

# Using Mass Reconstruction along a Four-Site Transect as a Method to Interpret PM<sub>10</sub> in West-Central Scotland, United Kingdom

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## ABSTRACT

Concurrent 24-hr samples of particulate matter of median aerodynamic diameter less than 10  $\mu\text{m}$  (PM<sub>10</sub>) were collected over a 10-day period in August 2000 at four sites

### IMPLICATIONS

This study highlights the utility of a multisite transect aligned with the prevailing wind to identify changes in PM<sub>10</sub> chemical composition in air masses moving inland from a coastal region, through urban and periurban regions. Local, marine, and long-range PM<sub>10</sub> components were identified. The CMB calculation offers a pragmatic method for accounting for the major chemical sources contributing to PM<sub>10</sub> at a receptor. Interpreting the CMB of PM<sub>10</sub> is of policy relevance not only in helping identify sources but also because of the implications for health impacts.

along a transect in west-central Scotland, UK (passing from the coast through the city of Glasgow) in line with the prevailing southwesterly wind. Each sample was analyzed for chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), calcium (Ca<sup>2+</sup>), iron (Fe), and organic hydrocarbon material (OHM). The contribution from elemental carbon (EC) was estimated. Sampling days were categorized according to local wind direction, synoptic flow, and air mass back trajectories. Chemical mass balance (CMB) reconstruction of the following PM<sub>10</sub> components was derived for each wind direction group and at each transect location: ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), sodium chloride (NaCl), gypsum (CaSO<sub>4</sub>), OHM, EC, soil/surface dusts, and particle-bound water. The results showed that PM<sub>10</sub> at the coastal site was dominated by the marine background (NaCl) compared with the urban sites, which were dominated by local primary (EC and soil/resuspension) and

secondary sources ( $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and OHM). There was evidence of  $\text{Cl}^-$  depletion as NaCl aerosol passes over urban areas. There was also evidence of long-range transport of primary  $\text{PM}_{10}$  (EC and OHM); for example, at the coastal site from transport from Ireland. The work demonstrates how the general approach of combining mass reconstruction along a transect with other information such as wind/air-mass direction generates insight into the sources contributing to  $\text{PM}_{10}$  over a more extended spatial scale than at a single receptor.

## INTRODUCTION

Numerous studies published over the last 20 yr have demonstrated a significant, linear association between the concentration of airborne particulate matter (PM) of median aerodynamic diameter less than  $10\ \mu\text{m}$  ( $\text{PM}_{10}$ ) and cardiopulmonary mortality and morbidity.<sup>1-3</sup> There appears to be no lower threshold in the dose response between  $\text{PM}_{10}$  concentrations and health effects.<sup>4</sup> Evidence suggests that particle size, number, and chemical composition all ultimately determine the PM toxicological impact.<sup>5</sup>

$\text{PM}_{10}$  has many sources, including anthropogenic, biogenic, geogenic, primary and secondary, local, and long-range.<sup>6,7</sup> To determine the source contribution to  $\text{PM}_{10}$  present at any given receptor, it is necessary to gain as much knowledge as possible regarding the chemical composition, meteorological factors, and an appreciation of the local and long-range sources impacting the receptor.<sup>8,9</sup> Several methods to apportion  $\text{PM}_{10}$  sources have been applied. These include deterministic approaches utilizing emission inventories and forward process modeling of the subsequent expected atmospheric concentration.<sup>10</sup> However, these models are computationally and input-data demanding and often exclude contributions from resuspended mineral dusts and marine-derived salt particles.<sup>9</sup> Other approaches use receptor models based on multivariate statistics, including principal component analysis and the more sophisticated positive matrix factorization method.<sup>11-15</sup>

The chemical mass balance (CMB) approach to receptor modeling offers a relatively simple method for source apportionment of airborne PM. Knowledge of the CMB of PM not only helps to elucidate their source but can provide insight into their potential toxicology effects.<sup>16</sup> Additionally, the CMB information can aid air quality managers in the identification of particular anthropogenic emissions and subsequent management strategies to reduce them. Several studies have used CMB to account for the collected  $\text{PM}_{10}$  mass through measured and inferred major chemical constituents.<sup>17-19</sup> For example, a "pragmatic" mass closure model was applied to the source apportionment of PM of aerodynamic diameter less than  $1\ \mu\text{m}$  ( $\text{PM}_1$ ), less than  $2.5\ \mu\text{m}$  ( $\text{PM}_{2.5}$ ), and  $\text{PM}_{10}$  collected at roadside, urban background, and rural sites within and outside of Birmingham, UK.<sup>20</sup> This study concluded that the pragmatic CMB approach developed previously<sup>9</sup> was suitable for application to new datasets at new locations and times.

