Environmental RTDI Programme 2000–2006

AIR POLLUTION – Nature and Origin of PM_{10} and Smaller Particulate Matter in Urban Air

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Final Report

Prepared for the Environmental Protection Agency

by

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Summary

The major source categories contributing to particulate air pollution in urban as well as non-urban areas of Ireland were studied over an 18-month period (July 2001 to December 2002) using measurements at five sites including urban roadside (Site A), urban centre/background (Sites B and E), rural (Site D) and coastal (Site C) environments. Daily fine and coarse aerosol samples were collected at each site using dichotomous Partisol samplers. The measurements included gravimetric mass (PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$), soluble ions (SO_4^{2-}, NO_3^-, Cl^-, $CH_3SO_3^-$, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}), elemental carbon (EC) and organic carbon (OC). Measurements of polycyclic aromatic hydrocarbon (PAH) content as well as trace metal concentration of samples were also carried out. In addition, more intensive measurements were carried out over a 4-week period at three of the sites (rural, city centre and coastal), which included size-resolved (12 size categories) impactor sampling as well as condensation particle count (CPC) and SO_2, NO, NO_2, NO_x, O_3 and CO gaseous measurements.

An annual averaged PM_{10} mass of 35.4 µg/m^3 for 2002 was a maximum at the Dublin city kerbside site, with values of 22–24 µg/m^3 for the Dublin and Cork city centre sites. Corresponding $PM_{2.5}$ mass concentration values were 21.5 µg/m^3 and 11.5–12.5 µg/m^3, respectively. The coastal site had averaged annual values for PM_{10} and $PM_{2.5}$ mass concentration of 20 µg/m^3 and 12.5 µg/m^3, while the rural background site had values of 10.5 and 6.3 µg/m^3, respectively.

Mass closure procedures using reconstructed chemical components were used to identify major source categories contributing to the aerosol mass, namely primary marine aerosol (NaCl), secondary inorganic materials ($NH_4NO_3 + (NH_4)_2SO_4$), primary anthropogenic combustion materials (EC), primary and secondary organic materials, and resuspended dusts. Source component contributions differed for fine and coarse particles and at different locations. In urban areas, the major components contributing to fine particle mass (together accounting for 79–84% of $PM_{2.5}$ mass) were, in order, organic compounds, EC, ammonium sulphate/ammonium nitrate, whilst in the coarse fraction resuspended material and sea salt were predominant (56–66%). At the rural and coastal sites, $PM_{2.5}$ mainly consisted of ammonium sulphate/ammonium nitrate and organic materials (65%), whilst sea salt was the largest contributor to coarse particles (39% rural, 56% coastal). Unexplained materials, accounting for about 7–28% of the mass, were attributed mainly to resuspended materials at urban sites and organic materials at the other sites, as well as unmeasured water content.

Chemical component analysis (for secondary aerosol components of sulphate, nitrate and ammonium), according to air mass origin from data in Chapter 5, indicates that long-range transport from an easterly direction – mainly from the continent and the UK – to Dublin City (Site B) accounts for up to about 30% of the $PM_{2.5}$ mass (as a fraction of the total mass) **over and above** that obtained under westerly or maritime air mass conditions, and about 25% of PM_{10} mass. Results also show that local sources account for at least 50% of $PM_{2.5}$ and of PM_{10} mass for the city centre sites.

The levels of PAHs were largest at the Dublin roadside (Site A), whilst similar concentrations were observed at the urban background sites in Dublin (B) and Cork (E) due to the large number of combustion sources. Very low concentrations of the PAHs were observed at the coastal and rural sites due to the lack of significant sources. The concentrations of the particle-phase PAHs measured at the five sites are similar to those observed at other locations around the world. The concentration of benzo(*a*)pyrene is of particular interest because a threshold value of 1 ng/m^3 will be introduced as part of a new EU directive. The average monthly concentration exceeded the threshold value on a number of occasions at all urban sites. This EU Directive 2004/107/EC of the European Parliament and Council of 15 December 2004 relates to arsenic, cadmium, mercury, nickel and PAHs in ambient air and it sets a target for PAHs (using B(a)P as a marker) of 1.0 ng/m^3 to be achieved by 31 December 2012.

The highest concentrations for all metals, except magnesium, were detected at the kerbside city centre site (Site A). This was expected, mainly due to the large

number of vehicles passing the site. Within the urban sites, Site A had the highest concentration of the crustal elements Ca and Fe. Average Ca levels in Site B were almost equal to those at Site A. The concentrations at these Dublin sites were almost double those observed in Site E (Cork). This difference could be due to higher amounts of resuspended road dust in the Dublin sites, probably due to the higher volumes of traffic.

The Ca concentrations at Sites C, D and E were quite similar, with higher values for the urban sit (Site E). Fe concentrations are highest at Site A, with Sites B and E possessing higher levels than the rural and coastal sites. Since Fe is associated with vehicle emissions, then these results are not surprising. Site A showed higher concentrations for the toxic trace metals (Mn, Pb, Cd, Zn, Ni, Cr, V and Cu) than either of the other urban sites. In general, the rural site (Site D, Co. Galway) showed the lowest level of all metals. This was to be expected as this site was removed from any direct vehicle emissions and had no industry within the vicinity. The coastal site showed the highest concentration of magnesium in the coarse fraction in comparison to all other sites. Normally there are high levels of magnesium in sea spray so these observations are consistent with other results.

As with the coarse fraction, the higher concentrations of trace metals in the fine fraction were usually observed at Site A. Within the urban sites (A, B and E), Site A had consistently higher concentrations than B and E, except for Ni (highest at Site B). Sites B and E showed similar concentrations for all metals in this fraction. This was expected since B and E are both urban background sites. The coastal (C) and rural (D) sites generally showed lower fine fraction concentrations of the metals than the urban sites.

Intensive measurements were carried out during four weeks in February–March 2002 (19 February–21 March) at three sites: the rural (D), coastal (C) and city (Dublin) centre (B) sites. Additional measurements were carried out:

- condensation particle number concentration – total number of particles larger than 10 nm in size;
- SO_2, NO, NO_2, NO_x, O_3, CO gaseous measurements;
- cascade impactor (micro-orifice uniform deposit impactor – MOUDI) for collection and analysis of size-resolved particles (12 size categories);
- meteorological data: temperature, wind speed and direction, relative humidity.

On average, chemical species concentrations measured in the size-resolved impactor samples are very similar to those measured for the daily samples. Comparison between chemical mass balance and gravimetric mass allowed for calculation of the percentage of unresolved mass for the different size fractions. Missing sub-micrometre mass was up to 40% for the city centre site (and greater for the other sites) and is attributed to non-analysed OC. Unresolved mass is of the order 30–40% for the diameter range from 1 to 10 µm and is in excess of that for larger sizes.

1 Introduction

From a human perspective the importance of small atmospheric particles (PM_{10}, those particles having an aerodynamic diameter of less than 10 µm at a 50% cut-off) lies in their influence on health. Mortality rates, particularly in urban areas, have been linked to levels of atmospheric particulates (Pope *et al.*, 1992; Dockery *et al.*, 1993: Schwartz *et al.*, 1996). PM_{10} are generated from incomplete combustion processes, industry, construction and natural sources and, in many cities, the principal source is road traffic emissions, particularly from diesel vehicles. Such PM_{10} are thought to carry surface-adsorbed carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAHs); however, knowledge of their exact chemical composition remains to be fully explored. It is expected that PM_{10} will consist of inorganic elements, ions, trace metals, elemental carbon (EC), organic compounds and water although in a variety of proportions depending upon their origin, chemical processes in the atmosphere, long-range transport effects and meteorological conditions (Chow *et al.*, 1994; Eldred *et al.*, 1997; Müller, 1999).

The European Union limit value for PM_{10}, for which compliance should be reached by 2005, is 50 µg/m^3, as measured over 24-h periods, which should not be exceeded more than 35 times per year. In addition, the annual mean should not exceed 40 µg/m^3. Future limit values, for which compliance is required before 2010, are 50 µg/m^3 (to be exceeded no more than seven times per year) and an annual mean of 20 µg/m^3.

Air quality is one of the major environmental issues facing Ireland due to the country's rapid development, particularly in the transport, energy and building/road construction sectors (Keary *et al.*, 1998; EPA, 2000). Emissions from road traffic, such as NO_x, PM_{10} and benzene have become the greatest potential threat to air quality, particularly in urban areas. Very limited available information shows that these pollutants will present a difficult challenge if the future EU limits are to be met. In order to ensure future compliance, the EPA funded work, the main phase of which commenced in July 2001, to study the nature and origin of PM_{10} and $PM_{2.5}$ (aerodynamic diameter less than 2.5 µm) particles at five sites including urban roadside, urban background/centre, rural and coastal environments. This is a collaborative study carried out by the University of Birmingham (UB), the National University of Ireland, Galway (NUI, Galway), University College Cork (UCC), Dublin City Council (DCC) and Cork City Council (CCC).

Twenty-four-hour PM_{10} and $PM_{2.5}$ aerosol samples were collected using dichotomous Partisol samplers. Gravimetric masses and concentrations of chemical species were obtained. Nine ions including SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, $CH_3SO_3^-$, Na^+, K^+, Mg^{2+} and Ca^{2+} were analysed using a Dionex DX500 ion chromatograph for anions and a Dionex DX100 for cations. Sixteen PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenz(*a,h*)anthracene, indeno(*1,2,3-ck*)pyrene, fluoranthene and benzo(*ghi*)perylene) were determined by Gas Chromatography–Mass Spectrometry (GC–MS). Eleven metals (calcium, manganese, iron, nickel, zinc, magnesium, lead, chromium, vanadium, cadmium and copper were analysed with ICP–MS). EC measurement was conducted using an EEL reflectometer calibrated against a LECO RC412 carbon analyser, whilst organic carbon (OC) was estimated using ratios OC/EC, derived from results over intensive measurement periods. The size-segregated chemical composition of the aerosol was also obtained using micro-orifice uniform deposit impactors (MOUDIs) at selected sites during an intensive period to provide up to 12 size fractions within the range 0.054–18 µm, for which the same chemical analysis was conducted. In addition to the aerosol measurements, nitric oxide, nitrogen dioxide, sulphur dioxide and carbon monoxide were also measured at one of the urban sites (Dublin) over the intensive campaign to provide additional information on the sources of particles. Details of sites, measurements and analyses are provided in Chapter 2.

The main aims of the study were to characterise the processes producing the particles present in urban air, principally those in the PM_{10} fraction but also those within the finer $PM_{2.5}$ size range, and provide estimates of the importance of the different main source categories. The method used was a combined measurements and modelling approach, as outlined in the following chapters of this report, and the principal objectives of the project are given below.

i. Determine the contributions to the urban atmosphere of PM_{10} from sources within and outside of the urban perimeter.

ii. Use chemical composition measurements to determine the contributions to urban PM_{10} of the following:

    - Primary anthropogenic combustion aerosols
    - Secondary anthropogenic aerosols
    - Resuspended surface dusts and primary industrial particles
    - Marine aerosols
    - Naturally produced secondary aerosols.

iii. Use appropriate meteorological information to assess the contributions of local, regional, national, European and North Atlantic sources of $PM_{2.5}$, $PM_{2.5–10}$ and PM_{10}.

iv. Determine any seasonal variability in the major chemical source components.

v. Determine the relative importance of PM_{10} and $PM_{2.5}$ in air masses having different origins, at both urban and rural locations.

vi. Obtain size-resolved particle chemical composition measurements in order to assign accurate size distributions to the major source categories.

2 Measurement Methodologies

2.1 Aerosol Sampling

2.1.1 Sampling locations

Five sampling locations were selected to represent typical urban, rural and coastal environments (Fig. 2.1). Two urban stations (roadside and background) were established in Dublin, and one in Cork (roadside). A rural site was established in central Ireland and an east coast site was set up to sample arriving air masses crossing the Irish Sea. A full description is given below.

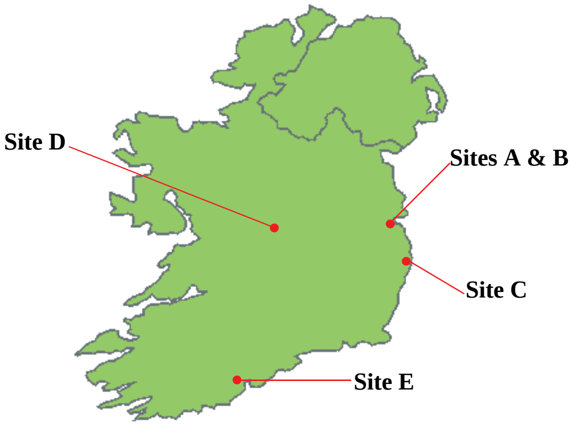


Figure 2.1. Geographical site locations.

2.1.1.1 Site A – urban roadside site

Site A (53° 21' N, 6° 16' W) is an urban roadside site situated at College Street, Dublin and surrounded by heavy traffic (Fig. 2.2). The traffic volume is around 29,000 vehicles per day.

Figure 2.2. College Street site, Dublin.

2.1.1.2 Site B – urban background/centre site

Site B (53° 21' N, 6° 17' W) is an urban background/centre site at Coleraine Street, Dublin (Fig. 2.3).

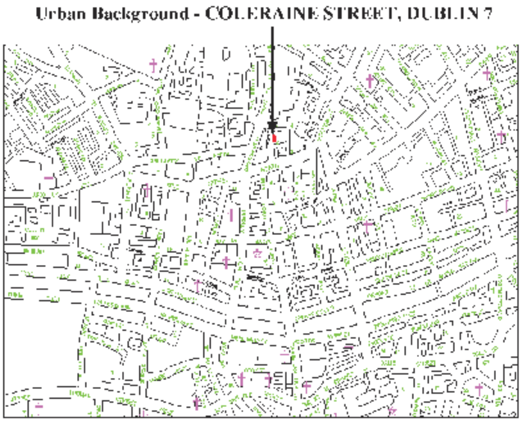


Figure 2.3. Coleraine Street site.

2.1.1.3 Site C – coastal site

Site C (52° 58' N, 5° 56' W) is a coastal site at Wicklow Head on the East Coast (Fig. 2.4), and samplers sit on the cliff top adjacent to the Irish Sea.

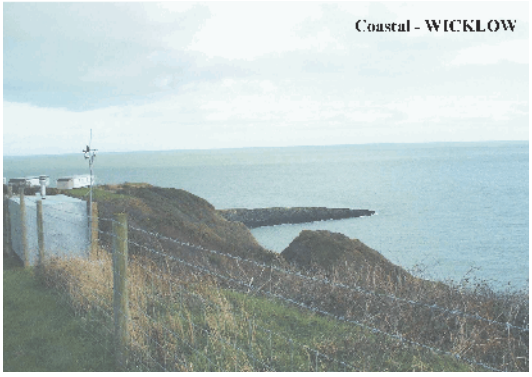


Figure 2.4. Wicklow Head site.

2.1.1.4 Site D – rural site

The rural site (53° 21' 6'' N, 8° 18' 30'' W) is located in central Ireland (Fig. 2.5), a region unaffected either by industrial or significant road traffic activities, or by unrepresentative intensive agricultural practices. It is

Figure 2.5. The rural Galway site.

about 70 km from Galway City and the western coast. The surrounding area is mainly grazing land and pasture with a few trees separating fields. There are a few farmhouses both east and west of the site. The sampler is located at a disused farmhouse. A minor road is about 200 m away from the sampler. The closest town is Ballinasloe, with a population of some 6,500, 5–6 km south-east (100°) from the site.

2.1.1.5 Site E – urban road/centre site

Site E in Cork (51° 53' 45" N, 8° 27' 57" W) is another urban roadside site, on the south side of Old Station Road, a link road between Anglesea Street and the South City Link Road (Fig. 2.6). The sampler inlet is about 5 m from the centre of the nearest traffic lane and about 4.5 m high. It is a highly trafficked roadway. Although some housing exists at 50 m, the area is commercial with much urban traffic. The best estimate for traffic on Old Station Road is 15,000 vehicles per day. On the eastern end of Old Station Road at about 50 m from the monitoring station is a junction that carries an extra 26,000 vehicles per day. On the western end of Old Station Road at about 120 m is a junction that carries about 10,000 extra vehicles per day. Meteorological sensors are located about 1 m higher than the intake at about 5.5 m above ground level.

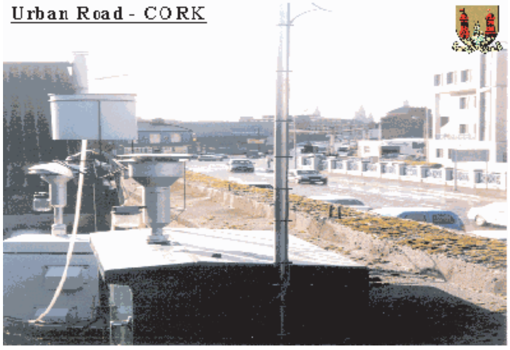


Figure 2.6. The Cork urban site.

Sampling was carried out at ground level (inlets at 2 m) except at the Cork and Dublin city centre sites, where the inlets were located at about 4.5 m and 4 m, respectively, above the ground.

