate matter, $PM_{2.5}$, PM_1 and $PM_{0.1}$. As might be expected, the relative importance of road traffic emissions increases with decreasing particle size to the point where road transport accounts for an estimated 61% of national $PM_{0.1}$ ultrafine particle emissions. The inventories do not include resuspended dusts which currently are not reliably quantifiable.

The available urban emission inventories show a very wide range of contributions of road traffic to primary PM_{10} ranging from 12% in Merseyside to 77% in London. The large differences arise from the inclusion of major industrial sources in some of the inventories (especially Merseyside). These are normally located well away from the urban centre and emit high above the ground, therefore having only a modest impact upon ground-level urban concentrations. The main uncertainties in the source inventories for PM_{10} are in the estimates for industrial processes, mining, quarrying and construction where the emission rates can be locally high. Emission estimates from light duty diesel vehicles are probably the most reliable in the inventories. Several primary particulate emission sources are not included in the inventories. These are entrainment of road dust, certain agricultural sources, such as harvesting and ploughing, and biological sources. This is due to the lack of emission factor measurements in conditions appropriate to the UK or the lack of relevant activity data.

Verification of the inventories shows a good relationship between measured annual PM_{10} (subtracting secondary contributions) and the estimated local emissions from road traffic. The situation is rather different in Belfast where household solid fuel use is a low-level source responsible for emitting more particulate matter than road traffic. A European inventory of PM_{10} emissions has been published by TNO on behalf of the European Environment Agency. It uses different, but generally less sophisticated methodology than the UK National Atmospheric Emissions Inventory, and whilst its estimates are broadly comparable with those of the national inventory, its projections of trends appear incorrect. Future trends in UK emissions estimated by the National Atmospheric Emissions Inventory for road traffic project a major reduction from 47.7 kilotonnes in 1996 to 22.6 kilotonnes in 2005 and 15.6 kilotonnes in 2025. For urban road traffic exhaust emissions of PM_{10}, the reduction is also substantial from 21.8 kilotonnes in 1996 to 11.1 kilotonnes in 2005, and 7.1 kilotonnes in 2025. These reductions are due to the fleet penetration of new diesel vehicles meeting tighter emission standards and the introduction of regulations further limiting particulate emissions from new diesel vehicles in 2000 and 2005. The phasing out of leaded petrol consumption and the penetration of cars fitted with three-way catalysts in the fleet also contribute to the reductions. The benefits of new vehicle emission abatement technologies will eventually be offset by the continuous growth in traffic after around 2015. Future projections of emissions from other sectors are not currently available.

6.3 PRIMARY PARTICULATE MATTER

In addition to that arising from the UK sources outlined above, primary particulate matter can reach the UK as a result of emissions in mainland Europe. These long range transport processes have been modelled based on the TNO inventory and indicate an annual average contribution of PM_{10} from mainland Europe of 1.9 µg m^{-3} in London and 1.0 µg m^{-3} in Edinburgh. These contributions