## AIM AND OBJECTIVES

The aim of this study was to investigate chemical mass reconstruction as a method to gain insight into the factors

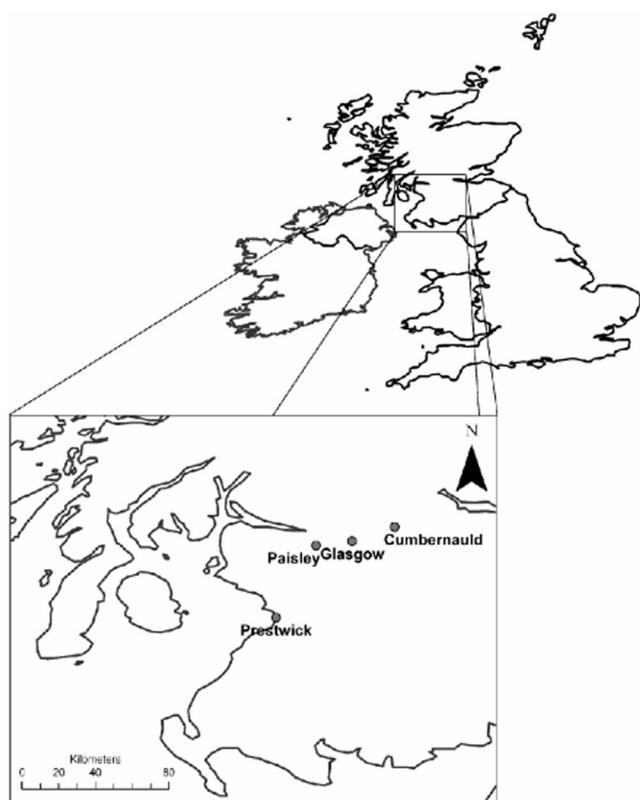
(local emissions, long-range transport, chemistry, etc.) influencing changes to  $\text{PM}_{10}$  chemical composition along a transect through a major conurbation in the United Kingdom, specifically a southwest to northeast transect through the towns of Prestwick, Paisley, Glasgow, and Cumbernauld in west-central Scotland. This is the first analysis of  $\text{PM}_{10}$  for a transect in Scotland, with only one such analysis previously reported for the UK in southwest England.<sup>21</sup>

The determination of ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), sodium ( $\text{Na}^+$ ), calcium ( $\text{Ca}^{2+}$ ), chloride ( $\text{Cl}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), and iron (Fe) extracted from collected  $\text{PM}_{10}$  is relatively straightforward, with recognized standard methods well documented in the literature.<sup>22-24</sup> However, the measurement of organic carbon (OC) and elemental carbon (EC) is problematic and there is no internationally agreed upon standard analytical procedure.<sup>25</sup> Some current methods use a combination of thermal and optical techniques to differentiate between the OC and EC fractions within a sample of  $\text{PM}_{10}$ ,<sup>26,27</sup> but there are recognized problems with these methods.<sup>25,28</sup> An alternative approach to estimate EC is via filter reflectance, but this is not a well-quantified metric and suffers from issues of colored metal oxides and overloaded filters.<sup>29</sup> In this work, a loss on ignition approach was used to quantify total organic hydrocarbon material (OHM) without requirement for further scale-up of an OC mass to total organic material mass.

## METHODS

### Sampling

Site selection was based on a transect aligned with the prevailing southwesterly wind direction,<sup>30</sup> with sites of contrasting coastal and urban environments including suburban zones upwind and downwind of a major urban center. The sampling locations are shown in Figure 1 and descriptive data in Table 1. Prestwick is a small coastal town with low vehicle density. The sampler was located approximately 240 m from the shore. Although Prestwick International Airport (PIA) is 1.5 km to the north-northeast, this is predominantly downwind of the site, and the airport has low passenger numbers compared with Glasgow International Airport (GIA) (PIA: 905,000 in 2000; GIA: 6,924,000).<sup>31</sup> Apart from the airport and local traffic there are few local anthropogenic sources of  $\text{PM}_{10}$  in Prestwick. Paisley is a larger urban area; the  $\text{PM}_{10}$  sampler was centrally located on the town hall veranda, 4 m above the ground and surrounded by urban roads carrying a total of 10,000 vehicles/day. The city of Glasgow is one of the largest urban conglomerations in the UK. The monitoring site was located in the center of the city, but 30 m above street level to represent urban background. Glasgow has one of the highest vehicle densities in the UK because of the convergence of four major transport routes (M8, M80, M77, and M74). The M8 (which has the highest vehicle density) bisects Glasgow, the nearest point of which lies 860 m to the northwest of the sampling site. There are two major railway termini in Glasgow that operate many diesel trains and are a considerable local source of EC. The predominantly downwind, suburban Cumbernauld monitoring site was located in a residential housing estate, adjacent to a road with a vehicle density of approximately 3000 vehicles/day.