2.1.2 Aerosol sampling

Twenty-four-hour fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$) particle samples were collected onto 47-mm diameter Whatman PTFE filters on alternate days continuously at each site using R&P Dichotomous Partisol-Plus Model 2025 Sequential Air Samplers. The system contains a virtual impactor and flow controllers located in the inlet line, separating the flow into fine and coarse fractions, at flow rates of 15.0 l/min and 1.7 l/min, respectively. Sampling was conducted over the period from July 2001 to June 2003 with filter exchange taking place at GMT 00:00 h each 48 h to obtain one 24-h sample every 48 h. However, this report only covers analysis of data taken over the period from July 2001 to December 2002. The Partisol instruments were operated by Dublin City Council at Sites A, B and C, by NUI, Galway at Site D and by Cork City Council at Site E, respectively.

Weekly aerosol samples were also collected onto 37-mm PTFE filter substrates during an intensive period (21 February 2002–21 March 2002) using MOUDI impactor samplers. The MOUDI uses circular jets to separate particles aerodynamically onto impaction stages (up to 11 size fractions) plus an inlet stage within a range of 0.056–18 µm (equivalent aerodynamic cut-off diameters at 50% efficiency: 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10 and 18 µm at a flow rate of 1.8 m^3/h). A 12-stage MOUDI was used at Sites B and D, whereas at Site C a 10-stage MOUDI was deployed. Similar chemical analysis was conducted as for the samples from the Partisol instruments, and comparison has been made between the two data sets derived from the MOUDI and Partisol samplers at each site. In addition to the aerosol measurements, nitric oxide, nitrogen dioxide, sulphur dioxide and carbon monoxide were also measured at Site B during the intensive campaign.

PM_{10} aerosol was also collected using filter holders attached to a small size-selective inlet containing a PM_{10}

impactor at a flow rate of 8.5 l/min (Luhana, 1995). The collection was conducted for two periods before the main sampling campaign and during the intensive period, and the samples used to provide information on the ratios of OC to EC and on the calibration of EC content of the exposed Partisol and MOUDI filters, determined using an EEL reflectometer. Details of measurement, analysis and calibration are described in Section 2.2.3.

2.2 Analytical Methods

2.2.1 Gravimetric analysis of PM_{10} and $PM_{2.5}$ masses

Particulate matter mass concentration was determined by weighing of the Teflon filters before and after air sampling using a Sartorius model MC5 microbalance, with a readability of 1 µg and a precision of approximately 1 µg/m^3 for 24-h samples of PM_{10} collected using the Partisol. Filters were pre-weighed in the University of Birmingham (for Sites A, B, C and D) and Cork City Council (for Site E) laboratories prior to installation in the Partisol or MOUDI samplers, and re-weighed under identical conditions after exposure. All filters were equilibrated at a relative humidity of 35–45% (30% at Cork) and a temperature of 20 ± 2°C in the weighing room for at least 24 h before weighing commenced. An ionising blower and a α-particle source (Po^{210}) were used to eliminate the effects of static electricity on the weighing process. The mass of the coarse fraction from the Partisol was corrected for fine fraction particles contained in the carrier flow.

Quality control of gravimetric procedures is assured by the inclusion of control filters during the weighing procedure. Controls are treated in an identical manner to samples, but are not exposed in the field. A typical weighing sequence consists of an initial control filter, a sequence of six sample filters, a further control filter, etc. This procedure effectively eliminates the effect of drift resulting from either instrumental anomalies or other environmental variables and, together with the use of anti-static measures, ensures accurate measurements of particle mass.

2.2.2 Chemical analyses for ionic species

Ionic species from the Partisol or MOUDI samples, including chloride, sulphate, nitrate, methanesulphonate (MSA), ammonium, sodium, potassium, magnesium and calcium were measured in aqueous filter extracts using ion chromatography in the University of Birmingham laboratory. One half of the PTFE filter was wetted with propan-2-ol (0.5 ml) and then extracted with distilled de-ionised water (10 ml) with mechanical agitation for 40 min to ensure thorough removal of the water-soluble aerosol. The resulting solutions were analysed for the anions using a Dionex DX500 chromatography system with an AS4A-SC analytical column and a GP40 gradient pump, which generates one eluent from two different solutions, de-ionised distilled water (DDW) and sodium hydroxide solution (0.1 M). Calibration was by construction of a calibration curve using a series of standards of known concentration (in the range 0.01–10 ppm). The same sample solution was also used for determination of cations using a Dionex DX100 chromatography system fitted with a CS12A analytical column. Isocratic elution of cations was achieved using 30 mN sulphuric acid as eluent.

Stock analytical standard solutions for both anion and cation calibration were prepared on a monthly basis from pure analytical grade chemicals, with dilution to working concentrations on the day of use. Detection limits were determined for each species as three times the standard deviation, calculated from the analysis of at least seven blank filters. The average values were 0.013, 0.026, 0.038, 0.017, 0.015, 0.031, 0.013, 0.011 and 0.054 ppm (solution concentrations) for MSA, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}, respectively. The sample concentrations were mostly well above the detection limits; values under the detection limit were all replaced with zero in the data analyses. Such replacements mostly represented under 5% of the total data set, but higher percentages were found for MSA (13%), coarse mode ammonium (11%) and fine mode calcium (8%). The uncertainties of the analytical methods in determining the concentrations were less than 10% (at 99% confidence level) for all ionic species measured.

2.2.3 Determination of carbonaceous compounds

A thermal method was used to quantify OC and EC (Yin *et al.*, 2005). A LECO Instruments Model RC412 Carbon Determinator was used for identifying carbonaceous compounds according to the temperature at which they oxidise while exposed to an oxygen atmosphere in a programmable furnace. By measuring the emission of carbon dioxide as the temperature is raised, a quantitative infrared absorption spectrum can be obtained. Two main temperature phases of 100–350°C and 350–800°C have been found to be suitable for identifying OC and EC. For eliminating moisture, a short phase at 100°C was used initially. The instrument was calibrated using calcium carbonate (which contains 12% carbon) as a standard and also checked against organic compounds of known composition. The detection limits for OC and EC were 6.1 and 4.5 µg, respectively, with method uncertainty about ±8.2% (at 99% confidence level). QMA (quartz) filters were used for the above analysis during an initial phase of the project and intensive periods. Pre-heating of filters at 500°C in air using a furnace prior to air sampling was performed for eliminating any volatilisable impurities and reducing the carbon blank values. It is noted that this method may cause some overestimation of EC due to charring of OC during pyrolysis (Schmid *et al*., 2001); however, no established standard procedure has been published.

The EC content of the exposed PTFE Partisol and MOUDI filters was determined using an EEL reflectometer by measuring their blackness (i.e. light absorbance). These absorption data were calibrated against the thermal method (above), based on the assumption that EC is the principal light-absorbing species in ambient air (Horvath, 1993, 1997).

Organic carbon from the PTFE samples was estimated using EC data and the ratios of OC/EC. The ratios will vary spatially and temporally, but a clear minimum ratio, which increases from 1.1 in larger cities to 1.5 at rural and remote sites, has been found in urban and rural European atmospheres (Castro *et al*., 1999). OC/EC ratios were determined according to season, either winter (October to March) or summer (April to September), and independently for fine and coarse fractions. Ratios were based on direct measurements of PM_{10} elemental and OC content at Sites B and C during an intensive measurement period in February and March 2002, and of PM_{10} and $PM_{2.5}$ elemental and OC content at all sites during January 2003. OC/EC ratios used for calculation of the OC contents during summer (April to September) were adjusted (separately for urban and non-urban sites) using previously reported seasonal values for European sites (Castro *et al*., 1999; Yin, 2002). In urban areas, the ratios used were 1.0 and 1.5 for fine and coarse particles in winter, with corresponding values of 1.5 and 2.5 in summer. At the non-urban sites (C and D), values employed were 2.0 in winter and 3.0 in summer for both fine and coarse particles. We estimate an OC/EC ratio uncertainty of around 30%.

2.2.4 Chemical analysis for PAHs

Polyaromatic hydrocarbons (PAHs) were extracted from the PTFE filters using the Soxhlet extraction method. The filters were placed in the glass vessel and extracted with dichloromethane (150 ml) for 18 h. The resulting mixture was placed in a rotary evaporator to remove the dichloromethane. The residue, containing the PAHs, was dissolved in *n*-hexane (10 ml) and then reduced to a volume of 1 ml through evaporation of the solvent. The efficiency of the Soxhlet extraction procedure was tested by using an appropriate Standard Reference Material (Urban Particulate Matter 1649, NIST). Recoveries in the range 90–107% were obtained thus confirming the high efficiency of the method.

Determination of PAH concentrations was carried out by GC–MS using a Varian GC3800 coupled to a Saturn 2000 ion trap mass spectrometer. The instrument was equipped with an auto-sampler (CP-8400 series) and controlled with Varian Saturn software. The GC–MS was operated in electron ionisation (EI) mode over the mass range 75–320 *m/z*. Chromatographic separation was achieved was a CP-Sil8CB fused silica capillary column (Chrompak, 30 m, 0.25 mm i.d., 0.25 µm film thickness) which was operated at 35°C for 1 min and then increased to 320°C at a rate of 10°C per minute and held for 5 min. Samples were placed in the auto-sampler and volumes of 1 µl were injected using the splitless mode with an injector temperature of 250°C. GC–MS calibration was carried out using standard solutions containing 0.01–0.6 ng of the 16 US EPA priority PAHs in 1 µl of acetonitrile. Each sample, including the calibration solutions, was injected three times and an average value for the concentration was obtained.

2.2.5 Chemical analysis for metals

Trace metals were extracted from the PTFE filters using a microwave-assisted acid digestion method. The filters were placed in fluoroplastic vessels, which were mounted in ceramic supporting vessels, and a standard acid digestion mixture consisting of HNO_3 (65%, 2 ml), HF (40%, 100 µl) and H_2O (2 ml) was added (Jalkanen and Hasanen, 1996; Robache *et al*., 2000). One reagent blank for each digestion was also performed to check for contamination during the process. The vessels were inserted into the microwave (Anton Paar MULTIWAVE) and a four-step programme, lasting 51 min, was used for the digestion process. The digested samples were transferred to volumetric flasks, the reaction vessels washed out with distilled water and the flask volume made up to 15 ml with distilled water. The reaction vessels were cleaned before each digestion using HNO_3 (65%, 5 ml) heated in the microwave at 1000 W for 30 min. The efficiency of the microwave digestion procedure was tested by using an appropriate Standard Reference Material (Urban Particulate Matter 1648, NIST). Recoveries in the range 91–102% were obtained thus confirming the high efficiency of the method.

Metal determination was carried out by Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) using a Perkin Elmer Optima 2000 DV Optical Emission Spectrometer fitted with a pneumatic nebuliser and a Scott spray chamber. The instrument was equipped with an auto-sampler (AS-90 series) and controlled with PE Winlab software. ICP–AES calibration was carried out using standard solutions with concentrations of 21 elements between 10 ppb and 1 ppm in 5% nitric acid. The solutions were prepared from a multi-elemental standard solution containing 21 elements at levels of 100 mg/l in 5% nitric acid (Glen Spectra Reference Material). Each sample, including the calibration solutions, was sampled three times and an average value for the concentration was obtained. In this work, the elements analysed were crustal and anthropogenic trace metals (Ca, Fe, Ni, Zn, Mg, Pb, Mn, Cr, V, Cd, Cu) chosen for their biogeochemical impact on the terrestrial ecosystems and their potential effects on human health. The quantitation limits (based on 10δ of the blank) were calculated in µg/l for each element and were 14, 2, 1, 6, 1, 3, 120, 2, 5, 2 and 2 for Ca, Mn, Fe, Ni, Zn, Mg, Pb, Cr, V, Cd and Cu, respectively.

3 Overview of Concentration Levels of PM_{10} and $PM_{2.5}$ Masses and their Chemical Components in the Irish Atmosphere

3.1 Atmospheric Concentrations of Particle Mass

3.1.1 Long-term and short-term variation of PM mass concentrations

Due to the effect of road traffic, substantial elevations of both PM_{10} and $PM_{2.5}$ concentrations were recorded at the Dublin roadside site (College Street) in comparison with the Dublin background site (Coleraine Street) and the Cork City site. The long-term average PM_{10}, $PM_{2.5}$ and coarse particle concentrations were 37.8, 22.4 and 15.4 µg/m^3, respectively, at Site A, which were about 1.5 times the concentrations at the other two urban sites, and nearly four times those at the rural site (Fig. 3.1). The observed PM_{10} elevation at Site A was 15.2 and 13.4 µg/m^3 compared to Sites B and E. These are consistent with results found at UK urban sites, showing a typical roadside elevation of around 10–20 µg/m^3 (Jones, 1996; QUARG, 1996; Yin, 2002). Roadside elevations were recorded for both fine and coarse particles, indicative of both particle fractions being affected by traffic activities. However, much higher increments of fine particle concentrations, at 10.7 and 9.9 µg/m^3, were observed than of coarse particle concentrations, at 4.5 and 3.5 µg/m^3. In comparison with the urban sites, the rural site (D) showed much lower concentrations, at 10.4, 6.1 and 4.3 µg/m^3, while the average concentrations at the coastal site were intermediate between those at urban and rural sites.

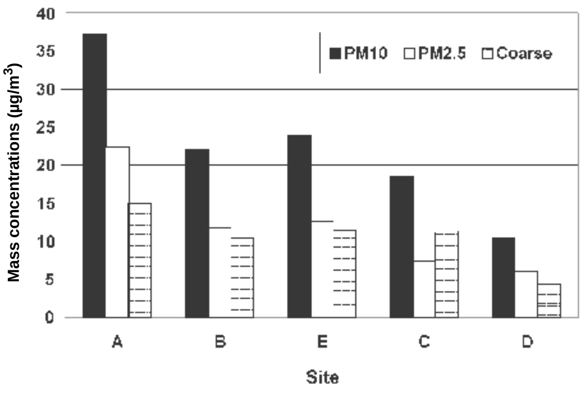


Figure 3.1. Mean particle mass concentrations at five sites in Ireland, July 2001–December 2002.

PM_{10} mass is composed of higher contributions from fine than coarse particles at these sites, except that a higher proportion of coarse particles was found at the coastal site due to a large contribution from sea salt.

Daily measurements of PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$ mass are shown in Fig. 3.2. Temporal similarity has been found at these sites, particularly at the two Dublin urban sites where the daily variation was more or less the same. Fluctuations in particle mass concentrations can be seen from season to season and year to year due largely to meteorological conditions. Pollution episodes are more likely to occur during colder weather periods and on both regional and local scales. National pollution episodes appeared to be common, when the PM was composed largely of fine particles of secondary origin formed locally or during long-range transportation. High PM_{10} concentration events were mostly dominated by fine particles at most of the sites; however, both coarse and fine fractions could contribute equally at the coastal site. Higher aerosol number concentration in the accumulation or fine particle mode for continental air masses – normally associated with anticyclonic high pressure systems, which can set themselves up as blocking highs (Jennings *et al*., 2003) – have also been found by Jennings *et al.* (1991) at Mace Head.

Monthly variation of the PM mass is shown in Fig. 3.3. As seen from the daily data, in general, winter months exhibited higher concentrations of $PM_{2.5}$ and hence PM_{10} than summer months at all sites, although this is most apparent in urban areas due to higher emissions from combustion processes such as vehicle exhaust under conditions of low dispersion in the shallow winter atmospheric boundary layer. Coarse particle concentrations were also higher in winter than during the summer period at Sites A, B, E and C due mainly to high wind speeds increasing sea salt concentrations at both

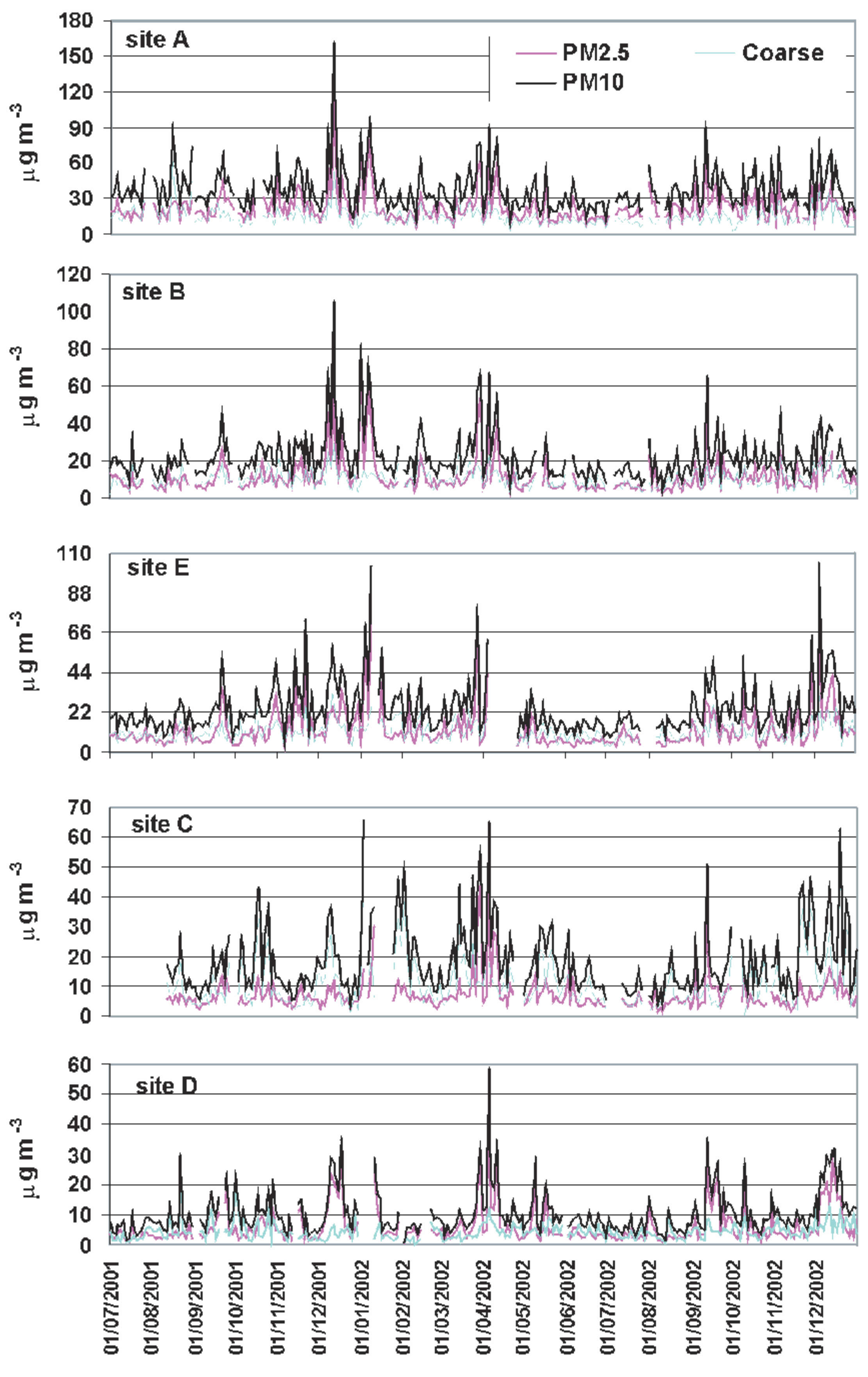


Figure 3.2. Daily variation of particle mass at five sites in Ireland, July 2001–December 2002.