may, however, be very much larger during short-term episodes. Measurements of black smoke from the north Norfolk coast are consistent with these estimates. Since the TNO inventory has estimates of $PM_{2.5}$ and $PM_{0.1}$ as well as PM_{10}, the transport of the smaller size fractions can be modelled showing that the long range transport is predominantly of $PM_{2.5}$. A re-analysis of co-located measurements of $PM_{2.5}$ and PM_{10} from the Birmingham Hodge Hill site confirms the earlier observations in the Third Report of QUARG that fine particles in the $PM_{2.5}$ range comprise the major part of PM_{10} with a seasonally variable contribution of coarse particles which peaks in the summer months. Recently available data from four DETR-funded sites gives further insights into the relationship between $PM_{2.5}$ and PM_{10} showing a substantial elevation of fine particles due to exhaust emissions and coarse particles by resuspension at the roadside Marylebone Road site relative to the urban background site at London Bloomsbury. A comparison of data from roadside sites with that from nearby urban background locations shows a long-term roadside elevation in concentration varying from 2 – 15 µg m^{-3} at the TEOM instrumented sites. Based on hourly TEOM data, the difference between Marylebone Road and London Bloomsbury can exceed 50 µg m^{-3}. An analysis of the fine ($PM_{2.5}$) and coarse (PM_{10} – $PM_{2.5}$) size fraction data, taking the difference between Marylebone Road and London Bloomsbury as representative of emissions on the road, indicates that traffic-induced resuspension of coarse particles is of a similar magnitude at Marylebone Road to the exhaust emissions of $PM_{2.5}$. Analysis of data from sites adjacent to the M4 and M25 motorways indicates that the annual average background concentration of PM_{10} of about 20 µg m^{-3} is increased by about 1 µg m^{-3} for each 1000 vehicles per hour. Maximum hourly average concentrations at the M4 and M25 sites in 1996/97 were 173 and 184 µg m^{-3} respectively, comparable with hourly maxima for central urban background sites. Analysis of diurnal profiles of PM_{10}, carbon monoxide and NO_x show a generally closer relationship between PM_{10} and NO_x than that between PM_{10} and carbon monoxide. This is reflective of the impact of diesel emissions on both PM_{10} and NO_x with petrol vehicles showing a different diurnal pattern which strongly influences the carbon monoxide, but has less influence on the diurnal profile of PM_{10} and NO_x. Local industrial sources can also impact substantially on PM_{10} concentrations in some areas, as can domestic coal burning, where this still takes place.

It is recognised in the National Air Quality Strategy that Bonfire Night celebrations may lead to exceedences of the PM_{10} standard. An analysis of data from 1994-1997 suggests that Bonfire Night pollution episodes can occur on several nights within an individual year depending upon which day of the week November 5th falls. The dominant factor is the prevailing meteorology, but during 1994, 1995 and 1997 exceedences of 50 µg m^{-3} over four or more days occurred at at least one site in the national monitoring network. Indeed, in 1995 the national air quality objective would not have been met at 25% of the monitoring sites in operation (exceedances greater than four days).

Data on the chemical and biological composition of airborne particles have been reviewed. Information on the contribution of biological particles to suspended particle mass is almost non-existent. A recent evaluation of biological particles collected in London over one week in July 1996 indicates that biological particles accounted for 5% of PM_{10} mass averaged over the week and up to 12% of PM_{10} mass within individual hours. Data from Germany are indicative of a contribution of about 10% to the coarse particle fraction. Due to the seasonality of biological particles, the annual average contribution is likely to be significantly lower. Chemical measurements are useful in elucidating the sources of particles and the chemical processes influencing airborne particulate matter. Work in Leeds has shown that the contribution of elemental carbon, presumed largely from road traffic, to total particle mass varies from 17 – 27% at urban sites, but comprises only 9% at a rural site. Comparison of the size distributions of airborne particulate matter in Leeds and at a rural site outside of the city show the impact of the

urban area to be primarily on the very small and very large particles consistent with knowledge of the physical processes affecting particles in the atmosphere. Data from Cardiff show clearly the important contribution of crustal elements such as iron, silicon and aluminium to the mass of airborne particulate matter reflecting the contribution of road dusts and soils.

6.4 SECONDARY PARTICULATE MATTER

Secondary particles are those formed within the atmosphere. The major contributors are sulphates arising from sulphur dioxide oxidation and nitrates from oxidation of NO_x. There is also a poorly quantified contribution from secondary organic matter derived from the atmospheric oxidation of VOCs. Concentrations of sulphate across the UK are reasonably well known as a result of measurements made for the EMEP network. This network does not provide information on particulate nitrate and ammonium which can only be determined by inference. A study in Leeds has determined both sulphate and nitrate, and if both are assumed present in the atmosphere as ammonium salts, they contributed 12.7 µg m^{-3} to the total particle mass (measured with an unheated sampler) during the period of the survey, comprised of 5.2 µg m^{-3} ammonium nitrate and 7.5 µg m^{-3} ammonium sulphate. Urban sulphate concentrations are very similar to rural levels, whilst the rural to urban ratio for nitrate varies from 0.46 – 0.84 suggesting an urban source of nitrate. The mass median diameters of sulphate, nitrate and ammonium measured in Leeds were 1.1 µm, 1.6 µm and 1.0 µm respectively.