**Figure 1.** Map of the PM<sub>10</sub> sampling locations.

Samples of PM<sub>10</sub> were collected concurrently at the four sites using U.S. Environmental Protection Agency (EPA) Federal Reference Method filter samplers (Thermo Partisol 2000) each fitted with an EPA-approved SA246b Graseby Andersen PM<sub>10</sub> size-selective inlet and sampling at a flow rate of 16.7 L min<sup>-1</sup>. Samples were collected daily (starting at 8:00 a.m. each day) from August 7 to 17, 2000.

### Gravimetric and Chemical Analysis

Samples were collected onto 47-mm diameter Whatman QMA quartz fiber filters with 0.6- $\mu$ m diameter pore size. All filters were baked for 4 hr at 900 °C in a muffle furnace before use,<sup>27</sup> then washed with 18 M $\Omega$  water, air-dried in Petri dishes, and placed in a desiccator to equilibrate for 48 hr at 35–45% relative humidity (RH) and 20  $\pm$  2 °C before weighing. The filters, including blanks and six control filters, were weighed using a Sartorius MC5 microbalance following the protocol used by Heal et al.<sup>32</sup> An antistatic dissipater was used to eliminate weighing artifacts due to electrostatic charge. Gravimetric imprecision was calculated to correspond to 1  $\mu$ g m<sup>-3</sup> for a 24-hr sample.

After re-weighing, the loaded filters were cut into thirds for chemical analysis: one third for the analysis of cations (Na<sup>+</sup>, Ca<sup>2+</sup>, and NH<sub>4</sub><sup>+</sup>) and anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>), one third for the analysis of Fe (and other trace metals), and one third for indirect quantification of OHM via mass loss on ignition at 550 °C. Blank filters were used to check for background contamination for all analyses.

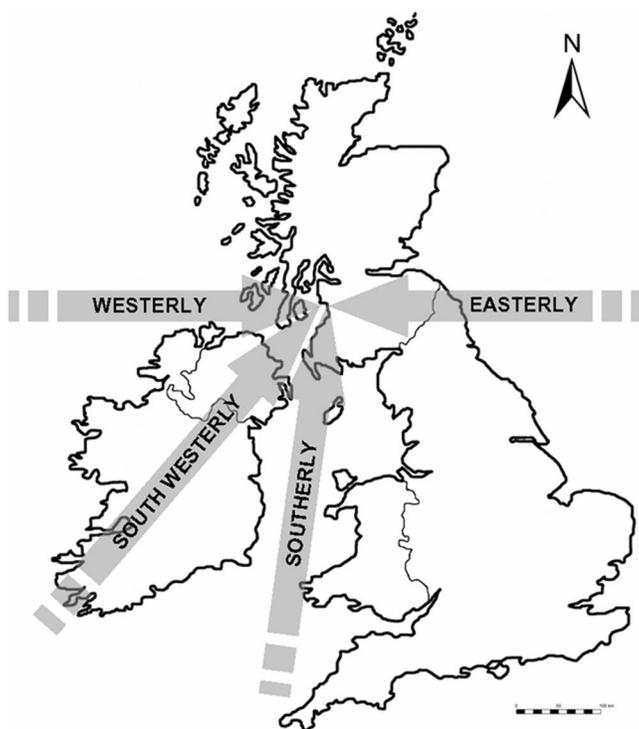
The filter portions for anion and cation determination were extracted with sonication into 5 mL of 18-M $\Omega$  water and the solution was analyzed using a Dionex 2000i ion chromatography system with conductivity detection.<sup>8</sup> For cation analysis, a Hamilton PRP-X200 separation column (Phenomenex) was used, with a mobile phase of 4 mM nitric acid (HNO<sub>3</sub>) in 3:7 methanol:water at a flow rate of 2 mL min<sup>-1</sup>. For anion analysis, a Dionex AS4A separation column preceded by a Dionex AG4A guard column was used, with a mobile phase of 1.8 mM sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and 1.7 mM sodium bicarbonate (NaHCO<sub>3</sub>) at a flow rate of 2.5 mL min<sup>-1</sup>. A Dionex AMMS-II Anion Micro Membrane Suppressor was also used, with a suppressor regenerant consisting of 25 mM sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) at a flow rate of 6 mL min<sup>-1</sup>. In both cases, sample injection volume was 100  $\mu$ L. Fe and other trace metals were extracted from the filter using a mixed acid solution (5 mL) prepared by mixing concentrated HNO<sub>3</sub> (65 mL) and concentrated hydrochloric acid (HCl; 185 mL) and diluting to 1:1 with 18-M $\Omega$  water. Four drops of concentrated perchloric acid were added to each 5-mL extract solution to aid the extraction process. The extracts were heated to 40 °C for 2 hr, followed by 1 hr at 90 °C and 2 hr at 140 °C, then diluted to 10 mL with 18-M $\Omega$  water and centrifuged at 10,000 revolutions per minute (rpm) for 10 min. Metal concentrations were determined using inductively coupled plasma-optical emission spectrometry (Jobin-Yvon 138) against seven-point standard calibration curves. The loss on ignition at 550 °C provides a good estimate of the organic hydrocarbon content of PM<sub>25</sub>,<sup>27</sup> once corrected for loss of other volatile material (see later). It is recognized that some hydrocarbons may char rather than be driven off at this temperature and thus lead to an underestimation of OHM and an overestimation of EC (as derived here from the remaining “unaccounted for” mass of PM<sub>10</sub>).