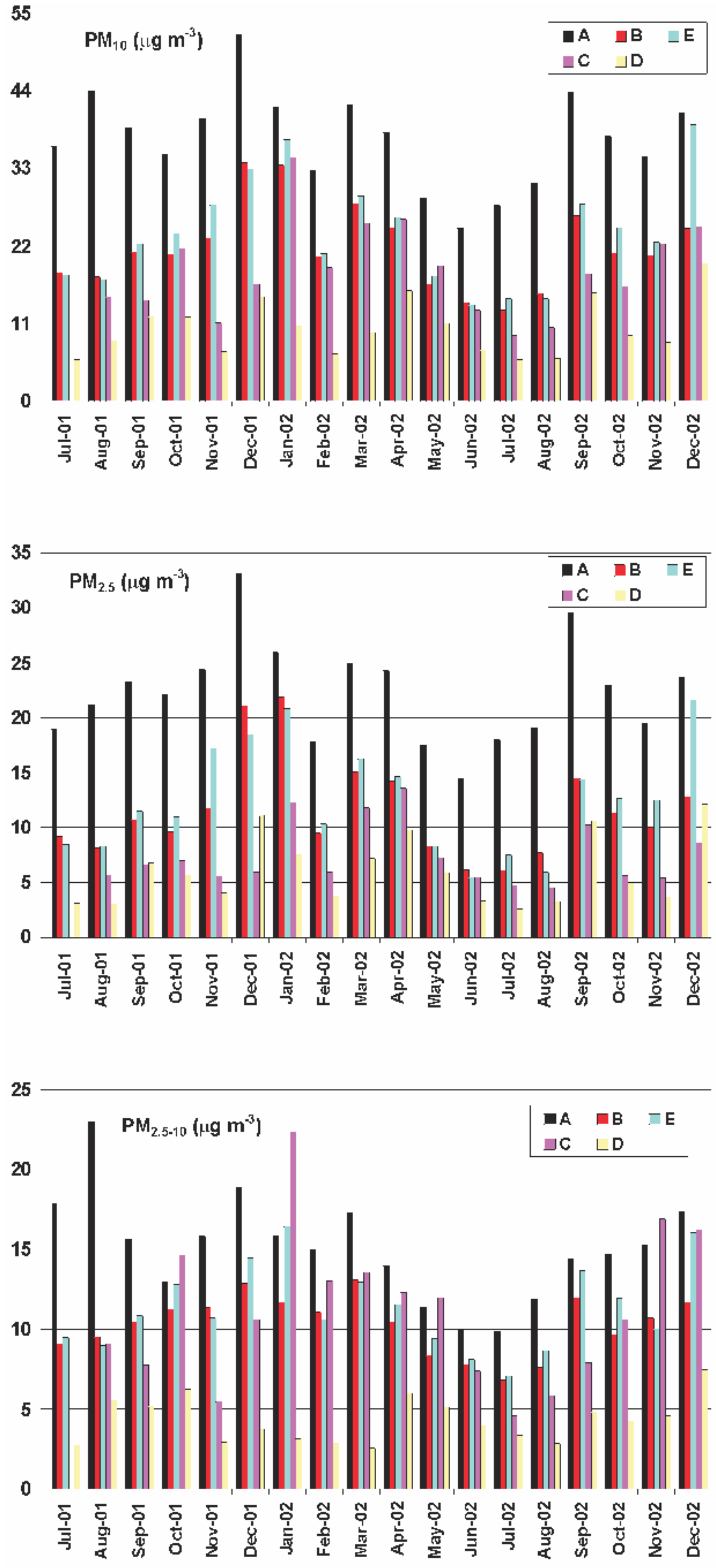


Figure 3.3. Monthly variation of particle mass at five sites in Ireland, July 2001–December 2002.

the coastal and the nearby Dublin and Cork sites. In comparison, the central rural site showed the least effect of this component. In addition, summer 2001 showed higher coarse particle and hence PM_{10} levels at Site A, presumably due to traffic or construction activity induced resuspension of dust materials under dry and hot weather conditions.

3.1.2 Number of exceedances of the PM_{10} standard limit

The 24-h PM_{10} limit value of 50 µg/m^3 was frequently exceeded (47 days) at the Dublin roadside site (Site A), whilst at the other two urban sites (Sites B and E) the number of exceedances (11 and 15 days) were much lower (Table 3.1). Since samples were taken on alternate days, if the measurement is extrapolated to all days, the number of PM_{10} exceedances is estimated as about 98 days during an 18-month period, equivalent to 65 days per year (assuming that the exceedance rate was similar for days on which measurement did not take place) at Site A. This number exceeds the EU limit application of 35 days per year to be achieved by 1 January 2005 (EU Council Air Quality Framework Directive 1999/30/EC – http://europa.eu.int/comm/environment/air/ambient.htm), indicating a current need for reducing PM concentrations to within limit values at more polluted urban locations. It should be noted, however, that Site A at College Street, Dublin is less than 4 m from the centre of the nearest traffic lane, as suggested by the siting guidelines of Directive 1999/30/EC, and so the site does not meet the EC Air Quality Directive as regards siting.

The extrapolated annual counts of the EU PM_{10} limit exceedances at Sites B and E were 15 and 21 days, which are below the limit application number of 35 days set by the year 2005, but are considerably above the limit application number of 7 days to be reached by the year 2010. At the non-urban sites (C and D), PM_{10} levels are more rarely likely to exceed the limit value, although an annual number of exceedances of more than 7 days was also recorded at Site C during the measurement period.

3.2 Atmospheric Concentrations of Particle Chemical Components

The annual average of PM fine and coarse mass concentration (µg/m^3) as well as annual averaged mass concentration of individual chemical components are given in Table 3.2. Data based on the year 2002 are used to construct the annual average.

The mean seasonal concentrations of measured chemical components based on the period from December 2001 to November 2002 are presented in Table 3.3 and in Fig. 3.4a–e separated as autumn (September–November), winter (December–February), spring (March–May) and summer (June–August) seasons for the fine and coarse fractions.

Primary sea salt (Na^+ and Cl^-), mostly present in the coarse fraction, has the highest average concentration at the coastal site (C) and lowest at the central rural site (D), although all sites are influenced by sea salt in the Irish atmosphere. Large spatial and seasonal variations were observed, with seasonal coarse concentration ranges of 0.78–6.24 µg/m^3 for Cl^- and 0.56–3.68 µg/m^3 for Na^+. The concentration levels were always higher in winter than in summer months at Sites A, B, C and E due to higher wind speeds blowing sea salt over inland areas; however, at Site D similar seasonal levels were found (Fig. 3.4a). Na^+ and Cl^- in the fine fractions showed similar seasonal trends as in the coarse fractions but less spatial variation, especially for fine chloride (which may arise from sources other than sea salt). Concentrations of coarse magnesium and potassium were low, with maximum seasonal values of 0.52 and 0.13 µg/m^3, respectively, and showed similar seasonal and spatial

Table 3.1. PM_{10} mass statistics at five sites in Ireland (data based on unadjusted alternate day measurements, July 2001–December 2002).

	Number of days exceeding 50 µg/m^3	Period	Highest 24-h concentration (µg/m^3)	Data capture (%)
Site A	47	July 2001–December 2002	161.1	95.7
Site B	11	July 2001–December 2002	105.8	94.6
Site E	15	July 2001–December 2002	104.2	93.8
Site C	5	August 2001–December 2002	66.1	84.0
Site D	1	July 2001–December 2002	57.9	94.9

Table 3.2. Annual (2002) averages of measured component concentration (µg/m^3).

		Mass	Cl^-	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	$CH_3SO_2^-$	EC
Site A	PM_{10}	35.41	1.95	1.35	0.22	0.11	1.27	0.96	2.14	1.94	0.08	8.19
	$PM_{2.5}$	21.49	0.42	0.36	0.05	0.06	0.13	0.94	1.71	1.27	0.06	7.71
	$PM_{2.5–10}$	13.92	1.53	1.00	0.17	0.05	1.14	0.03	0.43	0.67	0.03	0.48
Site B	PM_{10}	21.54	1.87	1.36	0.21	0.10	0.98	0.87	2.04	1.70	0.08	3.06
	$PM_{2.5}$	11.48	0.36	0.33	0.05	0.06	0.10	0.84	1.65	1.01	0.06	3.04
	$PM_{2.5–10}$	10.06	1.51	1.03	0.16	0.05	0.87	0.03	0.40	0.69	0.02	0.33
Site E	PM_{10}	23.92	2.67	1.67	0.27	0.11	0.80	0.93	2.05	1.75	0.08	2.93
	$PM_{2.5}$	12.55	0.53	0.34	0.05	0.05	0.09	0.87	1.54	1.16	0.06	2.81
	$PM_{2.5–10}$	11.37	2.14	1.33	0.22	0.06	0.71	0.08	0.51	0.60	0.03	0.28
Site C	PM_{10}	19.87	4.85	3.17	0.45	0.14	0.28	0.83	2.62	1.77	0.10	0.44
	$PM_{2.5}$	7.98	0.72	0.64	0.10	0.05	0.08	0.75	1.93	0.93	0.09	0.44
	$PM_{2.5–10}$	11.88	4.12	2.53	0.35	0.09	0.21	0.08	0.69	0.84	0.03	–
Site D	PM_{10}	10.49	1.48	0.93	0.16	0.06	0.22	0.69	1.42	1.31	0.08	0.52
	$PM_{2.5}$	6.25	0.46	0.31	0.05	0.03	0.07	0.64	1.17	0.92	0.07	0.52
	$PM_{2.5–10}$	4.23	1.02	0.63	0.10	0.03	0.16	0.06	0.25	0.39	0.02	–

– indicates below detection limit.

variations as sodium and chloride due to a similar source. Interestingly only for the fine fraction were higher potassium concentrations apparent at urban sites compared to the coastal site (Fig. 3.4a), indicating that fine potassium arises from combustion processes as well as from natural sources.

In contrast to sea salt, a significant urban increment of calcium was observed, particularly for coarse fractions, with concentration levels at the different sites in the order A > B > E > C > D (Fig. 3.4b). Fine calcium concentrations were generally higher in urban than in non-urban areas, although differences between sites were less distinct than for coarse mode calcium. These results support the notion that calcium may be used as a marker element for resuspended materials, since traffic contributes significantly to particle resuspension (APEG, 1999; Harrison *et al.*, 2001). It is also noticed that the concentrations of coarse calcium are higher at Site B than at Site E due to better ventilation at Site E, whereas higher levels at Site C than at Site D may be attributed to sea salt effects. Fine calcium concentrations were much lower than that of the coarse mode, and only contribute approximately 10% to the total PM_{10} calcium mass.

Elemental carbon, mostly present in the fine fraction (about 91%), exhibited the highest concentrations at Site A (6.54–7.81 µg/m^3), about half or less than half of the Site A concentrations at Sites B and E (2.31–3.79 µg/m^3 and 1.79–3.62 µg/m^3), and very low concentrations at Sites C and D (0.29–0.55 µg/m^3 and 0.17–0.66 µg/m^3). Large spatial variation reflects the fact that EC arises mostly from local combustion sources, largely vehicle exhaust emissions in urban areas (Fig. 3.4c). In comparison, seasonal variation in EC was fairly small although higher levels were found in winter and autumn than in spring and summer time.

Secondary component sulphate, ammonium and nitrate showed less spatial variability (Fig. 3.4d), but larger seasonal differences, particularly for nitrate. The highest concentrations for the fine fraction were observed in spring, whilst the lowest levels were found in summer months. Previous studies conducted in the UK also recorded higher activities of secondary particle formation

Table 3.3. Seasonal mean concentrations (μg/m^3) of measured chemical components at five sites in Ireland, December 2001–November 2002.

			Cl^-	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	$CH_3SO_3^-$	EC
Site A	Fine	Autumn	0.46	0.35	0.05	0.10	0.16	0.95	1.70	1.06	0.01	7.65
		Winter	0.88	0.50	0.08	0.08	0.18	0.92	1.96	1.28	–	7.81
		Spring	0.32	0.45	0.06	0.05	0.12	1.39	1.85	2.00	0.05	6.54
		Summer	0.16	0.23	0.04	0.06	0.18	0.65	1.58	0.47	0.10	7.10
	Coarse	Autumn	1.34	0.87	0.15	0.06	1.32	0.03	0.41	0.66	–	0.71
		Winter	2.16	1.32	0.22	0.05	1.31	0.01	0.59	0.56	–	0.62
		Spring	1.65	1.27	0.19	0.03	1.22	0.03	0.42	0.78	0.01	0.48
		Summer	0.82	0.60	0.12	0.07	1.58	0.01	0.36	0.47	0.02	0.53
Site B	Fine	Autumn	0.30	0.30	0.04	0.08	0.15	0.81	1.66	0.74	0.01	3.37
		Winter	0.77	0.45	0.07	0.08	0.15	0.91	1.83	1.30	–	3.79
		Spring	0.28	0.46	0.06	0.05	0.11	1.21	1.83	1.69	0.05	2.56
		Summer	0.14	0.22	0.03	0.04	0.09	0.57	1.47	0.28	0.10	2.31
	Coarse	Autumn	1.45	0.99	0.15	0.06	1.09	0.04	0.39	0.76	–	–
		Winter	2.14	1.34	0.22	0.05	0.93	0.02	0.56	0.61	–	0.19
		Spring	1.55	1.32	0.18	0.03	1.01	0.02	0.37	0.79	0.01	–
		Summer	0.78	0.58	0.11	0.05	0.84	0.02	0.28	0.47	0.02	–
Site E	Fine	Autumn	0.51	0.33	0.05	0.07	0.15	1.15	1.72	0.98	0.01	3.43
		Winter	0.93	0.45	0.07	0.07	0.11	1.01	1.65	1.12	–	3.62
		Spring	0.53	0.40	0.06	0.04	0.09	1.17	1.85	2.42	0.04	2.46
		Summer	0.21	0.24	0.04	0.05	0.13	0.37	0.97	0.16	0.09	1.79
	Coarse	Autumn	2.00	1.34	0.20	0.08	0.76	0.06	0.42	0.64	–	–
		Winter	2.96	1.85	0.30	0.08	0.77	0.11	0.76	0.68	–	0.28
		Spring	2.20	1.39	0.22	0.05	0.68	0.05	0.51	0.70	0.02	–
		Summer	1.18	0.86	0.13	0.06	0.65	0.01	0.27	0.25	0.06	–
Site C	Fine	Autumn	0.65	0.59	0.08	0.05	0.09	0.68	1.72	0.45	0.01	0.48
		Winter	1.17	0.93	0.14	0.05	0.11	0.51	1.62	0.93	–	0.51
		Spring	0.67	0.69	0.11	0.04	0.05	1.10	2.33	1.82	0.06	0.55
		Summer	0.24	0.36	0.06	0.04	0.06	0.55	1.61	0.30	0.12	0.29
	Coarse	Autumn	3.58	2.38	0.30	0.10	0.22	0.08	0.59	0.72	–	–
		Winter	6.24	3.68	0.52	0.13	0.27	0.06	1.04	0.72	–	–
		Spring	4.07	2.66	0.35	0.07	0.21	0.11	0.67	1.13	0.01	–
		Summer	1.69	1.28	0.19	0.07	0.13	0.03	0.33	0.54	0.02	–
Site D	Fine	Autumn	0.32	0.26	0.04	0.04	0.06	0.68	1.16	0.67	0.01	0.42
		Winter	0.80	0.43	0.07	0.04	0.12	0.77	1.23	1.25	–	0.66
		Spring	0.46	0.35	0.06	0.02	0.05	0.80	1.30	1.42	0.04	0.44
		Summer	0.19	0.20	0.03	0.02	0.04	0.31	0.77	0.18	0.09	–
	Coarse	Autumn	1.12	0.74	0.10	0.04	0.19	0.07	0.28	0.43	–	–
		Winter	0.96	0.60	0.10	0.03	0.18	0.04	0.29	0.34	–	–
		Spring	1.14	0.73	0.12	0.02	0.16	0.03	0.23	0.41	0.01	–
		Summer	0.80	0.56	0.09	0.05	0.16	0.02	0.21	0.22	0.02	–

– indicates below detection limit.

