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USING ARCHIVE DATA TO INVESTIGATE TRENDS IN THE SOURCES AND COMPOSITION OF URBAN PM₁₀ PARTICULATE MATTER: APPLICATION TO EDINBURGH (U.K.) BETWEEN 1992 AND 1997

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Abstract. By extending the method of Stedman (1998), daily data of atmospheric concentrations of gravimetric PM₁₀, black smoke (BS) and sulphate aerosol (SA) from national networks were analysed to determine the trends in time of the contribution of different sources of particulate matter to total PM₁₀ measured in central Edinburgh. Since BS is an indicator of combustion-related primary sources of particulate matter, the quantity obtained by subtraction of daily BS from daily PM₁₀ is indicative of the contribution to total PM₁₀ from other primary sources and from secondary aerosol. This PM₁₀-BS statistic was regressed on SA, since SA is an indicator of variation in secondary aerosol source. For Edinburgh, SA is a considerably better indicator of PM₁₀-BS during summer than winter (reflecting the much greater photochemical generation of secondary aerosol in summer) and there is evidence that the contribution of other secondary aerosol (presumably nitrate aerosol) has increased relative to SA between 1992 and 1997. The concentration of non-combustion primary particulate material (marine aerosol, suspended dust) to PM₁₀ in Edinburgh has not changed over this period but is about twice that calculated as the U.K. national average. The increasing input to PM₁₀ from secondary aerosol sources at regional rather than urban scale has important implications for ensuring local air quality compliance. The method should have general applicability to other locations.

Keywords: network atmospheric data, primary aerosol, secondary aerosol

1. Introduction

The concentration of airborne particulate matter is subject to regulation in many countries. In the United Kingdom the current air quality standard (still under review) for concentration of PM₁₀ particulate matter (fraction with aerodynamic diameter <10 μm) is 50 $\mu\text{g m}^{-3}$ calculated as a 24 h running mean. However, the single gravimetric measure of PM₁₀ concentration masks the considerable intrinsic heterogeneity in particle source, size distribution and chemical composition. PM₁₀ includes particles emitted directly into the atmosphere from primary sources (for example, carbonaceous and organic particles from traffic-related and stationary combustion, direct emissions from other industrial sources, or mineral particles from wind-blown dust) as well as secondary particles formed by chemical reaction within the atmosphere (for example, sulphuric acid and ammonium sulphate and nitrate particles) (Harrison and Jones, 1995). The U.K. Quality of Urban Air Review Group have highlighted the need to quantify the relative contribution of primary and secondary sources to receptor-measured PM₁₀ before further progress can be made towards understanding both the impact of present policies in respect of PM₁₀ air quality and the emissions reductions required to meet the specified standard (QUARG, 1996). Information on airborne particulate matter speciation is also required to further understanding of specific health risks (COMEAP, 1997). The U.K. is fortunate in having fairly extensive rural and urban networks for air pollutant measurements. The data routinely recorded by these networks represent a valuable resource for analysis of trends and relationships in air pollutant behaviour. For example, in two recent papers it was suggested that secondary aerosol generation

and long-range transport processes contributed significantly to two periods of elevated PM₁₀ concentration during the period January to March 1996 (King and Dorling, 1997; Stedman, 1997). Subsequently, Stedman (1998) used daily data of PM₁₀, black smoke (BS) and sulphate aerosol (SA) concentrations, averaged over all sites in the U.K., to derive a method to distinguish between the contribution of primary and secondary particles during this period. BS data are obtained from the extent of light reflectance from filter samples. The reflectance optical units are converted by the network operators to a concentration of particulate matter in $\mu\text{g m}^{-3}$ using a British Standard (non-linear) smoke calibration curve (Edwards *et al.*, 1983). In addition, the nature of the air sampling inlet restricts particle size range collected on the filters to $<4 \mu\text{m}$. Together these two biases towards particle blackness and smaller particle size make BS a very good indicator of the contribution to airborne particulate matter of the fine carbonaceous fraction emanating from primary combustion-related sources (Edwards *et al.*, 1983; Erdmann *et al.*, 1993). Conversely, SA concentration data from the rural non-automated networks are indicative of the extent of contribution from secondary particulate matter generation.

The Stedman (1998) analysis used national averages of PM₁₀, BS and SA concentrations from all U.K. sites. The aims of the work reported in this paper were, a) to investigate if the national approach accurately reflected data specific to the city of Edinburgh and its immediate environs and b) to extend the analysis for Edinburgh over the whole period 1992–1997 to investigate regional trends. The results show that a regional scale approach is necessary, but that important conclusions can be drawn regarding changes in particulate matter composition with time in a specific area.