### Meteorological Data

Temperature and RH were recorded by each Partisol unit at each monitoring location. Other meteorological data (local wind direction, wind speed, and rainfall) were obtained from a meteorological station 12.2 km west of the Glasgow monitoring site, 5.9 m above mean sea level.

**Table 1.** Summary of PM<sub>10</sub> monitoring site characteristics.

Location	Site Characteristics	Site Coordinates Latitude/Longitude	Distance from Adjacent Site Running Southwest to Northeast (km)	Elevation (m)	Population	Area (km <sup>2</sup> )
Prestwick	Coastal	55.49527° north/4.61768° west	0	4.9	15,476	10
Paisley	Urban	55.84524° north/4.42147° west	42	9.0	77,000	40
Glasgow	Urban	55.86175° north/4.24453° west	8	30.0	611,440	110
Cumbernauld	Suburban	55.93493° north/4.03643° west	17	86.0	51,500	50



**Figure 2.** Four wind direction groups defined during sampling between August 7 and 17, 2000.

Synoptic charts were obtained from the Royal Meteorological Society (<http://www.rmets.org>) and used to classify wind direction according to the Lamb weather type, which contains eight main directional types: north, northeast, east, southeast, south, southwest, west, and northwest.<sup>30</sup>

In addition, 5-day air mass back trajectories were calculated for arrival every 6 hr at the 950-hPa pressure level at each site using software and data at the British Atmospheric Data Centre (<http://badc.nerc.ac.uk>). Air mass back trajectories are a useful tool for determining potential upwind sources of air pollutants reaching a receptor.<sup>33,34</sup> Trajectories were visualized using the AGIS Geographical Information System<sup>35</sup> and categorized according to the broad geographical sector over which they had passed before reaching each site, with categorization defined by having at least 70% of the trajectory in that sector.<sup>30</sup>

## RESULTS

### Meteorology

Generally there was little rainfall during the study period. August 7, 8, 11, 12, 14, and 17, 2000 had little rain, ranging between 2 and 4 mm; the remaining days were dry. The RH was unusually high, between 95 and 100% at all of the monitoring locations, compared with the normal range of 71–90% for this location.<sup>36</sup> The winds were predominately from the west and southwest with a fairly uniform wind speed of approximately  $3 \text{ m sec}^{-1}$ .

### Data Groupings

Daily air mass back trajectories could be consigned as described above to one of the following four categories, illustrated in Figure 2:

- Westerly: Five days spent over the Atlantic before making landfall in the vicinity of Prestwick.
- Southwesterly: From the Atlantic, then crossing Ireland from southwest to northeast before crossing the Irish Sea before making landfall in the vicinity of Prestwick.
- Southerly: From the Atlantic, through the Irish Sea avoiding Ireland, England, and Wales before making landfall in the vicinity of Prestwick.
- Easterly: Originating in eastern Europe and crossing the North Sea and central Scotland before reaching the transect sites.

Scrutiny of the local wind direction plots, Lamb weather types, and chemical compositional data revealed similarities for certain sampling events (e.g., for August 7 and 8). These days were characterized by a westerly wind and low levels of  $\text{PM}_{10}$  at Prestwick and Paisley. The air mass back trajectories confirmed similar geographical categorization. On this basis, these two days were grouped within the westerly classification. Days were grouped together only if both the meteorological parameters and the PM chemical composition were similar. This approach to grouping yielded the classification shown in Table 2. In the case of August 14, the local wind direction was highly variable and it was not possible to assign it into a well-defined category.

### Transect $\text{PM}_{10}$ Gravimetric Concentrations

The descriptive statistics of the  $\text{PM}_{10}$  concentrations at each location along the transect are illustrated as box plots in Figure 3.