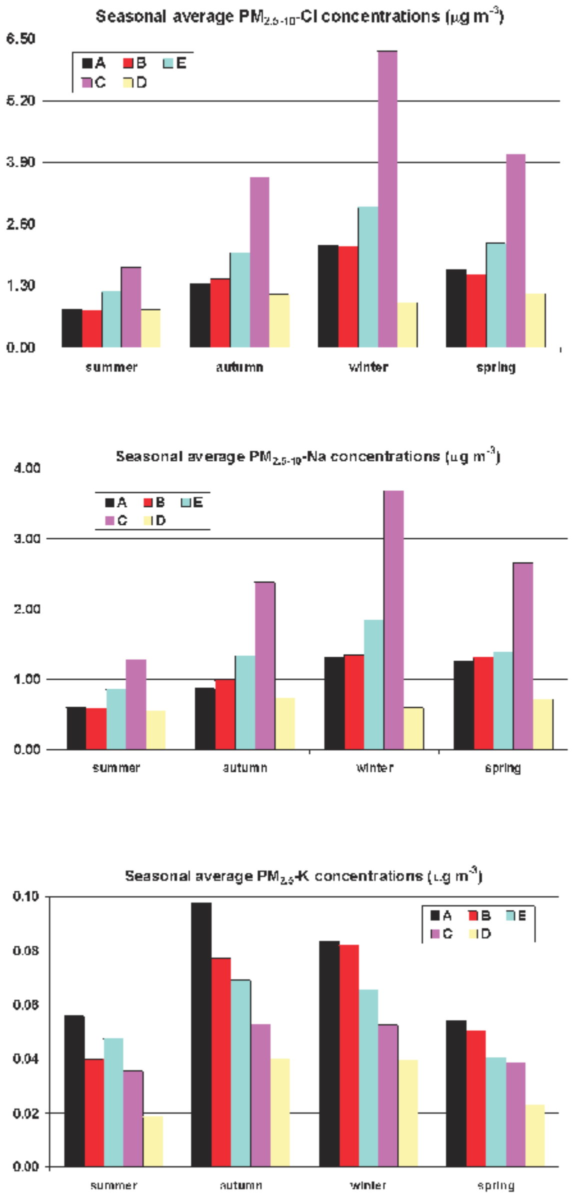


Figure 3.4a. Mean seasonal sea salt concentrations at five sites.

in spring (Yin, 2002). About three-quarters to four-fifths of SO_4^{2-} and two-thirds of NO_3^- were present in the fine fractions at these sites, and very little NH_4^+ was found in the coarse fractions.

Despite very low concentrations (0.0–0.12 µg/m^3), the maximum production of MSA occurred in summer, with little production in spring and autumn while wintertime often showed zero values. There was no clear spatial trend although higher levels were observed at Site C for fine MSA and at Site E for the coarse fraction (Fig. 3.4e).

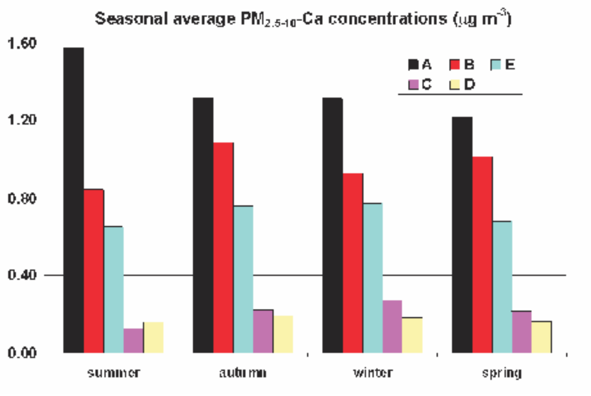


Figure 3.4b. Mean seasonal calcium concentrations at five sites.

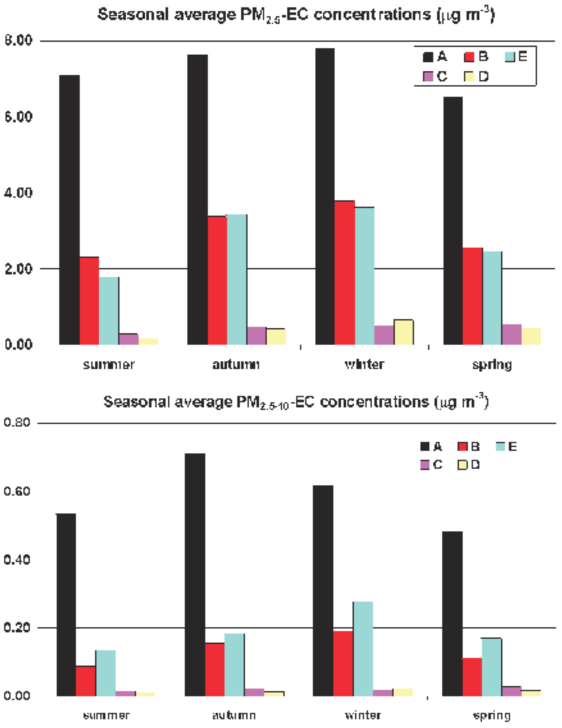


Figure 3.4c. Mean seasonal elemental carbon concentrations at five sites.

MSA can be present in both fine and coarse fractions but a higher proportion was normally found in the fine mode.

3.3 Relationship between Monthly PM Mass and its Major Chemical Component Concentrations

The monthly average mass concentrations (µg/m^3) of measured chemical components at the five sites over the

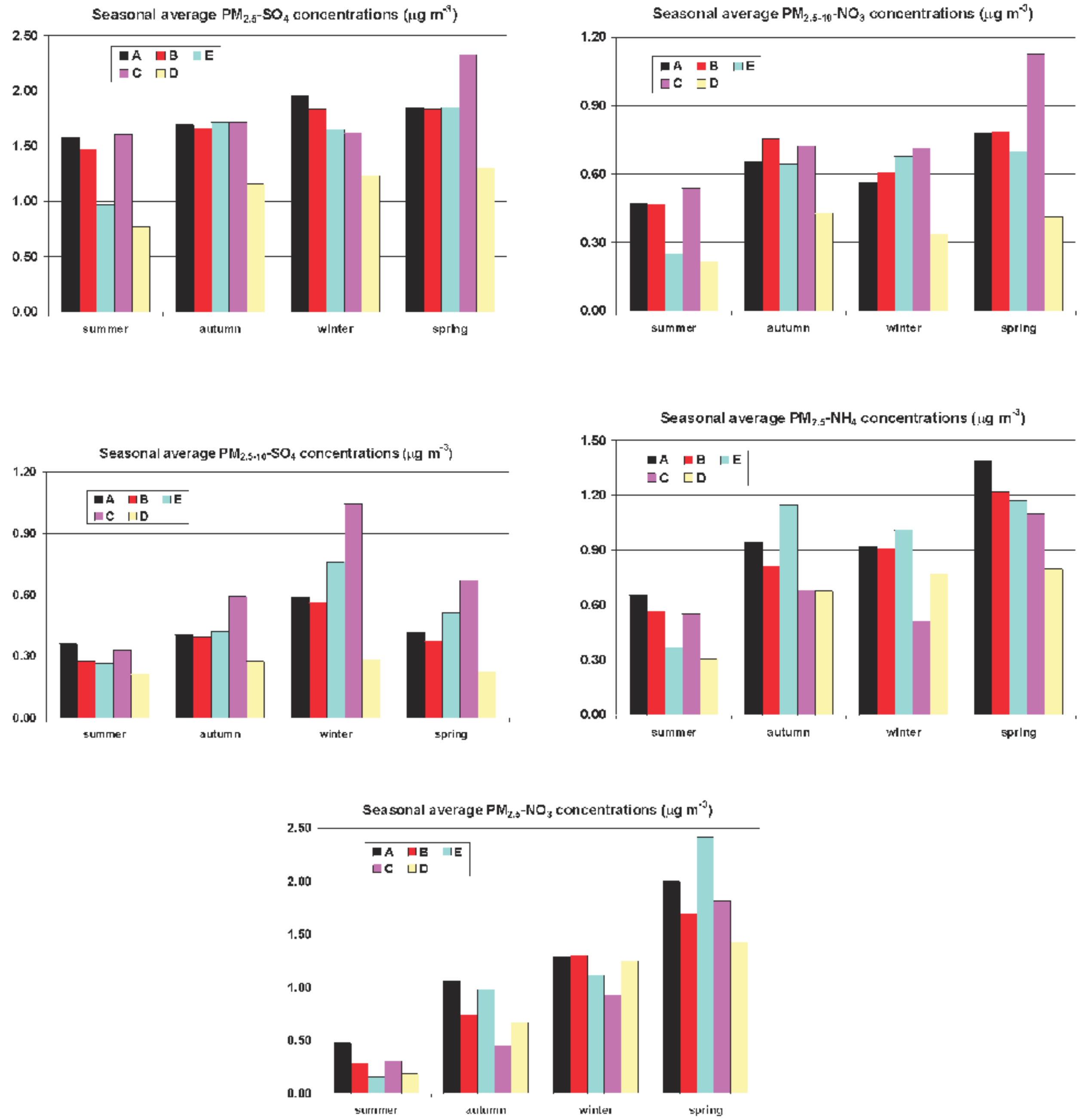


Figure 3.4d. Mean seasonal sulphate, nitrate and ammonium concentrations at five sites.

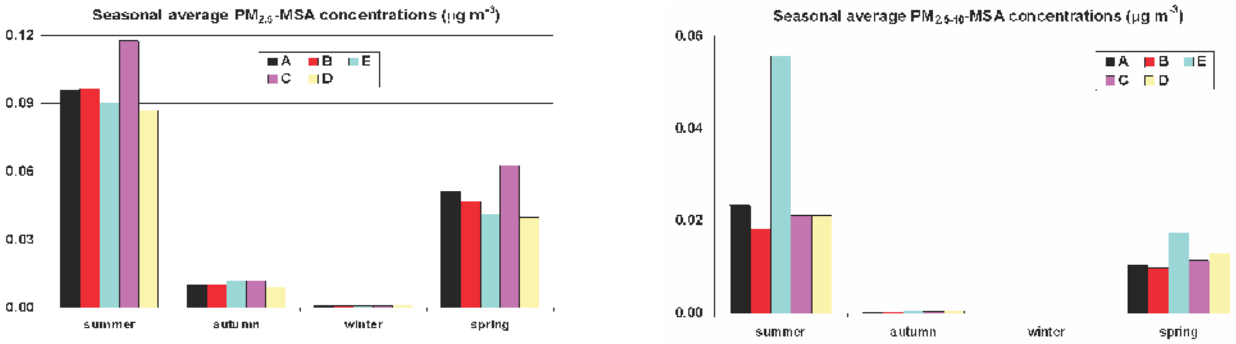


Figure 3.4e. Mean seasonal MSA concentrations at five sites.

period from June 2001 to December 2002 are presented in Tables 3.4–3.6 for fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$ and PM_{10}) mode particles. Total mass concentration ($\mu g/m^3$) for the three modes is also given.

Monthly time series are illustrated in Figs 3.5a and 3.5b for both fine and coarse particle fractions at each site. The correlation between the total mass and its chemical component mass, and the relative importance of a chemical component in contributing to the aerosol mass, were examined at each site.

The major chemical species contributing to fine particles are EC, sulphate, nitrate and ammonium (Fig. 3.5a). In general, good correlation was observed between $PM_{2.5}$ and these chemical components at all sites except at Site E where temporal inconsistency was observed. In urban areas, a greater contribution to the fine mass was found from primary EC than from inorganic secondary materials. This is particularly apparent at the Dublin roadside site. At non-urban locations, it is found that secondary source particles make a greater contribution than EC to the fine mass .

The correlation between coarse particle mass and its major chemical components (calcium, chloride, sodium and nitrate) was less clear (Fig. 3.5b). At Sites A and B, a better relationship was found between $PM_{2.5–10}$ and calcium, although both sea salt and calcium were the most significant chemical components. Conversely at Sites E and D, sea salt exhibited the highest correlation with coarse mass and calcium was less important. It must be pointed out that very good correlation between sea salt and the coarse mass was only found at the coastal site (C), where sea salt is also the major chemical component of the aerosol mass.

Table 3.4. Monthly averages of measured $PM_{2.5}$ component concentration (µg/m^3).

Month	Site code	Mass	Cl^-	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	$CH_3SO_3^-$	EC
Jul 2001	A	18.99	0.16	0.31	0.04	0.06	0.33	0.66	1.97	0.34	0.09	6.05
	B	9.21	0.16	0.30	0.04	0.05	0.11	0.60	1.92	0.35	0.09	2.41
	D	3.12	0.14	0.17	0.03	0.02	–	0.29	0.90	0.15	0.07	–
	E	8.46	0.15	0.22	0.03	0.05	0.15	0.49	1.41	0.12	0.07	2.02
Aug 2001	A	21.16	0.17	0.35	0.05	0.11	0.22	0.71	1.87	0.46	0.06	6.43
	B	8.15	0.15	0.33	0.05	0.08	0.12	0.64	1.70	0.24	0.06	2.45
	C	5.72	0.33	0.57	0.09	0.06	0.03	0.31	1.47	0.33	0.07	0.29
	D	3.04	0.15	0.23	0.03	0.03	0.02	0.26	0.66	0.13	0.04	0.20
	E	8.27	0.24	0.34	0.05	0.09	0.20	0.30	1.01	0.22	0.05	2.01
Sep 2001	A	23.28	0.41	0.40	0.05	0.09	0.05	1.22	1.74	0.96	0.02	5.97
	B	10.72	0.34	0.33	0.04	0.08	–	1.10	1.84	0.70	0.02	2.78
	C	6.64	0.49	0.44	0.06	0.05	–	0.97	1.57	0.29	0.02	0.49
	D	6.79	0.43	0.37	0.05	0.04	0.04	0.96	1.17	0.59	0.02	0.36
	E	11.51	0.46	0.36	0.05	0.08	0.14	1.34	1.67	1.03	0.03	2.12
Oct 2001	A	22.10	0.90	0.52	0.07	0.19	0.39	0.77	1.74	0.47	–	6.47
	B	9.61	0.38	0.51	0.07	0.09	0.46	0.57	1.54	0.45	–	2.53
	C	7.01	1.08	1.18	0.15	0.06	0.31	0.48	1.56	0.38	0.01	0.34
	D	5.67	0.40	0.43	0.06	0.03	0.13	0.49	1.13	0.22	0.01	0.27
	E	11.02	0.75	0.60	0.08	0.07	0.24	0.91	1.59	0.48	0.01	2.73
Nov 2001	A	24.41	0.45	0.37	0.05	0.06	0.17	0.97	1.32	0.95	–	6.99
	B	11.80	0.38	0.29	0.04	0.05	0.16	0.84	1.27	0.87	–	3.08
	C	5.61	0.40	0.39	0.05	0.03	0.09	0.45	1.13	0.36	–	0.66
	D	4.07	0.31	0.25	0.03	0.02	0.06	0.39	0.62	0.38	–	0.34
	E	17.25	0.70	0.27	0.03	0.06	0.25	1.62	1.45	1.20	–	4.76
Dec 2001	A	33.19	0.91	0.36	0.05	0.08	0.21	1.16	2.29	1.43	–	7.82
	B	21.12	0.74	0.28	0.04	0.07	0.15	1.16	2.11	1.49	–	4.91
	C	5.98	0.55	0.49	0.08	0.03	0.09	0.40	1.29	0.55	–	0.59
	D	11.14	0.53	0.21	0.04	0.05	0.14	0.99	1.11	1.69	–	0.93
	E	18.52	0.76	0.33	0.05	0.08	0.15	1.17	1.71	1.45	–	3.95
Jan 2002	A	25.98	1.30	0.61	0.09	0.15	0.29	1.15	2.43	1.60	–	8.36
	B	21.89	1.24	0.54	0.09	0.16	0.27	1.32	2.49	1.86	–	4.57
	C	12.29	1.80	1.35	0.20	0.09	0.22	0.99	2.10	2.22	–	0.54
	D	7.59	1.09	0.60	0.09	0.05	0.19	0.58	1.27	1.11	–	0.35
	E	20.83	1.55	0.73	0.11	0.09	0.18	1.22	2.10	1.35	–	3.86
Feb 2002	A	17.85	0.89	0.62	0.10	0.04	0.11	0.34	0.97	0.54	–	6.26
	B	9.48	0.84	0.60	0.10	0.03	0.10	0.28	0.85	0.48	–	2.29
	C	5.97	1.59	1.05	0.17	0.02	0.07	0.14	0.94	0.28	–	0.31
	D	3.83	1.07	0.67	0.11	0.01	0.06	0.04	0.49	0.16	–	–
	E	10.38	0.95	0.57	0.09	0.03	0.07	0.32	0.77	0.33	–	2.77
Mar 2002	A	24.94	0.46	0.72	0.08	0.07	0.19	2.08	2.16	2.67	0.04	6.79
	B	15.06	0.43	0.77	0.08	0.07	0.19	1.80	2.09	2.43	0.04	3.13
	C	11.82	1.02	0.90	0.14	0.04	0.07	1.26	2.36	2.52	0.04	0.53
	D	7.20	0.46	0.34	0.06	0.02	0.07	0.75	1.35	1.40	0.02	0.61
	E	16.27	0.54	0.35	0.05	0.04	0.08	1.24	2.21	2.62	0.04	3.48