2. Methodology

Since BS is a measure of primary combustion-derived particulate matter it is proposed that the statistic (PM₁₀-BS) (i.e. the difference between PM₁₀ concentration and BS concentration) represents the contribution to PM₁₀ from non-combustion derived primary material and secondary aerosol (Stedman, 1998). It is further proposed that the value of SA is an indicator of the variation in secondary aerosol within the (PM₁₀-BS) statistic. Additional information on the composition of PM₁₀ particulate matter is derived from the quantitative nature of the regression relationship between PM₁₀-BS and SA.

All data for monitoring sites within or near to Edinburgh were obtained from the U.K. National Air Quality Archive (see ref. DETR). The Enhanced Urban Network includes one site in the centre of Edinburgh (classified as urban centre) at which concentrations of PM₁₀ (expressed in units of $\mu\text{g m}^{-3}$) are measured by Tapered Element Oscillating Microbalance. Daily averages of these PM₁₀ data were used. Data for daily BS (in $\mu\text{g m}^{-3}$) were obtained from two sites within Edinburgh contributing to the Non-Automatic Monitoring Network. One site is classified as lying within a commercial area, or an area with predominantly central heating, while the other is classified as residential with medium-density housing surrounded by, or interspersed with, areas of low potential air pollution output (parks, fields, coasts). The average of both daily BS values was used, or the actual value from a single site when data from the other was missing. (N.B. data collection at the former site ceased on 31st March 1997 and was replaced by a site classified as surrounded by high-density housing). Although the BS sites are not coincident with the PM₁₀ site, all monitors are located in 'urban background' areas and therefore not subject to the influence of strong local sources.

Daily concentrations of rural SA (units of $\mu\text{g SO}_4^{2-} \text{ m}^{-3}$) were obtained from the Acid Deposition Network. The SA data refer specifically to airborne particulate sulphate collected from air drawn through a filter, and are not derived from precipitation measurements of bulk or wet-only deposition. Daily data from the two rural sites at Eskdalemuir and Glen Dye in east Scotland were averaged. The two sites are approximately 90 km SSW and 120 km NNE of Edinburgh, respectively, and provide a representative measure of background SA in remote locations unaffected by primary sources.

3. Results and Discussion

Regressions of $\text{PM}_{10}\text{-BS}$ against SA were plotted and analysed for each year for the period 1992–1997 using all daily data for that year. There was considerably greater correlation between $\text{PM}_{10}\text{-BS}$ and SA data during summer months than for winter months. The seasonal correlation and regression coefficients are summarised in Table I. Summer refers to 1st April – 30th September, inclusive. An example plot is illustrated in Figure 1.