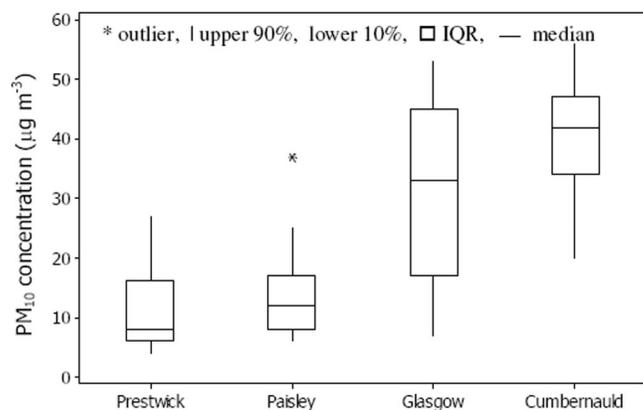
### Mass Reconstruction

The numerical procedures used to reconstruct  $\text{PM}_{10}$  chemical composition from measured components are detailed in Table 3 and were based on the work of Harrison et al.<sup>9</sup> but with minor modifications. First,  $\text{NH}_4^+$  content was measured explicitly in this work so it was possible to independently calculate contributions from each of ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), and  $\text{NaNO}_3$ . Secondly, total OHM was derived indirectly. The loss on ignition method drives off hydrocarbon species, but also drives off particle-bound water and volatilizes  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  (which all have volatilization temperatures well below the  $550^\circ\text{C}$  temperature used). The mass of OHM in each sample is therefore the mass lost during the heating after subtraction of the masses of these latter components. Any other

**Table 2.** Data group categories.

Air Flow Data Group	Dates (August 2000)
Westerly	10
Westerly	7 and 8
Southwesterly	11, 15, 16, and 17
Southerly	9
Southerly	12 (spanning Saturday and Sunday)
Easterly	13

*Notes:* August 14 could not be categorized because of too much deviation in the air flow.



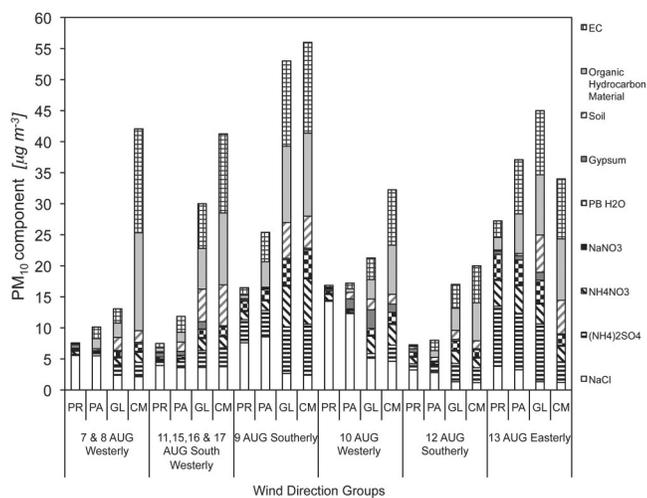
**Figure 3.** Box plots of the PM<sub>10</sub> concentrations measured at each site in the transect over the period August 7–17, 2000.

unidentified component that might also be lost on combustion will have small mass contribution compared with the major chemical species accounted for in Table 3. After accounting for all of the other components detailed in Table 3, the remaining mass in each PM<sub>10</sub> sample was assigned as EC. Thus, the CMB approach used here reconstructs the entire PM<sub>10</sub> mass by definition. As discussed in the introduction, any OHM that chars in situ on the filter rather than being driven off will erroneously be assigned as EC, but this is also an issue for more sophisticated thermal/optical OC-EC analyzers.

The PM<sub>10</sub> reconstructed mass (as defined above), for each site and for each wind direction categorization, are shown in Figure 4 and expressed as percentage fractions of each reconstructed mass in Figure 5.

### PM<sub>10</sub> Dispersion along the Transect

SCREEN VIEW, an EPA Gaussian dispersion screening model,<sup>37</sup> was used to assess the dispersion of primary surface emissions of PM<sub>10</sub> from an upwind site downwind to the next site along the transect. The meteorology observed during southwest airflow was used in the model because this is in alignment with the transect sites. The model assumes that PM<sub>10</sub> does not change state over the time scale modeled and that wind direction remains constant. The model does not