Application of the NAME model to prediction of sulphate concentrations shows a good capability for predicting episodic sulphate during the summer months. The results show clearly that both UK and continental European sources of sulphur dioxide make important contributions to episodes of sulphate pollution within the UK. Using the EMEP model to predict secondary particulate matter in the UK shows an over-prediction of total sulphate, nitrate and ammonium concentrations in London, but rather more accurate predictions for Edinburgh. The major contributions of precursor emissions to secondary inorganic PM_{10} on an annual average basis arise from the UK, Germany and France respectively. Projected concentrations of secondary inorganic particulate matter predicted by the EMEP model based on emissions in 2010 anticipated from current policies show substantial reductions in this basis in sulphate with lesser reductions in nitrate, and we estimate a probable reduction in UK secondary PM_{10} of 30% by 2010.

6.5 RECEPTOR MODELLING

An examination of relationships between PM_{10} and carbon monoxide at urban background sites following the methodology developed in the Third Report of QUARG has shown generally good relationships despite the decoupling of the petrol and diesel contributions to air pollution at some sites mentioned above. Extrapolation of the PM_{10}: CO relationship to northern hemisphere background carbon monoxide concentrations allows estimation of the non-traffic PM_{10} concentration and thereby the traffic contribution by difference. Traffic contributions to the annual average at city centre sites estimated by this method typically lie in the 30 – 40% range but are much higher during episodes of locally generated pollution. Correlations of PM_{10} and $PM_{2.5}$ with NO_x at the Birmingham Hodge Hill site show especially strong correlations for $PM_{2.5}$ consistent with a strong source of both pollutants in road traffic. These show that many of the highest winter PM_{10} concentrations are also associated with very high NO_x and hence must arise from local road traffic. An intercept for $PM_{2.5}$ and PM_{10} concentrations at zero NO_x of 8.5 and 14.1 µg m^{-3} respectively reflects mainly the contribution of secondary particles in the former case and secondary plus coarse particles in the latter. The coarse particle mass is poorly correlated with NO_x indicative of sources in resuspension rather than vehicle exhaust emissions. An attempt to identify a component of coarse particles which increases with

windspeed, and is therefore attributable to wind-driven resuspension, shows seasonally variable concentrations of around 1 – 3 µg m^{-3}. This is less than the other component which is diluted rather than increased by increasing windspeed and appears to represent contributions both from soil, street dust and sea spray. An examination of the episodicity of coarse particle concentrations shows that coarse particle pollution events on their own are very unlikely to lead to exceedence of the current UK ambient PM_{10} standard of 50 µg m^{-3} 24-hour running mean. Analysis of data from Marylebone Road, London, highlights the importance of coarse particle resuspension by road traffic which adds appreciably to PM_{10} concentrations at this site. Recent work evaluating particle numbers as opposed to mass has shown that particle number, which reflects mainly particles less than 0.1 µm diameter, is a very good tracer of road traffic emissions in the urban environment, and more clearly related to road traffic than PM_{10} mass. Diesel vehicles contribute far more to particle number than petrol vehicles within the urban environment, and significantly more than is indicated by the urban road transport mass-based PM_{10} inventories.

A number of studies have estimated the mass of seasalt particles in the atmosphere. Whilst concentrations are higher at coastal sites, the influence of seasalt is seen at even the most inland sites amounting to around 1.5 – 2.0 µg m^{-3} long term average with around three quarters in the coarse particle size range. Preliminary estimates of the contribution of secondary organic matter to PM_{10} show average winter and summer concentrations in Birmingham of 0.8 and 3.7 µg m^{-3} of PM_{10} mass measured with a High Volume sampler.

A new receptor modelling technique has given considerable new quantitative insights into the sources of airborne particulate matter. The technique uses measurements of black smoke to estimate combustion-generated particles, which the inventories show to come mainly from road traffic. Secondary particulate mass is estimated from sulphate measurements, and a third component estimated by difference corresponds well with coarse particle mass. The technique has been used especially to examine periods of high PM_{10} concentration showing that these can arise as a result of local traffic emissions with poor dispersion or from secondary pollutants, or a combination of both. Whilst coarse particles contribute to high airborne concentrations, they do not on their own cause exceedences of the air quality standard.