Table 3.4. ***Contd.***

Month	Site code	Mass	Cl^-	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	$CH_3SO_3^-$	EC
Apr 2002	A	24.30	0.26	0.29	0.05	0.06	0.09	1.45	2.02	2.59	0.07	7.04
	B	14.22	0.21	0.29	0.05	0.05	0.06	1.28	2.02	2.23	0.06	2.73
	C	13.61	0.30	0.54	0.09	0.06	0.04	1.58	3.13	2.61	0.08	0.70
	D	9.75	0.55	0.38	0.07	0.03	0.05	0.98	1.24	2.14	0.06	0.47
	E	14.63	0.61	0.47	0.08	0.05	0.09	1.49	1.76	3.90	0.06	2.06
May 2002	A	17.52	0.24	0.34	0.05	0.03	0.09	0.62	1.38	0.74	0.05	5.78
	B	8.34	0.22	0.30	0.04	0.03	0.08	0.56	1.39	0.41	0.04	1.82
	C	7.28	0.70	0.64	0.09	0.02	0.05	0.45	1.50	0.33	0.06	0.40
	D	5.92	0.36	0.32	0.05	0.02	0.05	0.66	1.32	0.73	0.03	0.26
	E	8.30	0.43	0.38	0.05	0.04	0.11	0.77	1.59	0.73	0.03	1.84
Jun 2002	A	14.51	0.16	0.21	0.04	0.02	0.10	0.53	1.36	0.28	0.09	5.90
	B	6.19	0.14	0.20	0.03	0.01	0.08	0.43	1.25	0.17	0.11	1.70
	C	5.50	0.30	0.39	0.06	0.01	0.14	0.49	1.70	0.23	0.12	0.25
	D	3.30	0.29	0.27	0.05	–	0.05	0.20	0.71	0.17	0.09	–
	E	5.49	0.35	0.32	0.05	0.01	0.11	0.25	0.81	0.13	0.09	1.25
Jul 2002	A	18.03	0.16	0.12	0.03	0.03	0.09	0.58	1.27	0.40	0.17	8.68
	B	6.14	0.12	0.10	0.02	0.02	0.09	0.52	1.14	0.28	0.15	2.40
	C	4.75	0.11	0.17	0.03	0.02	0.04	0.77	1.93	0.33	0.20	0.25
	D	2.61	0.19	0.14	0.03	0.01	0.05	0.29	0.65	0.25	0.16	–
	E	7.51	0.14	0.12	0.02	0.02	0.08	0.42	0.91	0.18	0.17	1.69
Aug 2002	A	19.11	0.15	0.17	0.03	0.07	0.16	0.79	1.41	0.88	0.07	8.43
	B	7.73	0.12	0.15	0.02	0.04	0.06	0.64	1.35	0.39	0.08	2.57
	C	4.56	0.24	0.30	0.05	0.05	0.05	0.63	1.33	0.32	0.09	0.38
	D	3.27	0.17	0.18	0.03	0.03	0.06	0.48	0.92	0.21	0.07	0.21
	E	5.95	0.18	0.23	0.04	0.06	0.08	0.37	0.69	0.14	0.08	1.96
Sep 2002	A	29.54	0.13	0.14	0.03	0.09	0.08	1.66	3.30	2.21	0.03	9.85
	B	14.50	0.08	0.13	0.02	0.09	0.06	1.39	3.24	1.02	0.03	4.03
	C	10.26	0.12	0.24	0.04	0.07	–	1.48	3.80	0.73	0.03	0.64
	D	10.64	0.12	0.11	0.02	0.07	–	1.50	2.82	1.71	0.02	0.65
	E	14.38	0.13	0.17	0.03	0.08	0.06	1.64	3.49	1.39	0.03	2.92
Oct 2002	A	22.97	0.25	0.24	0.05	0.09	0.15	0.69	1.31	0.99	0.01	9.16
	B	11.37	0.16	0.19	0.03	0.08	0.08	0.62	1.25	0.68	0.01	4.08
	C	5.65	0.39	0.39	0.06	0.05	0.06	0.52	1.42	0.57	–	0.49
	D	5.03	0.19	0.12	0.02	0.04	0.05	0.54	0.73	0.81	–	0.55
	E	12.69	0.38	0.22	0.03	0.06	0.10	0.93	1.25	1.31	0.01	3.92
Nov 2002	A	19.47	0.63	0.40	0.06	0.07	0.13	0.36	0.78	0.77	–	7.43
	B	10.02	0.44	0.33	0.05	0.07	0.10	0.35	0.81	0.73	–	3.75
	C	5.47	1.41	0.90	0.13	0.05	0.07	0.18	0.82	0.37	–	0.23
	D	3.75	0.46	0.29	0.04	0.04	0.06	0.18	0.45	0.31	–	0.36
	E	12.53	0.64	0.34	0.05	0.06	0.08	0.44	0.85	0.45	–	4.11
Dec 2002	A	23.71	0.41	0.40	0.06	0.07	0.11	1.01	2.14	1.56	–	8.79
	B	12.84	0.27	0.36	0.05	0.07	0.07	0.88	1.88	1.38	–	3.39
	C	8.62	0.72	0.83	0.12	0.06	0.07	0.52	2.14	0.65	–	0.60
	D	12.14	0.50	0.24	0.04	0.06	0.07	1.47	2.07	2.04	–	1.24
	E	21.61	0.47	0.16	0.02	0.06	0.03	1.34	2.02	1.33	–	3.91

– indicates below detection limit.

Table 3.5. Monthly averages of measured $PM_{2.5–10}$ component concentration (µg/m^3).

Month	Site code	Mass	Cl$^-$	Na$^+$	Mg^{2+}	K$^+$	Ca^{2+}	NH$_4^+$	SO$_4^{2-}$	NO$_3^-$	CH$_3$SO$_3^-$	EC
Jul 2001	A	17.89	0.91	0.67	0.12	0.07	1.95	–	0.51	0.53	0.03	0.70
	B	9.08	0.76	0.58	0.10	0.05	0.78	–	0.29	0.50	0.01	–
	D	2.73	0.51	0.41	0.06	0.03	0.12	0.01	0.12	0.14	0.01	–
	E	9.48	0.91	0.71	0.10	0.06	0.71	–	0.27	0.34	0.18	–
Aug 2001	A	23.02	0.82	0.87	0.17	0.15	3.10	0.01	0.48	0.51	0.01	1.07
	B	9.52	0.86	0.87	0.14	0.11	1.31	0.01	0.38	0.62	–	–
	C	9.12	2.38	2.19	0.30	0.14	0.07	0.02	0.50	0.54	0.01	0.02
	D	5.54	0.76	0.71	0.09	0.12	0.26	0.02	0.44	0.23	0.01	0.02
	E	8.98	1.29	1.20	0.17	0.10	0.67	–	0.30	0.23	0.01	–
Sep 2001	A	15.66	1.22	0.87	0.13	0.06	1.02	0.05	0.39	0.57	–	1.03
	B	10.47	1.24	0.90	0.13	0.06	0.71	0.07	0.36	0.60	–	0.26
	C	7.76	1.77	1.27	0.16	0.06	0.11	0.12	0.35	0.59	–	–
	D	5.18	1.35	0.96	0.11	0.05	0.19	0.04	0.29	0.37	–	–
	E	10.85	1.85	1.17	0.14	0.06	0.54	0.09	0.33	0.43	–	–
Oct 2001	A	12.97	1.58	1.13	0.16	0.08	1.39	–	0.37	0.35	–	0.85
	B	11.24	1.93	1.58	0.20	0.08	1.42	0.01	0.43	0.59	–	0.21
	C	14.66	5.91	4.86	0.50	0.16	0.44	0.06	0.89	0.57	–	–
	D	6.21	1.70	1.28	0.15	0.06	0.33	0.05	0.36	0.29	–	–
	E	12.80	3.22	2.54	0.29	0.11	0.71	0.06	0.58	0.42	–	–
Nov 2001	A	15.82	1.33	0.89	0.15	0.05	2.00	0.01	0.44	0.24	–	0.54
	B	11.37	1.31	0.87	0.14	0.05	1.67	0.00	0.38	0.28	–	–
	C	5.48	1.74	1.18	0.15	0.04	0.22	0.02	0.37	0.24	–	–
	D	2.91	0.69	0.46	0.06	0.02	0.08	0.03	0.15	0.12	–	–
	E	10.69	1.44	0.99	0.13	0.07	1.00	0.01	0.39	0.35	–	0.19
Dec 2001	A	18.91	1.53	0.97	0.18	0.05	1.58	–	0.51	0.62	–	0.90
	B	12.84	1.55	1.01	0.18	0.04	1.15	0.01	0.54	0.75	–	0.23
	C	10.62	4.13	2.27	0.32	0.07	0.21	0.05	0.65	0.78	–	–
	D	3.73	0.71	0.46	0.08	0.03	0.26	0.07	0.18	0.39	–	–
	E	14.48	1.95	1.31	0.22	0.07	0.81	0.06	0.45	0.99	–	0.26
Jan 2002	A	15.87	2.35	1.46	0.22	0.06	1.19	0.02	0.70	0.52	–	0.65
	B	11.67	2.22	1.41	0.22	0.07	0.87	0.02	0.65	0.55	–	0.33
	C	22.36	9.08	5.53	0.77	0.19	0.41	0.11	1.58	1.02	–	–
	D	3.12	0.66	0.40	0.07	0.02	0.16	–	0.25	0.12	–	–
	E	16.43	4.13	2.53	0.40	0.10	0.68	0.11	0.98	0.55	–	0.31
Feb 2002	A	15.01	2.47	1.41	0.24	0.03	1.17	–	0.52	0.19	–	0.54
	B	11.06	2.54	1.50	0.24	0.04	0.89	–	0.51	0.22	–	–
	C	13.01	5.25	3.07	0.44	0.08	0.23	0.01	0.88	0.22	–	–
	D	2.86	1.27	0.73	0.12	–	0.08	–	0.21	0.06	–	–
	E	10.60	2.99	1.79	0.27	0.05	0.60	0.01	0.57	0.17	–	–
Mar 2002	A	17.24	2.16	1.98	0.24	0.03	1.96	0.04	0.53	0.86	–	0.57
	B	13.09	1.94	2.12	0.24	0.05	1.71	0.02	0.45	0.80	–	–
	C	13.56	4.79	3.26	0.39	0.08	0.23	0.14	0.76	1.19	–	–
	D	2.52	0.73	0.48	0.09	–	0.12	0.03	0.14	0.32	0.01	–
	E	12.93	1.96	1.27	0.21	0.04	0.78	0.04	0.60	0.90	–	–

Table 3.5. ***Contd.***

Month	Site code	Mass	Cl^-	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	$CH_3SO_3^-$	EC
Apr 2002	A	13.98	1.49	1.00	0.19	0.03	0.93	0.02	0.42	0.91	0.03	0.50
	B	10.44	1.47	0.99	0.17	0.02	0.73	0.03	0.37	0.93	0.02	–
	C	12.30	3.51	2.34	0.36	0.06	0.23	0.15	0.66	1.47	0.03	–
	D	5.98	1.50	0.95	0.16	0.02	0.21	0.05	0.30	0.53	0.03	–
	E	11.54	2.57	1.61	0.27	0.05	0.66	0.09	0.52	0.75	0.05	0.28
May 2002	A	11.36	1.30	0.84	0.14	0.04	0.77	0.01	0.31	0.56	–	0.39
	B	8.33	1.24	0.84	0.13	0.03	0.60	0.02	0.30	0.63	–	–
	C	11.97	3.91	2.38	0.31	0.07	0.18	0.04	0.60	0.72	–	–
	D	5.12	1.18	0.75	0.11	0.02	0.16	0.03	0.24	0.39	–	–
	E	9.43	2.07	1.29	0.18	0.05	0.60	0.01	0.42	0.45	0.01	–
Jun 2002	A	10.05	0.87	0.56	0.11	–	0.80	–	0.29	0.39	0.01	0.24
	B	7.77	0.89	0.57	0.10	–	0.71	–	0.27	0.30	0.01	–
	C	7.36	1.94	1.30	0.19	0.04	0.14	0.02	0.39	0.58	0.01	–
	D	3.96	1.15	0.70	0.10	–	0.10	–	0.20	0.18	0.01	–
	E	8.09	1.99	1.22	0.17	0.04	0.59	–	0.35	0.23	0.01	–
Jul 2002	A	9.85	0.70	0.39	0.10	0.03	0.94	0.02	0.27	0.42	0.05	0.26
	B	6.79	0.62	0.36	0.09	0.03	0.68	0.03	0.21	0.40	0.05	–
	C	4.58	1.00	0.63	0.11	0.03	0.14	0.04	0.23	0.55	0.05	–
	D	3.31	0.80	0.45	0.09	0.03	0.14	0.03	0.17	0.27	0.05	–
	E	7.07	0.66	0.40	0.08	0.02	0.63	–	0.15	0.24	0.05	–
Aug 2002	A	11.89	0.79	0.52	0.12	0.07	1.09	0.04	0.26	0.51	0.02	0.40
	B	7.57	0.75	0.53	0.10	0.06	0.74	0.06	0.23	0.51	0.02	–
	C	5.84	1.43	1.01	0.16	0.08	0.15	0.05	0.20	0.48	0.02	–
	D	2.82	0.77	0.52	0.09	0.06	0.17	0.05	0.15	0.26	0.02	–
	E	8.64	1.05	0.77	0.14	0.07	0.67	0.05	0.26	0.20	0.03	–
Sep 2002	A	14.39	0.75	0.58	0.12	0.06	1.17	0.08	0.50	1.59	–	0.55
	B	11.96	0.72	0.60	0.12	0.06	1.12	0.09	0.46	1.70	–	–
	C	7.88	1.43	1.11	0.16	0.06	0.15	0.14	0.39	1.64	–	–
	D	4.82	0.45	0.35	0.07	0.03	0.26	0.19	0.32	1.09	–	–
	E	13.70	1.09	0.90	0.17	0.07	0.99	0.14	0.41	1.75	–	0.24
Oct 2002	A	14.74	1.16	0.73	0.14	0.05	1.12	0.04	0.31	0.80	–	0.64
	B	9.66	1.36	0.87	0.15	0.06	0.78	0.03	0.34	0.92	–	–
	C	10.62	3.43	2.08	0.30	0.09	0.18	0.08	0.56	0.90	–	–
	D	4.25	0.77	0.46	0.08	0.04	0.15	0.08	0.21	0.47	–	–
	E	11.93	1.64	1.01	0.17	0.07	0.77	0.05	0.37	0.77	–	–
Nov 2002	A	15.26	2.02	1.05	0.18	0.07	1.21	0.01	0.42	0.38	–	0.66
	B	10.70	2.13	1.10	0.18	0.06	0.83	0.01	0.41	0.45	–	–
	C	16.90	7.21	3.79	0.51	0.16	0.23	0.05	1.00	0.40	–	–
	D	4.59	1.76	0.92	0.14	0.05	0.14	0.02	0.32	0.24	–	–
	E	10.02	2.78	1.45	0.28	0.08	0.54	0.02	0.45	0.15	–	0.19
Dec 2002	A	17.37	2.31	1.45	0.22	0.07	1.31	0.02	0.62	0.92	–	0.38
	B	11.70	2.24	1.46	0.22	0.07	0.81	0.03	0.55	0.91	–	–
	C	16.24	6.51	3.86	0.52	0.16	0.23	0.08	1.06	0.85	–	–
	D	7.45	1.18	0.81	0.14	0.04	0.24	0.08	0.50	0.78	–	–
	E	16.07	2.78	1.77	0.30	0.11	1.00	0.24	1.04	0.99	–	0.37

– indicates below detection limit.

Table 3.6. Monthly averages of measured PM_{10} component concentration ($\mu g/m^3$).