**Figure 4.** PM<sub>10</sub> reconstructed mass by site and by wind direction group (August 7–17, 2000).

include background and/or long-range transported PM<sub>10</sub> sources. Additionally, only simple terrain can be incorporated into the model, whereas there are hills between Prestwick and Paisley. However, the terrain from Paisley to Glasgow to Cumbernauld does fit the “simple” category. Despite these simplifications, the model provides some useful insight into the extent to which dispersion of primary PM<sub>10</sub> emissions at the upwind site can impact the downwind receptor. Figure 6 illustrates the modeled dispersion of primary emissions of PM<sub>10</sub> in Glasgow downwind toward the Cumbernauld site. The modeled contributions, on average, to the total PM<sub>10</sub> concentrations at each site because of primary PM<sub>10</sub> emissions from the adjacent upwind urban area were as follows: Prestwick to Paisley = 0.34 µg m<sup>-3</sup>, Paisley to Glasgow = 3.6 µg m<sup>-3</sup>, and Glasgow to Cumbernauld = 8.5 µg m<sup>-3</sup>.

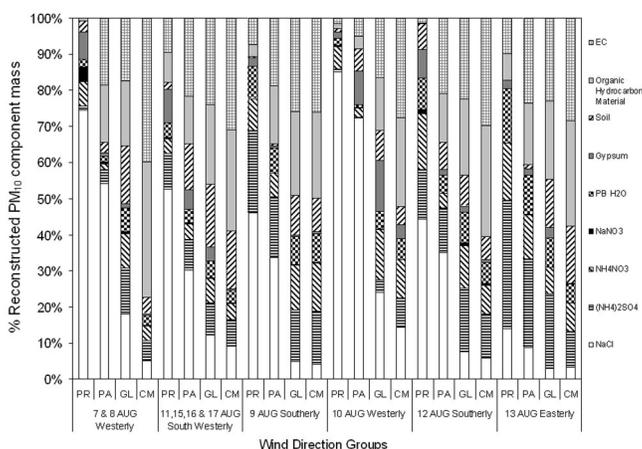
### DISCUSSION

Although the discussion here necessarily focuses on the data obtained in this study, it demonstrates the general approach that can be taken to analyzing PM compositional data from along a transect.

**Table 3.** Adjustment factors used in mass closure.

Analyte	Conversion to	Numerical Factor
SO <sub>4</sub> <sup>2-</sup>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Take measured mass of SO <sub>4</sub> and subtract (2.4 × Ca) to yield a corrected SO <sub>4</sub> <sup>2-</sup> not contained within gypsum. Multiply result by 1.375
Ammonia (NH <sub>3</sub> )	Particle-bound water	Multiply (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> by 0.29
	NH <sub>4</sub> NO <sub>3</sub>	Take measured mass of NH <sub>4</sub> <sup>+</sup> and subtract (0.375 × corrected mass of SO <sub>4</sub> <sup>2-</sup> as above) to yield NH <sub>4</sub> <sup>+</sup> not associated with (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . Multiply result by 4.44 to yield NH <sub>4</sub> NO <sub>3</sub>
NO <sub>3</sub> <sup>-</sup>	Particle-bound water	Multiply NH <sub>4</sub> NO <sub>3</sub> by 0.29
	NaNO <sub>3</sub>	Take measured mass of NO <sub>3</sub> and subtract (0.775 × derived mass of NH <sub>4</sub> NO <sub>3</sub> ) to yield NO <sub>3</sub> not associated with NH <sub>4</sub> NO <sub>3</sub> . Multiply result by 1.375 to yield NaNO <sub>3</sub>
Cl <sup>-</sup>	NaCl	Multiply Cl <sup>-</sup> by 1.648
Ca <sup>2+</sup>	CaSO <sub>4</sub> ·2H <sub>2</sub> O (gypsum)	Multiply Ca <sup>2+</sup> by 4.30
Fe	Soil/road dust	Multiply Fe by 7.50
Mass lost on filter combustion	OHM	Take mass of material lost on combustion and subtract (mass of (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + NH <sub>4</sub> NO <sub>3</sub> + associated particle-bound water).
Unexplained mass	EC	Remaining mass ~ EC

Notes: Adapted with permission from Harrison et al.<sup>9</sup> Copyright 2003 Elsevier, *Atmospheric Environment*.