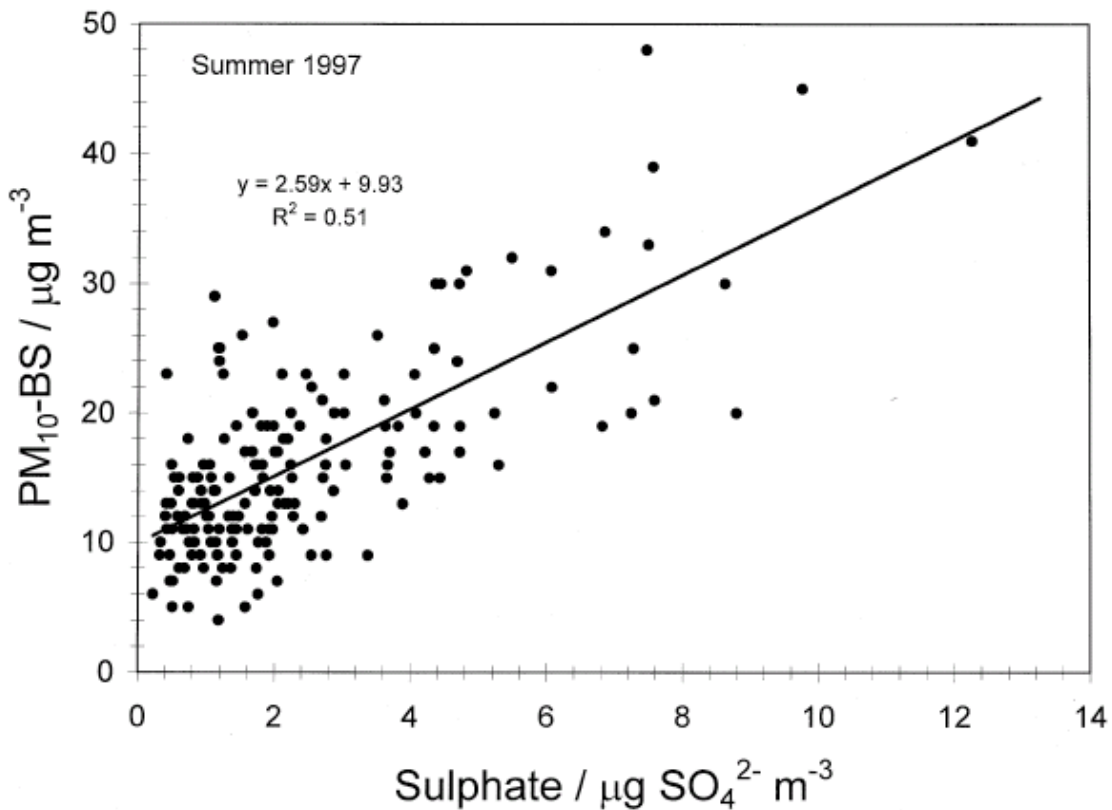


Figure 1. Example regression of $\text{PM}_{10}\text{-BS}$ vs. SA for data measured in Edinburgh (PM_{10} , BS) or at two rural sites in eastern Scotland (SA) for 1st April to 30th September 1997.

A stronger correlation between the non-BS fraction of PM_{10} and SA indicates that a greater proportion of variation in the non-BS fraction of PM_{10} is accounted for by the variation in SA. Consequently, that part of the non-BS fraction that is not specifically SA is likely to be other particulate matter with similar source characteristics, most probably nitrate aerosol (NA), which is generated by secondary reactions in the atmosphere under similar conditions to the generation of SA.

This conclusion is consistent with the stronger correlations observed for summer data since secondary aerosol generation is dependent on photochemical oxidation reactions which are considerably enhanced during summer.

The observation that PM₁₀ concentrations in the centre of Edinburgh during summer are strongly influenced by the extent of photochemically generated secondary aerosol in the surrounding rural area, confirms previous suggestions of the importance of long-range transport of particulate pollution (King and Dorling, 1997; Stedman, 1997) and demonstrates that urban air particulate concentrations are no longer determined just by local primary emission but are strongly affected by regional scale sources. A similar conclusion was reached by Hoek *et al.* (1997) who interpreted the significant correlations in daily PM₁₀ concentrations across 28

Data set	Slope	Intercept ($\mu\text{g m}^{-3}$)	Corr. coeff.	n
Summer 1993	2.1	10.9	0.61	147
Summer 1994	2.0	10.2	0.60	168
Summer 1995	2.9	9.0	0.68	181
Summer 1996	2.1	8.1	0.64	170
Summer 1997	2.6	9.9	0.71	171
Winter 1992/1993	1.3	9.8	0.27	134
Winter 1993/1994	0.5	10.3	0.11	180
Winter 1994/1995	1.0	10.8	0.14	147
Winter 1995/1996	1.9	9.5	0.55	179
Winter 1996/1997	1.3	9.7	0.19	157

TABLE I: Regressions of PM₁₀-BS on SA for data measured in Edinburgh (PM₁₀, BS) or at two rural sites in eastern Scotland (SA) during the period 1992–1997. Summer refers to 1 April to 30 September, inclusive

Year	Average PM ₁₀ ($\mu\text{g m}^{-3}$)	Average BS ($\mu\text{g m}^{-3}$)	Average SA ($\mu\text{g SO}_4^{2-} \text{ m}^{-3}$)
1992	22.6 ^a	9.2	2.0
1993	22.5	7.4	2.5
1994	19.6	6.4	2.2
1995	20.3	5.4	2.2
1996	19.4	5.7	2.6
1997	18.4	4.4	2.0

TABLE II: Annual average concentrations of PM₁₀, BS and SA during the period 1992–1997 for sites referred to in Table I

^aPM₁₀ data available only for the period 10 October – 31 December 1992.

separate urban and non-urban sites in western and central Europe as indicating the important contribution of the formation and transport of secondary aerosols to total particulate concentrations.