Month	Site code	Mass	Cl^-	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	$CH_3SO_3^-$	EC
Jul 2001	A	36.88	1.07	0.98	0.16	0.13	2.28	0.66	2.48	0.87	0.12	6.74
	B	18.29	0.91	0.89	0.14	0.10	0.89	0.60	2.21	0.84	0.10	2.41
	D	5.86	0.65	0.58	0.09	0.05	0.12	0.30	1.01	0.29	0.08	–
	E	17.94	1.07	0.93	0.13	0.11	0.86	0.49	1.68	0.46	0.25	2.02
Aug 2001	A	44.18	0.99	1.22	0.22	0.26	3.33	0.72	2.35	0.97	0.08	7.50
	B	17.67	1.01	1.20	0.19	0.19	1.42	0.65	2.07	0.86	0.06	2.45
	C	14.84	2.71	2.76	0.39	0.20	0.10	0.33	1.98	0.87	0.07	0.31
	D	8.58	0.91	0.94	0.12	0.15	0.29	0.28	1.10	0.36	0.05	0.22
	E	17.25	1.53	1.55	0.22	0.19	0.87	0.30	1.31	0.46	0.06	2.01
Sep 2001	A	38.94	1.63	1.28	0.18	0.15	1.07	1.27	2.13	1.53	0.02	7.00
	B	21.19	1.58	1.23	0.17	0.13	0.71	1.17	2.20	1.29	0.02	3.04
	C	14.40	2.26	1.72	0.21	0.11	0.11	1.09	1.91	0.89	0.02	0.49
	D	11.98	1.78	1.34	0.15	0.09	0.22	1.00	1.46	0.96	0.02	0.36
	E	22.36	2.31	1.53	0.19	0.14	0.68	1.43	2.00	1.46	0.03	2.12
Oct 2001	A	35.06	2.48	1.65	0.24	0.26	1.78	0.77	2.11	0.82	–	7.32
	B	20.85	2.31	2.08	0.27	0.17	1.88	0.57	1.97	1.04	–	2.74
	C	21.67	6.99	6.05	0.64	0.22	0.75	0.54	2.45	0.95	0.01	0.34
	D	11.88	2.09	1.71	0.21	0.09	0.46	0.53	1.49	0.52	0.01	0.27
	E	23.83	3.97	3.14	0.37	0.18	0.95	0.97	2.17	0.90	0.01	2.73
Nov 2001	A	40.24	1.78	1.26	0.20	0.12	2.17	0.98	1.75	1.19	–	7.53
	B	23.17	1.69	1.15	0.17	0.10	1.83	0.84	1.66	1.15	–	3.08
	C	11.09	2.13	1.57	0.20	0.07	0.31	0.47	1.50	0.59	–	0.66
	D	6.99	0.99	0.71	0.09	0.04	0.14	0.42	0.78	0.50	–	0.34
	E	27.94	2.14	1.26	0.16	0.13	1.24	1.63	1.84	1.55	–	4.94
Dec 2001	A	52.11	2.44	1.33	0.23	0.13	1.79	1.16	2.80	2.05	–	8.72
	B	33.96	2.29	1.29	0.22	0.12	1.30	1.17	2.65	2.24	–	5.14
	C	16.60	4.68	2.76	0.40	0.11	0.30	0.45	1.94	1.33	–	0.59
	D	14.86	1.23	0.67	0.12	0.08	0.40	1.06	1.29	2.08	–	0.93
	E	33.00	2.72	1.64	0.27	0.15	0.96	1.23	2.16	2.44	–	4.22
Jan 2002	A	41.84	3.65	2.07	0.31	0.20	1.48	1.18	3.13	2.12	–	9.00
	B	33.57	3.46	1.95	0.30	0.22	1.14	1.34	3.14	2.41	–	4.89
	C	34.65	10.89	6.88	0.98	0.28	0.62	1.10	3.68	3.24	–	0.54
	D	10.71	1.75	1.00	0.16	0.06	0.34	0.58	1.51	1.23	–	0.35
	E	37.26	5.68	3.25	0.51	0.19	0.86	1.33	3.08	1.90	–	4.17
Feb 2002	A	32.86	3.36	2.03	0.34	0.07	1.28	0.34	1.49	0.73	–	6.80
	B	20.53	3.37	2.10	0.34	0.07	0.99	0.28	1.36	0.70	–	2.29
	C	18.97	6.84	4.13	0.61	0.10	0.31	0.14	1.82	0.50	–	0.31
	D	6.70	2.35	1.40	0.23	0.01	0.14	0.04	0.70	0.21	–	–
	E	20.98	3.93	2.36	0.36	0.09	0.67	0.32	1.34	0.51	–	2.77
Mar 2002	A	42.18	2.62	2.69	0.32	0.11	2.15	2.12	2.69	3.54	0.04	7.36
	B	28.14	2.36	2.90	0.33	0.12	1.90	1.83	2.54	3.23	0.04	3.13
	C	25.38	5.81	4.16	0.53	0.12	0.30	1.41	3.13	3.71	0.04	0.53
	D	9.72	1.19	0.82	0.15	0.02	0.19	0.78	1.49	1.73	0.03	0.61
	E	29.19	2.51	1.63	0.27	0.08	0.86	1.28	2.80	3.52	0.04	3.48

Table 3.6. ***Contd.***

Month	Site code	Mass	Cl^-	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	$CH_3SO_3^-$	EC
Apr 2002	A	38.28	1.76	1.29	0.24	0.08	1.01	1.47	2.43	3.50	0.10	7.54
	B	24.66	1.68	1.28	0.22	0.08	0.79	1.32	2.39	3.17	0.08	2.73
	C	25.90	3.81	2.88	0.45	0.12	0.27	1.73	3.79	4.08	0.11	0.70
	D	15.73	2.05	1.34	0.23	0.05	0.26	1.03	1.54	2.67	0.09	0.47
	E	26.17	3.18	2.09	0.34	0.10	0.75	1.58	2.28	4.64	0.10	2.34
May 2002	A	28.89	1.54	1.17	0.18	0.07	0.86	0.63	1.69	1.30	0.05	6.16
	B	16.66	1.46	1.14	0.17	0.06	0.68	0.58	1.69	1.04	0.04	1.82
	C	19.25	4.61	3.02	0.40	0.09	0.23	0.49	2.10	1.05	0.06	0.40
	D	11.03	1.55	1.07	0.16	0.04	0.20	0.69	1.56	1.12	0.03	0.26
	E	17.73	2.50	1.67	0.23	0.08	0.70	0.78	2.01	1.19	0.03	1.84
Jun 2002	A	24.56	1.02	0.78	0.14	0.02	0.90	0.53	1.65	0.67	0.10	6.15
	B	13.96	1.03	0.77	0.14	0.01	0.79	0.43	1.52	0.47	0.11	1.70
	C	12.86	2.24	1.69	0.25	0.05	0.28	0.51	2.09	0.81	0.13	0.25
	D	7.26	1.45	0.98	0.15	-	0.14	0.20	0.91	0.35	0.10	–
	E	13.58	2.34	1.53	0.22	0.05	0.70	0.25	1.16	0.36	0.10	1.25
Jul 2002	A	27.88	0.86	0.51	0.13	0.06	1.03	0.60	1.54	0.82	0.21	8.94
	B	12.93	0.75	0.46	0.11	0.05	0.78	0.54	1.35	0.68	0.20	2.40
	C	9.34	1.11	0.80	0.14	0.05	0.18	0.80	2.16	0.88	0.24	0.25
	D	5.91	0.99	0.59	0.12	0.04	0.19	0.32	0.83	0.52	0.21	–
	E	14.58	0.81	0.51	0.10	0.05	0.71	0.42	1.06	0.43	0.22	1.69
Aug 2002	A	30.99	0.94	0.69	0.14	0.13	1.25	0.83	1.68	1.39	0.09	8.83
	B	15.30	0.87	0.68	0.12	0.10	0.80	0.70	1.58	0.90	0.10	2.57
	C	10.41	1.67	1.32	0.21	0.13	0.20	0.67	1.53	0.80	0.11	0.38
	D	6.09	0.94	0.71	0.13	0.09	0.22	0.53	1.07	0.47	0.09	0.21
	E	14.58	1.23	0.99	0.17	0.13	0.75	0.42	0.95	0.34	0.11	1.96
Sep 2002	A	43.93	0.87	0.71	0.15	0.15	1.25	1.74	3.80	3.79	0.03	10.40
	B	26.46	0.80	0.73	0.14	0.15	1.18	1.48	3.70	2.72	0.03	4.03
	C	18.13	1.55	1.36	0.20	0.13	0.15	1.62	4.19	2.37	0.03	0.64
	D	15.46	0.56	0.46	0.09	0.11	0.26	1.69	3.14	2.80	0.02	0.65
	E	28.08	1.22	1.07	0.20	0.15	1.05	1.78	3.89	3.14	0.03	3.16
Oct 2002	A	37.71	1.41	0.97	0.18	0.14	1.26	0.73	1.62	1.80	0.01	9.80
	B	21.03	1.52	1.06	0.19	0.14	0.86	0.66	1.59	1.60	0.01	4.08
	C	16.27	3.82	2.48	0.37	0.14	0.24	0.61	1.98	1.47	–	0.49
	D	9.28	0.97	0.58	0.10	0.08	0.20	0.62	0.94	1.27	–	0.55
	E	24.61	2.02	1.23	0.20	0.13	0.87	0.98	1.61	2.09	0.01	3.92
Nov 2002	A	34.73	2.65	1.45	0.24	0.13	1.34	0.37	1.20	1.16	–	8.09
	B	20.72	2.56	1.44	0.23	0.13	0.92	0.36	1.22	1.18	–	3.75
	C	22.36	8.63	4.69	0.63	0.21	0.30	0.23	1.82	0.76	–	0.23
	D	8.34	2.22	1.21	0.18	0.09	0.20	0.20	0.77	0.55	–	0.36
	E	22.56	3.41	1.79	0.33	0.13	0.62	0.46	1.30	0.60	–	4.30
Dec 2002	A	41.08	2.73	1.85	0.28	0.14	1.42	1.03	2.76	2.49	–	9.17
	B	24.54	2.52	1.82	0.27	0.14	0.88	0.91	2.43	2.29	–	3.39
	C	24.85	7.22	4.69	0.64	0.22	0.30	0.61	3.21	1.50	–	0.60
	D	19.59	1.69	1.05	0.17	0.10	0.31	1.55	2.58	2.82	–	1.24
	E	37.68	3.26	1.94	0.32	0.17	1.03	1.58	3.06	2.32	–	4.28

– indicates below detection limit.

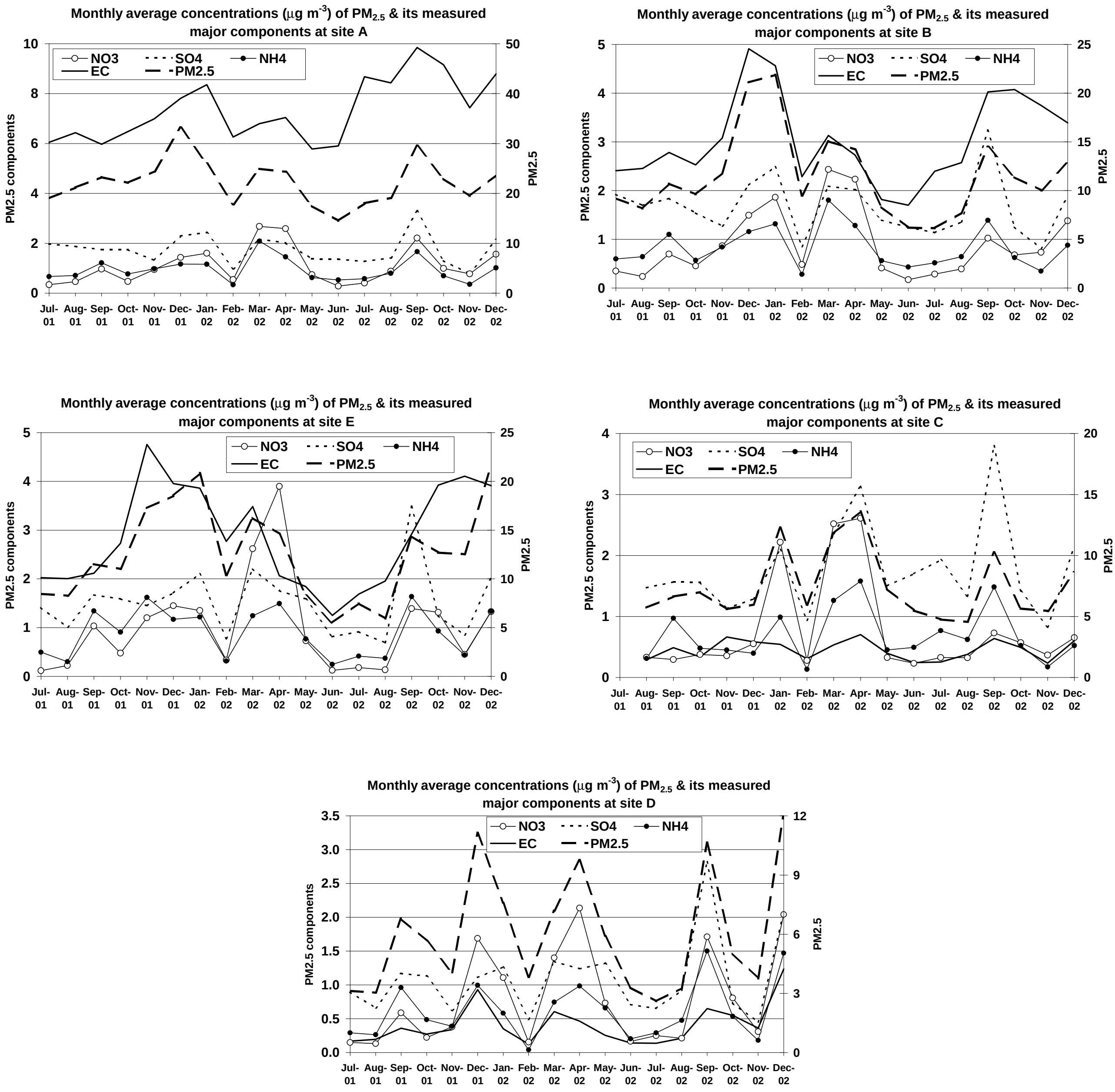


Figure 3.5a. Monthly measurements for fine particles at the five sites.

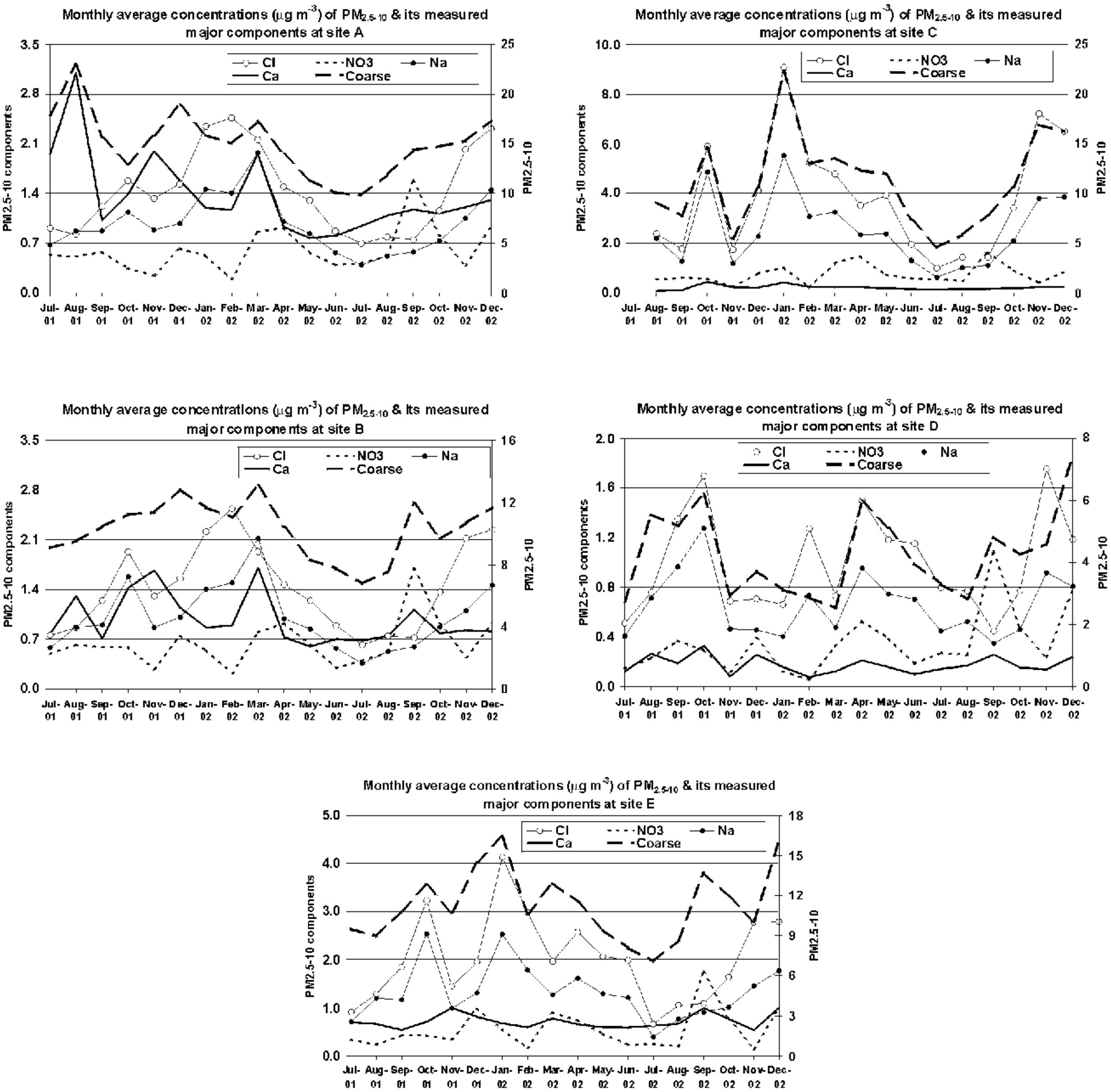


Figure 3.5b. Monthly measurements for coarse particles at the five sites.