**Figure 5.** Percent reconstructed  $PM_{10}$  mass by site and wind direction group (August 7–17, 2000).

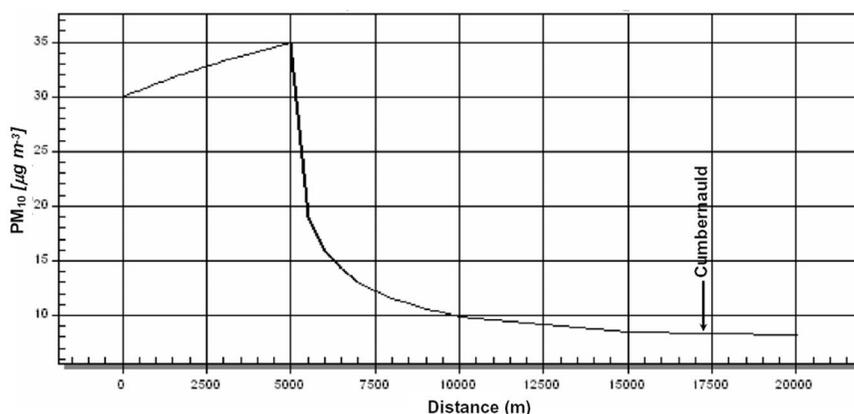
A multivariate analysis of variance confirmed the visual impressions gained from Figures 3–5; namely, that sampling site has a significant effect on the mean concentrations of NaCl,  $(NH_4)_2SO_4$ ,  $NH_4NO_3$ ,  $NaNO_3$ , OHM, soil, and EC in sampled  $PM_{10}$  ( $P = 0.015$ ), and that wind direction also has a significant effect upon the mean concentrations of the same components ( $P = 0.014$ ). The interpretations of the detail of the observed differences in  $PM_{10}$  composition sampled along the transect are given below.

Figure 3 shows that the highest average  $PM_{10}$  observed was in Cumbernauld ( $\bar{x} \pm 1 \text{ SD} = 40 \pm 10 \mu\text{g m}^{-3}$ ) and Glasgow ( $30 \pm 15 \mu\text{g m}^{-3}$ ). As shown in Figures 4 and 5,  $PM_{10}$  at these two locations is dominated by EC, OHM, soil/dust,  $NH_4NO_3$ ,  $(NH_4)_2SO_4$ , and associated particle-bound water. The lowest  $PM_{10}$  concentrations were observed at Prestwick under the conditions of the westerly airflow prevailing on August 7 and 8 ( $7.6 \mu\text{g m}^{-3}$ ); the southwesterly airflow prevailing on August 11, 15, 16, and 17 ( $7.3 \mu\text{g m}^{-3}$ ); and the southerly airflow prevailing on August 12 ( $8.8 \mu\text{g m}^{-3}$ ). Figures 4 and 5 show that under westerly airflow, the  $PM_{10}$  in the coastal town of Prestwick is dominated by NaCl, presumably of marine origin from the Atlantic. The outlier  $PM_{10}$  concentration for Paisley shown in Figure 3 is terminology assigned by the plotting

package and should not be interpreted as erroneous because the gravimetric value is consistent with the independent measurements of the major chemical components of this sample. This datum is for August 13, the one day of easterly airflow, when air masses arriving at Paisley had previously passed over Glasgow, central Scotland, and the European mainland.

The composition of  $PM_{10}$  at Prestwick and Paisley for EC, OHM,  $NH_4NO_3$ , and  $(NH_4)_2SO_4$ , was highly significant different ( $P < 0.0005$ ) under easterly airflow compared with all of the other wind direction groups (Figures 4 and 5). This suggests upwind sources of primary and secondary “aged” aerosol originating from continental Europe and central Scotland. Figures 4 and 5 also show evidence of transport of EC and OHM advected from Ireland during the period of August 11, 15, 16, and 17. These components have low concentrations at Prestwick for westerly airflow directly from the North Atlantic but missing Ireland (August 7 and 8), but they show a highly significant increase ( $P < 0.0005$ ) during southwesterly airflow that crossed Ireland and passed over the city of Belfast en route to Prestwick. Westerly airflow on August 10 also appears to have entrained some secondary aerosol (as revealed by  $NH_4NO_3$ ) before arrival at Prestwick. The air mass back trajectories showed that the air mass arriving on August 10 passed close to the north of Ireland’s coastline as compared with the westerly airflows on August 7 and 8. Despite this,  $PM_{10}$  on August 10 at Prestwick and Paisley still contained a predominant proportion from NaCl, demonstrating the significant contribution that marine aerosol makes to the total  $PM_{10}$  observed in maritime regions. Figures 4 and 5 also show that EC, OHM,  $NH_4NO_3$ , and  $(NH_4)_2SO_4$  concentrations at Prestwick and Paisley are somewhat elevated during southerly airflow (e.g., August 9) compared with westerly and southwesterly airflow, presumably because of advection of  $PM_{10}$  from England to all of the sites under these conditions.