Closer examination of the data in Table I lead to further conclusions. For the summer regressions of PM₁₀-BS on SA concentrations there is evidence (although not statistically significant) of an increase in magnitude of linear regression slope with time. (The 95% confidence intervals for the slopes of the regression are about ± 0.5 units). Between summer 1993 and summer 1997, the regression slope increases from about 2.0 to about 2.6. There is also a trend of increasing correlation with time. The increase in regression gradient over this period indicates: a) a greater proportion of PM₁₀ now consists of non-combustion (i.e. non-BS) secondary aerosol, and b) that the contribution of other secondary aerosol material to PM₁₀-BS has increased relative to the SA contribution.

These observations are not inconsistent with a rise in urban traffic emissions because the concurrent rise in NO_x (NO + NO₂) emissions has increased the generation of secondary NA across the U.K. in recent years (QUARG, 1996). The chemical reactions which lead to NA formation occur with a timescale of a few hours to a few days, within which time transport processes will disperse NA (and SA) over wider areas, particularly since secondary aerosol constitutes part of the 'fine' fraction of PM₁₀ (with aerodynamic diameter <2.5 μm) and consequently has lower surface deposition rates than the 'coarse' fraction (QUARG, 1996). The assertion that PM₁₀ is increasingly more influenced by other non-SA secondary aerosol is supported by examination of the statistical summaries of annual particulate concentration data given in Table II. Although there is a trend for a decrease of around 10–20% in average PM₁₀ concentration between 1992 and 1997, the average BS concentration has fallen by a factor of 2, whilst SA concentration has also remained fairly constant. Therefore there must be another component of total PM₁₀ that has increased with time and, as discussed above, this is most probably nitrate aerosol.

In contrast to the trend observed in the gradient of the regressions, the value of the regression y-intercept (Table I) does not indicate any systematic variation with year or with season but has remained within the range 8.1–10.9 $\mu\text{g m}^{-3}$ (The 95% confidence interval on the intercepts is about $\pm 1.5 \mu\text{g m}^{-3}$). The value of PM₁₀-BS at the intercept (i.e. when secondary aerosol contribution is zero) must represent the contribution of other, non-combustion primary particulate matter such as resuspension of crustal dust and/or sea-salt aerosol particles. There is no reason for the magnitude of these sources of particulate matter to have changed with time and this is reflected in the analyses.

In regard to other sources of primary particulate matter it is important to recognise that background aerosol in the U.K. contains a significant contribution from marine-derived sulphate. The annual variation in marine-derived sulphate is likely to be much less than the variation in other aerosol sources (particularly in coastal Scotland) and thus form a relatively constant background contribution. This conclusion is consistent with the essentially constant SA concentrations and y-intercepts presented in Tables II and I, respectively, for the 6 yr of available data. It is interesting to note further that the intercept obtained using Edinburgh data is around twice the magnitude of the intercept (4.6 $\mu\text{g m}^{-3}$) reported by Stedman (1998) using the average of all U.K. data between January and March

1996. This may reflect Edinburgh's specific windy, coastal location leading to above U.K.-average dust resuspension and contribution from marine aerosol. Similarly, the gradient of the regressions using Edinburgh data are lower than the value (3.0) reported by Stedman (1998) using U.K. average data for January to March 1996. The inference, based on the above hypotheses, is that other photochemically derived secondary aerosol contribute a smaller fraction to Edinburgh PM₁₀ than the national average. This may reflect both the lower photochemical activity and the lower ammonia emissions (which contribute to secondary particle formation) applicable to Edinburgh's higher latitude and more remote geographical location. In future work it may be instructive to try and correct the SA data for marine bias.

4. Conclusions

Inferences about changes with time in broad categories of sources of airborne particulates can be extracted from detailed examination of national air quality data sets collected by governments or other agencies. However, use of nationally-averaged data may not reflect airborne particulate matter issues within a given region. Analysis of data for Edinburgh indicates that between 1992 and 1997 there has been a change in particulate composition, with greater input now from sources at a regional scale rather than from local sources. This has implications for local regulators attempting to maintain local air quality within specified limits. It is highly recommended that monitoring of particulate matter concentration as PM₁₀, BS and SA be maintained in parallel since the different measures clearly provide complementary rather than duplicative information on airborne particulate composition. This may also have important benefits to understanding any adverse health consequences associated with exposure to ambient particulate matter. In addition, concurrent measurement of both PM₁₀ and PM_{2.5} fractions will provide further information since wind-blown inorganic material is likely to be predominantly in the coarse fraction of PM₁₀ and secondary aerosol predominantly in the fine fraction.

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