4 Measurements over an Intensive Period

Intensive measurements were carried out during 4 weeks in February–March 2002 (19 February–21 March) at three stations: Killure, Ahascragh, Ballinasloe (rural site D), Coleraine Street (Dublin site B) and Wicklow (coastal site C). The main objectives of the intensive campaign were to obtain a greater understanding of pollution sources, of their strength and impact on air quality and to obtain size-resolved particle chemical composition measurements in order to assign accurate size distributions to the major source categories. The following additional measurements were carried out:

- condensation particle concentration (CPC) – total number of particles larger than 10 nm in size;
- SO_2, NO, NO_2, NO_x, O_3, CO gas measurements;
- cascade impactor (MOUDI) for collection and analysis of size-resolved aerosol particles (12 size categories);
- meteorological data: temperature, wind speed and direction, relative humidity.

Gaseous measurements were made with 5-min time resolution, while MOUDI impactor samples were changed weekly. MOUDI impactors are capable of collecting particles in up to 12 size fractions within the range 0.054–18 µm. A 12-stage MOUDI was used at Sites B and D, whereas at Site C a 10-stage MOUDI was employed. The 10-stage MOUDI is essentially the same as the other two, but is missing the two smallest particle stages. Those smallest particles (<0.054 µm) were collected on the backup filter. MOUDI samples were first weighted gravimetrically, and then analysed for MSA^-, Cl^-, Mg^{2+}, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} and EC. Analytical procedures used were the same as those used for the ordinary samples (Section 2.2).

4.1 Local Meteorology during the Intensive Campaign

Regional meteorology during the intensive campaign was characterised by a westerly air flow from the Atlantic Ocean during the first 2 weeks and by an easterly flow at the end of the campaign. Westerly air flow brings the cleanest air into Ireland, while the easterly flow brings polluted air masses from the United Kingdom and continental Europe. The frequency distribution pattern of local wind direction throughout the campaign at Sites C and D is presented in Fig. 4.1. The meteorological situation was rather stable during the individual 4 weeks and therefore enabled estimation of the influence of air masses passing over Ireland from the west and from the east on pollutant levels in Ireland.

Other meteorological parameters (temperature, relative humidity and wind speed) were mostly affected by regional meteorology. The temperature at the rural site

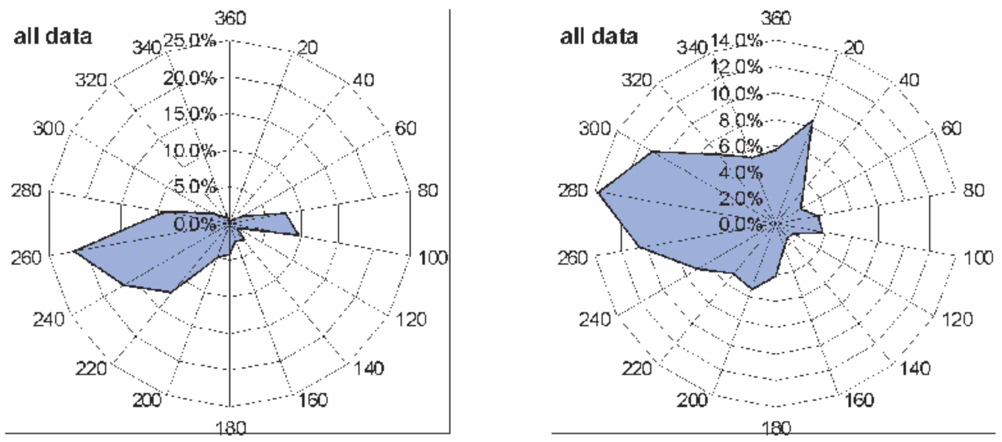


Figure 4.1. Frequency distribution pattern of local wind direction during the intensive campaign measured at the rural site (D) (left) and Site C (right).

was about a factor of 2 lower than that at the coastal site, where the warm sea water made temperature independent of the influence of air masses. The temperature at the rural site was at its lowest in northerly air masses and highest in the westerly air masses. Relative humidity was directly related to the temperature, with relative humidity values of between 60 and 80% at the rural site and between 40 and 60% at the coastal site. Wind speed was variable between 1 and 6 m/s on average, with a stronger variation at the rural site. Strongest winds appeared from the western sector, while the weakest winds generally came from the eastern sector. Meteorology at the Dublin site (Site B) had strong local character, affected by street canyons. Wind speed was very low, generally below 1 m/s, and therefore measured wind direction was not reliable. Due in part to the low wind speed, local temperature was rather high, above 15°C on the average, and relative humidity was around 40%.

4.2 Gaseous Measurements and Condensation Particle Counts during the Intensive Campaign

High-resolution gas measurements enabled estimation of the strength and impact of local and regional pollution sources on regional air quality. Figure 4.2 presents frequency distribution patterns of SO_2, NO, NO_2 and CPC counts at Site D during the intensive campaign. NO is a short-lived gas and it clearly shows the influence of the nearby sources. Elevated NO concentrations come from an easterly (around 100°) direction, where Ballinasloe town, with a population of about 6500 inhabitants, is situated at a distance of 5–6 km. NO_2 concentration does not follow the same pattern, as NO_2 is a photochemical product of NO, exhibiting a uniform concentration pattern produced by distant regional sources. The SO_2 concentration pattern reveals both local and regional sources, with slightly elevated concentrations from the eastern sector. SO_2 comes mainly from fossil fuel, mainly

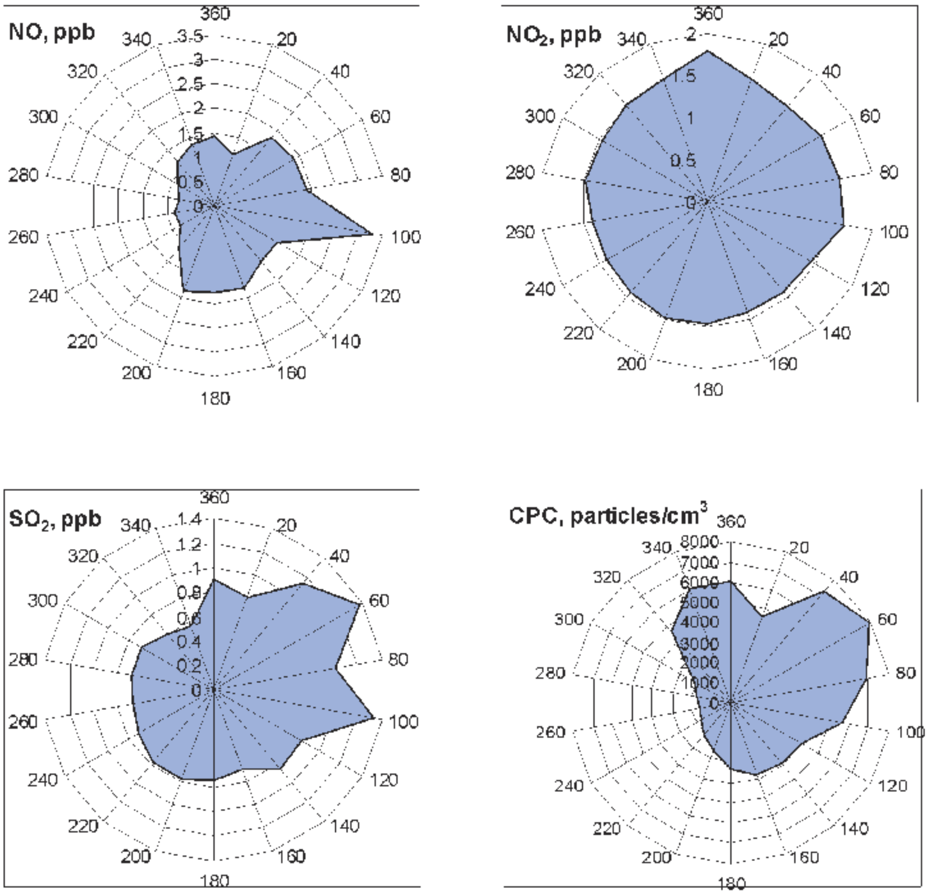


Figure 4.2. Frequency distribution of gases NO, NO_2, SO_2 and condensation particle concentration (CPC) measured during the intensive campaign at the rural site (D).

exhibiting influences of nearby sources (Ballinasloe and Athlone towns) and distant sources (Ireland, the United Kingdom and the rest of Europe). Gaseous measurements have shown that Site D is clearly rural and nearby local pollution sources had little impact on air quality. Despite clear concentration patterns in some cases, gaseous concentrations were generally very low (Table 4.1). CPC counts showed even more pronounced regional pollution with elevated counts for the north-eastern sector. It should be pointed out that the CPC pattern did not show a clear influence of the nearby town, Ballinasloe, and therefore it can be assumed that local sources had little influence on aerosol chemical composition at Site D. This rural site is certainly representative of regional background air quality. Note that pollutant concentrations which appeared in the western sector were generally low, e.g. CPC counts were about 1500 particles/cm^3. By comparison, in clean air masses advecting into Ireland from the Atlantic CPC counts are below 700 particles/cm^3. Therefore, it can be concluded that emissions from Galway City had a clear, but fairly limited, influence on the regional air quality due to the distance of 70 km from the rural site and favourable mixing conditions at higher wind speeds from the western sector. However, this conclusion is made based on concentration levels only. Despite low CPC concentrations in the western sector, the chemical composition of particles is different from the one expected in the clean marine air masses (Section 4.3).

Gaseous concentration patterns at the coastal site (C) were similar in their nature to those at the rural site, as shown in Fig. 4.3. Generally, concentrations were very low, with the lowest values in the western sector. Variation of SO_2 concentration at the coastal site exhibited a local character, with multiple concentration spikes associated with local emissions from either burnt domestic fuel or from ships. The latter emissions were dominating, as they have appeared from the seaside, but often lasted only for about 1 h (measurement resolution). Accompanying high CPC counts, despite supporting the aforementioned local emissions, may also have been coming from new particle formation events at the coast. CPC concentrations in the western sector were very similar, though slightly higher than at the rural site, implying that emissions during air mass passage over Ireland slightly enhanced particle concentration by about 20–25%. However, NO_x and SO_2 concentrations remained at a very low level in that sector.

The Dublin site (B) represented a background urban site with a local meteorology determined by a street canyon. Gaseous concentrations were not particularly high, as shown in Fig. 4.4, as the 95th percentile concentration did not come close to any limit value (Table 4.1). However, frequency distribution patterns revealed clear pollution sources. NO, NO_2 and CO emissions were advecting mainly from a southern direction where a busy North King Street is situated. SO_2 emissions did not follow that pattern, suggesting that urban emissions were coming mainly from domestic fuel consumption. Elevated SO_2 concentration in the south-eastern sector pointed to ship

Table 4.1. Summary of gaseous and CPC concentrations measured during the intensive campaign (19 Feb 2002–21 Mar 2002) at Sites B, C and D.

Site	CO ppm	NO_x ppb	NO_2 ppb	NO ppb	SO_2 ppb	O_3 ppm	CPC particles/cm^3
B (Dublin)							
Average	0.44	34.9	14.6	20.2	1.52	na	25,689
5th percentile	0.20	3.00	2.90	0.40	0.40	na	30
95th percentile	0.90	84.6	44.9	40.2	3.80	na	55,550
C (coastal)							
Average	0.21	1.77	1.58	0.19	0.48	30.3	2,981
5th percentile	0.04	–0.20	–0.20	–0.28	–0.07	21	419
95th percentile	0.31	6.94	6.30	0.95	1.46	39	11061
D (rural)							
Average	na	2.81	1.46	1.35	0.81	na	3024
5th percentile	na	1.49	0.57	0.17	0.36	na	360
95th percentile	na	5.57	2.34	3.91	1.53	na	9266

na: data not available.

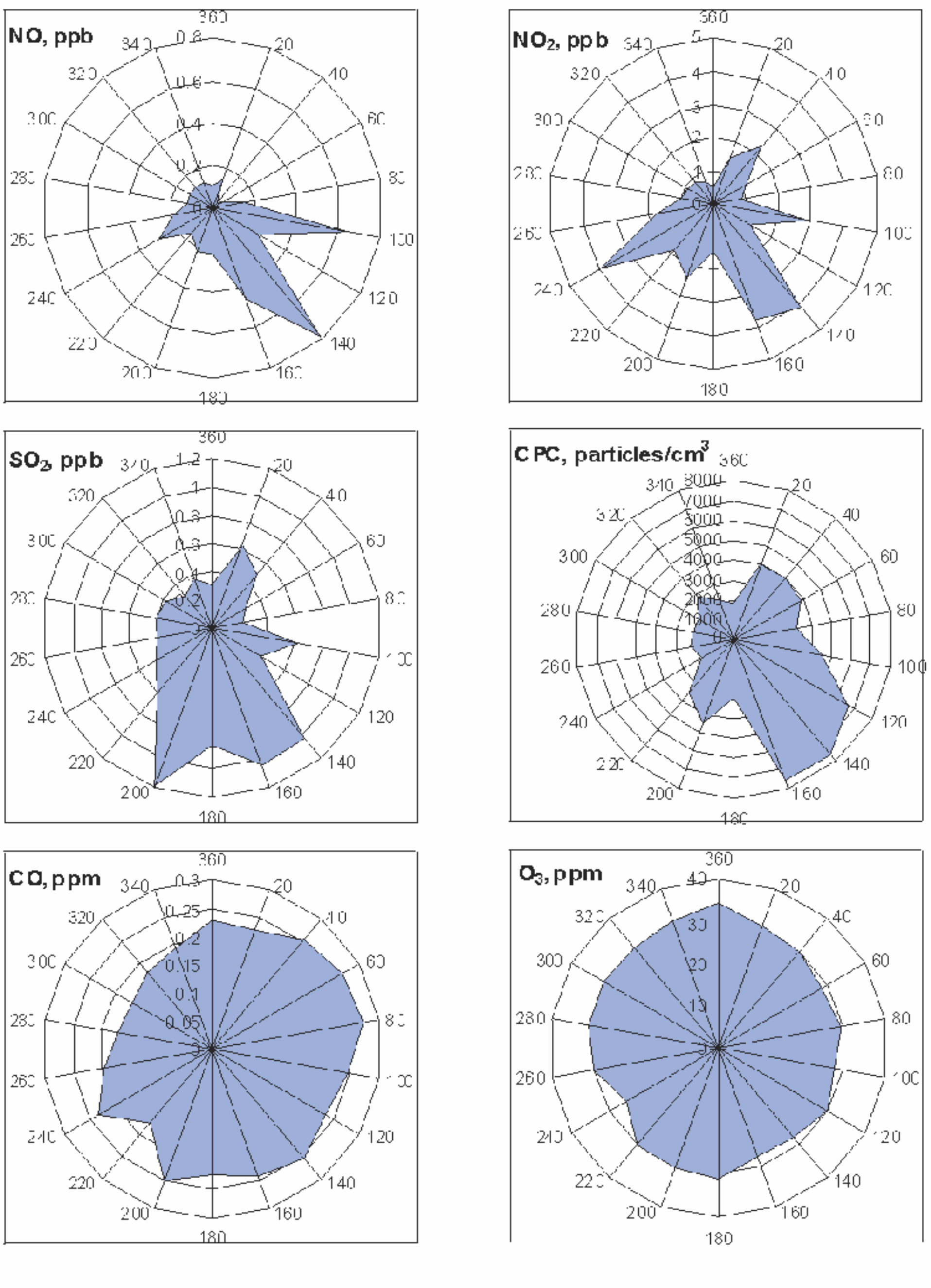


Figure 4.3. Frequency distribution patterns of certain gases NO, NO$_2$, SO$_2$, CO, O$_3$ and condensation particle concentration (CPC) at the coastal site (C).

emissions. Correlation coefficients between the pollutants confirmed the likely common sources. There was high correlation between CO and NO$_x$, NO$_2$, NO and CPC. Also, moderate correlation was observed between SO$_2$ and CPC, pointing to the fact that domestic fuel emissions contributed to particle emissions as well.

Overall, gaseous measurements performed during the intensive campaign showed that emissions sources in Ireland had mainly a local character and therefore were confined within a limited area of around 20–30 km radius, without affecting regional air quality. Even large emission sources such as Dublin City did not reveal any noticeable influence on concentration levels measured at the coastal site in Wicklow, just 40–50 km distant. This phenomenon could be explained by unstable meteorological conditions, favouring good mixing in the boundary layer, a high precipitation rate and a relatively good state of the car fleet not producing excessively high emissions.