An interesting observation is that, for most of the sampling campaign, the NaCl content of  $PM_{10}$  declines substantially between Paisley and Glasgow. It is assumed this is because of the numerous reactions that are known to occur between nitrogen dioxide ( $NO_2$ ),  $H_2SO_4$ ,  $HNO_3$ ,  $NH_4NO_3$ ,  $(NH_4)_2SO_4$ , and sodium chloride (NaCl) that



**Figure 6.** Screen view modeled  $PM_{10}$  dispersion downwind of Glasgow during southwesterly airflow. The initial rise in  $PM_{10}$  concentrations arises because Glasgow is a large area source and air continues to pick up  $PM_{10}$  primary emissions downwind from the center of the city before dispersion dominates beyond the conurbation boundary.

lead to removal of  $\text{Cl}^-$  from the particle phase via formation of gaseous HCl and nitryl chloride ( $\text{ClNO}_2$ )<sup>38,39</sup>; for example,  $\text{NaCl}_{(s)} + \text{HNO}_{3(g)} \rightarrow \text{NaNO}_{3(s)} + \text{HCl}_{(g)}$ . The loss of NaCl at Glasgow and Cumbernauld is supported by the greater  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  concentrations in Glasgow and Cumbernauld than Prestwick and Paisley (except for easterly airflow where they are comparable because of advection from more polluted terrestrial areas).

Another interesting observation is the general trend for the increased soil/resuspended component concentration from Prestwick to Paisley to Glasgow (Figure 4); this source contributes approximately 20% of the  $\text{PM}_{10}$  composition in Glasgow and Cumbernauld. The increasing trend is evidence that the soil component originates principally from local sources during passage along the transect, most likely vehicle-induced resuspension of surface soil on roads from the increased traffic density in the Glasgow and Cumbernauld area. There was no discernable site-specific or wind directional trend associated with the gypsum component because this is a marker of site-specific construction activity.

A further feature is the increase in the OHM/EC ratio moving inland from the coast. The OHM/EC ratios for all Prestwick and Paisley samples ranged from 0.20 to 0.88, whereas the OHM/EC ratios for Glasgow and Cumbernauld ranged from 0.89 to 1.00. The OHM/EC ratios observed for Glasgow and Cumbernauld are similar to those reported for other urban environments.<sup>25,40</sup> Figure 5 shows that the OHM has some spatial uniformity in Prestwick, Glasgow, and Cumbernauld, accounting for approximately 20%, on average, of total  $\text{PM}_{10}$ . This is also consistent with the findings of Jones and Harrison,<sup>41</sup> who observed that OC contributes approximately 22%, on average, to total  $\text{PM}_{10}$  with reasonable spatial uniformity across other sites in the UK. The OHM will comprise locally emitted primary OHM and secondary OHM generated on the regional scale. The lightly traffic-influenced coastal Prestwick site in this study shows lower OHM concentrations.

The simple Gaussian dispersion modeling showed that approximately  $8\text{--}9 \mu\text{g m}^{-3}$  of primary-emitted  $\text{PM}_{10}$  may be advected to Cumbernauld from Glasgow (for westerly and southwesterly wind directions). Although Figure 6 shows that primary  $\text{PM}_{10}$  emissions disperse rapidly in the first 10 km downwind, Glasgow is within this 10-km zone from Paisley; therefore, it inherits a significant  $\text{PM}_{10}$  contribution from Paisley (~12% of the mean  $\text{PM}_{10}$  concentration in Glasgow). Similarly, Cumbernauld, although 17 km downwind of Glasgow, receives considerable primary  $\text{PM}_{10}$  import from Glasgow (~20% of the total on average) because of the high primary emissions within Glasgow. These observations obviously have implications for effectiveness of local air quality management strategies.

Although the data for this study were collected several years ago and emissions of primary PM and precursors contributing to secondary PM have generally continued to decline in the UK and most of Europe, the major sources and atmospheric processes contributing to receptor-measured  $\text{PM}_{10}$  in the UK are broadly unchanged.<sup>42</sup> Thus, although the primary purpose here is to demonstrate a methodological approach, it is anticipated that the specific results for the example study area also remain valid.

## CONCLUSIONS

This work demonstrates how simultaneous sampling of  $\text{PM}_{10}$  along a transect, coupled with CMB, provides insights into the changes in  $\text{PM}_{10}$  chemical composition with prevailing wind direction; for example, in this study, on moving inland from the west coast of Scotland through the major conurbation of Glasgow. The upwind coastal site at Prestwick revealed the marine and long-range transport components, whereas  $\text{PM}_{10}$  in the city of Glasgow and at the downwind site near Cumbernauld included substantial primary material associated with high-density urban areas (EC, OHM, resuspended material). There was clear evidence of  $\text{Cl}^-$  loss from  $\text{PM}_{10}$  moving inland. Under easterly airflow, a component of long-range transport of secondary aged aerosol ( $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ) from continental Europe was apparent. Studies of the design reported can contribute to policy development by helping identify sources contributing to  $\text{PM}_{10}$  over a spatial scale more extended than at a single receptor and thus to more informed targeting of abatement measures.

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