6.6 THE FUTURE

Current annual average concentrations of PM_{10} at urban central background sites are made up of about one third by combustion sources (mainly road traffic), slightly more than one third from secondary particles (mostly sulphates and nitrates) with the contribution decreasing towards the north and west of Britain, and a little less than one third from coarse particles comprising seasalt, biological materials, construction dusts and windblown dusts and soils. Local sources, such as major roads or industries, can make a major impact on these concentrations with roadside elevations in annual average concentration going up to about 15 µg m^{-3} at current TEOM-instrumented sites. At rural sites, the contributions of road traffic and coarse particles are somewhat smaller than at urban centre sites, whilst the concentration of secondary particles is diminished by a small amount due to lower nitrate concentrations.

Considerably better information is now available on the contributions of the different sources to daily concentrations of PM_{10}. The receptor modelling technique described above shows daily episodes of primary combustion particles in Birmingham and Newcastle of up to 80 µg m^{-3} and of secondary particles of up to 50 µg m^{-3}. The technique has been extended to provide forecasts of PM_{10} concentrations in the years 2005 and 2010 by the multiplication of the individual contributions by the appropriate reduction factors reflecting the likely changes in emissions of PM_{10} from road traffic and contributions of secondary particulate matter resulting from existing policies

in place, based on model studies. Both annual means and percentiles of daily concentrations can be predicted. The results suggest a reduction in annual mean PM_{10}, as measured by TEOM, at London Bloomsbury from 28 µg m^{-3} in 1995 to 23 µg m^{-3} in 2005, and at Birmingham Centre from 23 µg m^{-3} in 1995 to 19 µg m^{-3} by 2005. The 99th percentile of maximum daily concentrations decline from 80 µg m^{-3} to 69 µg m^{-3} (London Bloomsbury) and 77 µg m^{-3} to 65 µg m^{-3} (Birmingham Centre). The interpretation of these data is made more difficult by changing proportions of sulphate and nitrate in airborne particulate matter in the future, with nitrate playing a progressively larger role. However, a predicted reduction in urban road traffic emissions of PM_{10} of 49% between 1996 and 2005 should have a substantial beneficial effect on winter episodes, and an approximately 30% reduction in secondary particles by 2010 should also improve summertime concentrations. The number of fixed daily means above 50 µg m^{-3} is probably a more robust statistic than the 99th percentile concentration. Estimates for London Bloomsbury show a reduction from 24 exceedences in 1995 to 9 in 2005 based on 1995 meteorology. For other cities it is predicted that between 2 and 9 fixed daily means will exceed 50 µg m^{-3} in 2005 with a greater number of exceedences (up to 13) when the predictions are based on the less favourable meteorology of 1996. Conformity with the objective of the National Air Quality Strategy implies that less than four exceedences should occur by 2005. The method used for projection does not account separately for Bonfire Night episodes and these alone in some years can form a significant proportion of as many as four exceedences of the daily 50 µg m^{-3} concentration. This total may reduce in future years as the background pollution from road traffic and secondary particles is reduced.

In order to compare predicted future UK concentrations of PM_{10} with the European Union Daughter Directive Limit Values for 2005 and 2010, the Group took a conservative approach of basing its future projections upon TEOM concentrations, measured in 1995 and 1996, multiplied by a factor of 1.3 to estimate concentrations as measured by the EU reference gravimetric method. Based on the more pessimistic 1996 data, the results indicate that with existing policies in place likely compliance with the EU Stage 1 limit values for 2005 at urban background locations, with the possible exception of central London (90th percentile of 24-hour concentrations, 54 µg m^{-3} compared to the limit value of 50 µg m^{-3}). However, predicted concentrations for 2010 based upon currently planned emissions reductions exceed the EU Stage 2 limit values by a considerable margin in most urban background locations in major cities.

The above projections can only be based upon the best current information available to the Group. If the uncertainties in our predictions are to be reduced, further research will be required on a number of topics. Most important amongst these are the behaviour of nitrates and secondary organic compounds in the TEOM instrument, measurement of current concentrations of nitrates and secondary organic compounds and prediction of future concentrations, quantification of resuspension processes and an evaluation of the sources and composition of coarse fraction particles.