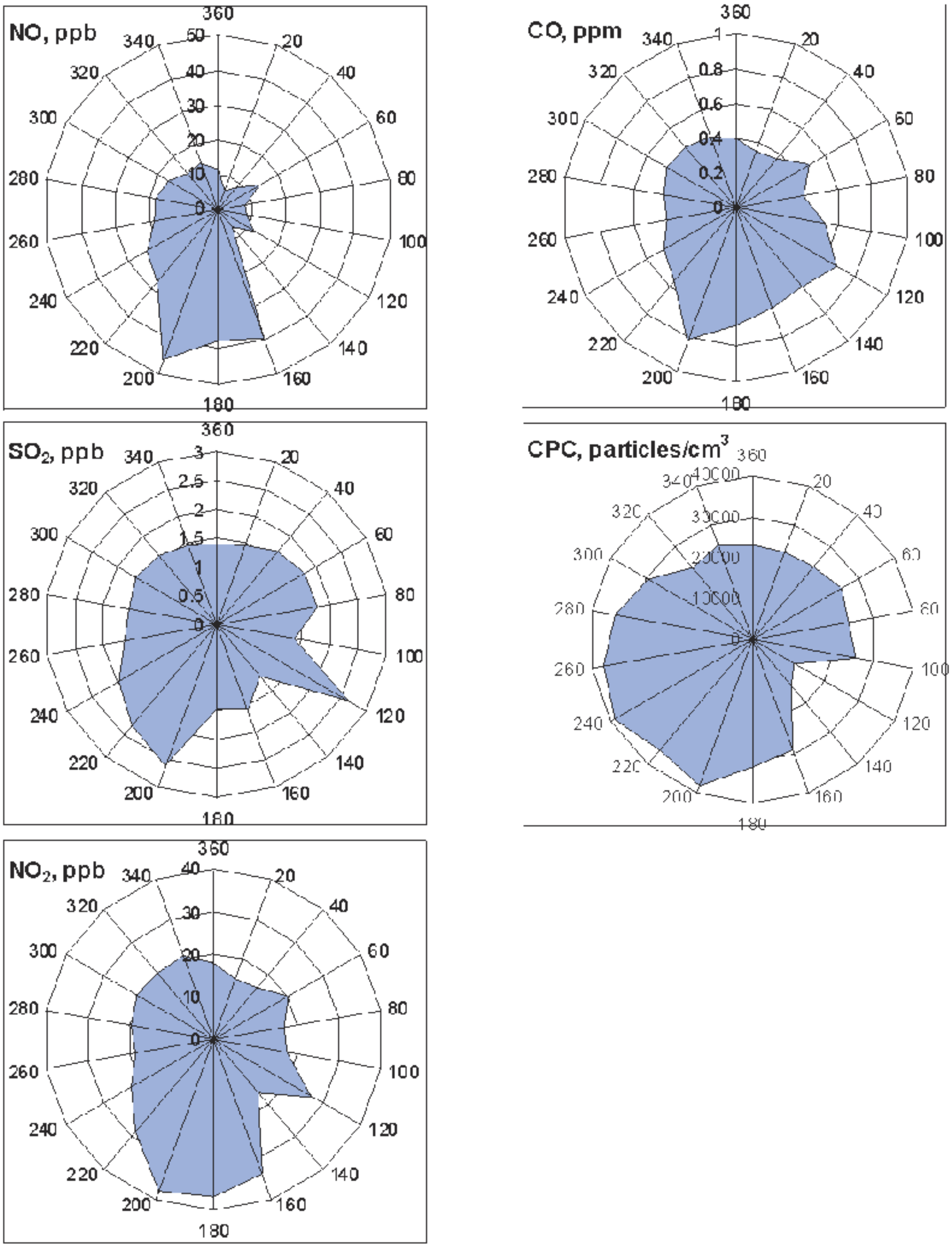


Figure 4.4. Frequency distribution patterns of certain gases NO, NO_2, SO_2, CO, and condensation particle concentration (CPC) at the Dublin site (B).

4.3 Size-Resolved Particle Distribution, Obtained by MOUDI Impactors, and Chemical Composition during the Intensive Campaign

Size-resolved particle distribution and particle chemical composition provide a better insight into assessing an influence of pollutant emissions in Ireland on aerosol chemistry. A comparison of gravimetric mass size distribution with size distribution of chemical species enabled an estimation of the importance of different pollution sources contributing to particulate chemical species. Stable regional meteorology during some of the weeks during the intensive campaign was also a favourable factor. As already mentioned in Section 4.2, there was a clear westerly flow during the first 2 weeks of the campaign, bringing clean marine air masses into Ireland across a west–east transect.

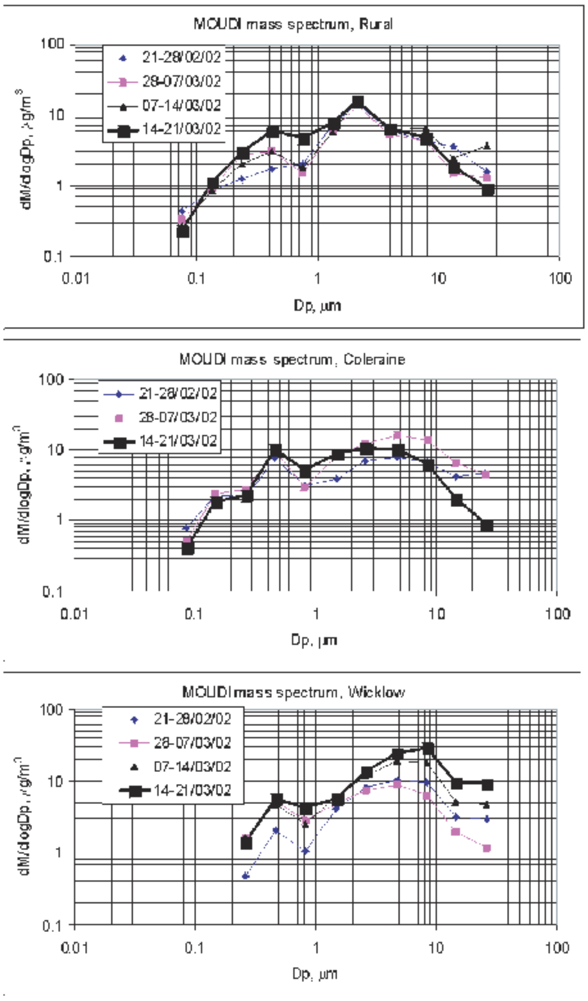


Figure 4.5. Particle mass size distributions for the rural site (D), the city site (B) and the coastal site (C).

Size-resolved gravimetric mass distribution showed clear differences between particle modes at the three sites. A demarcation between accumulation and coarse modes was at about 0.8 µm and was constant at all sites, as shown in Fig. 4.5. This finding places a new perspective on the value which is frequently used to separate fine and coarse particle modes – that of 2.5 µm. Note that the demarcation size of 0.8 µm represents a 'wet' diameter, as MOUDI impactors were run at ambient temperature. Therefore, the measurements suggest that dichotomous samplers should separate particles at a standard 1.0-µm size, at least under Irish conditions with a strong primary sea salt source.

An accumulation mode (between particle size diameter range from 0.1 to 1.0 µm) or fine particle mode mass was fairly similar at the rural and the coastal sites, while at the urban background site fine particle mass concentration was a factor of about 2 to 4 higher due to urban emissions. The accumulation mode concentration was very different depending on air mass history, which was factor of 2 to 3 higher in easterly air masses compared to the westerly ones. The exception was the Coleraine Street site (Site B), where the accumulation mode concentration was stable and fairly independent of the air mass sector. This pointed to the fact that particle mass was dominated by urban emissions, with only a relatively small difference attributed to air mass history.

The coarse particle mode was also characteristic of the different sites. The coarse particle mode at the rural site was dominated by sea salt particles of about 2 µm in size, while larger particles were washed out or deposited before reaching the site. At the coastal site (C), coarse mode particle mass was dominated by particles of 5–8 µm in size and was quite dependent on the wind direction, with a factor of 2 to 3 higher mass during the week of easterly air flow compared to the westerly flow. Coarse mode particle mass at the Coleraine Street site exhibited moderate variation depending on the wind direction, but much less than at the coastal site.

Chemical species contributing to the measured aerosol mass are presented in Figs 4.6–4.8 for Sites D, B and C. There is a clear size demarcation where particle chemical composition completely changes its distribution pattern. Particles up to 1.0 µm in size are predominantly composed of EC, nss SO_4^{2-} (non-sea-salt sulphate), NO_3^- and NH_4^+. Particles above 1.0 µm are almost entirely composed of sea salt (NaCl, ss SO_4^{2-} (sea-salt sulphate), Ca and Mg). There were only two exceptions: (1) at the rural site when due to the strong westerly winds during the first week of the campaign sea salt significantly contributed to even the 0.56- to 1.0-µm size range; and (2) at the urban background site, where Ca significantly contributed to the coarse mode due to resuspended road dust. The clear difference in chemical composition, which occurred at the 1.0-µm size, supports the critics of the 2.5-µm cut-off size utilised in dichotomous samplers.

On average, all chemical species concentrations measured in the size-resolved samples were very similar to the ones measured in the PM_{10} or $PM_{2.5}$ samples. Due to the effect of road traffic, substantial elevations of EC concentrations were recorded at the Coleraine Street site (Dublin) in comparison with the rural or coastal background sites, which were up to 10 times the

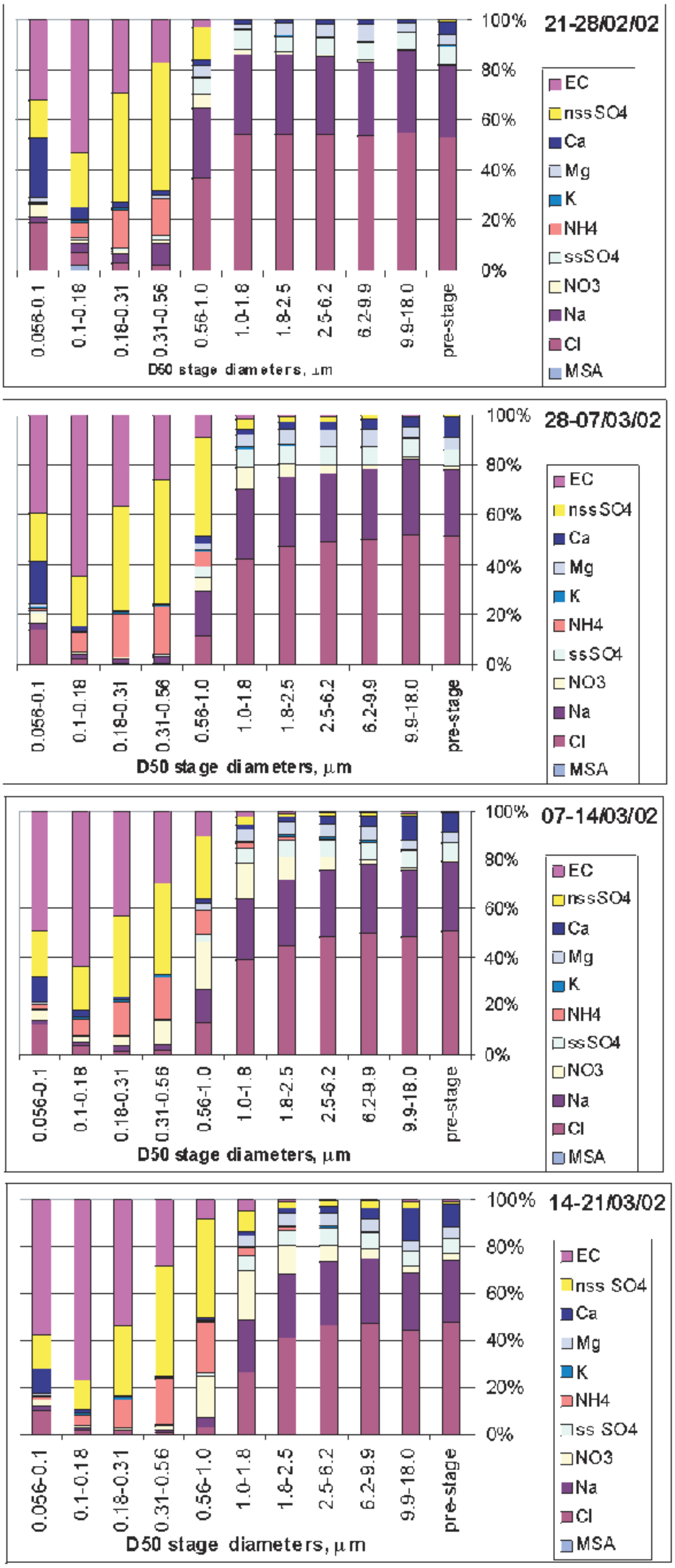


Figure 4.6. Mass fraction of aerosol chemical species as a function of particle size at the rural site (D).

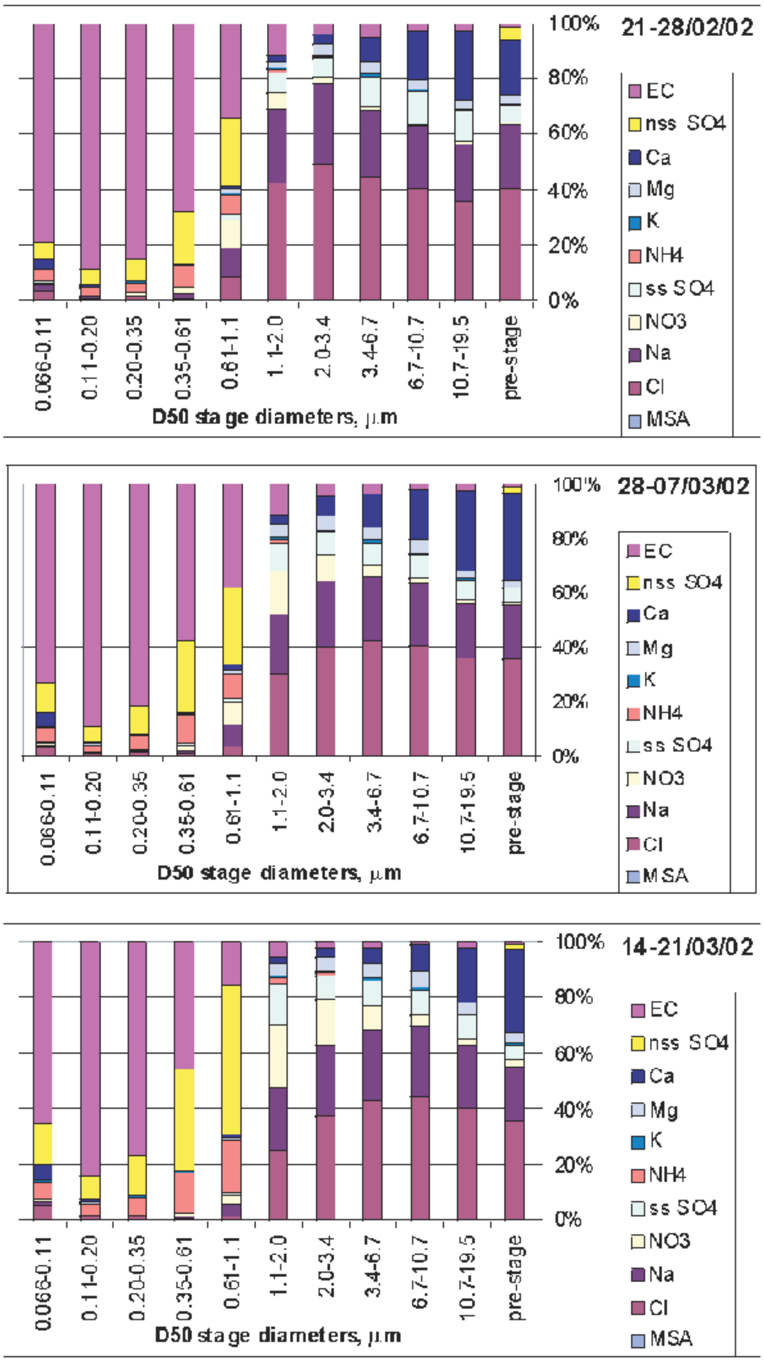


Figure 4.7. Mass fraction of aerosol chemical species as a function of particle size at the urban site (B).

concentrations at the other two sites. Consequently, EC concentration at the Coleraine Street site accounted for up to 90% of the particle mass in the size range of 0.1–0.2 µm. As EC comes primarily from burned fossil fuel it has a strong local character. There were much less differences between other chemical species at the different sites. Non-sea-salt SO_4^{2-} concentrations were only up to 50% higher at the urban site compared to the rural or coastal site, while NO_3^- and NH_4^+ concentrations were similar at the urban and coastal sites, but a factor of 2 to 3 higher than at the rural site. The only unusual finding was a noticeable contribution of calcium to the smallest sized particles at all sites.

Constant westerly air flow during the first week of the intensive campaign provided us with an insight into the influence of pollution sources in Ireland on aerosol chemical composition. Figure 4.9 shows an increase in

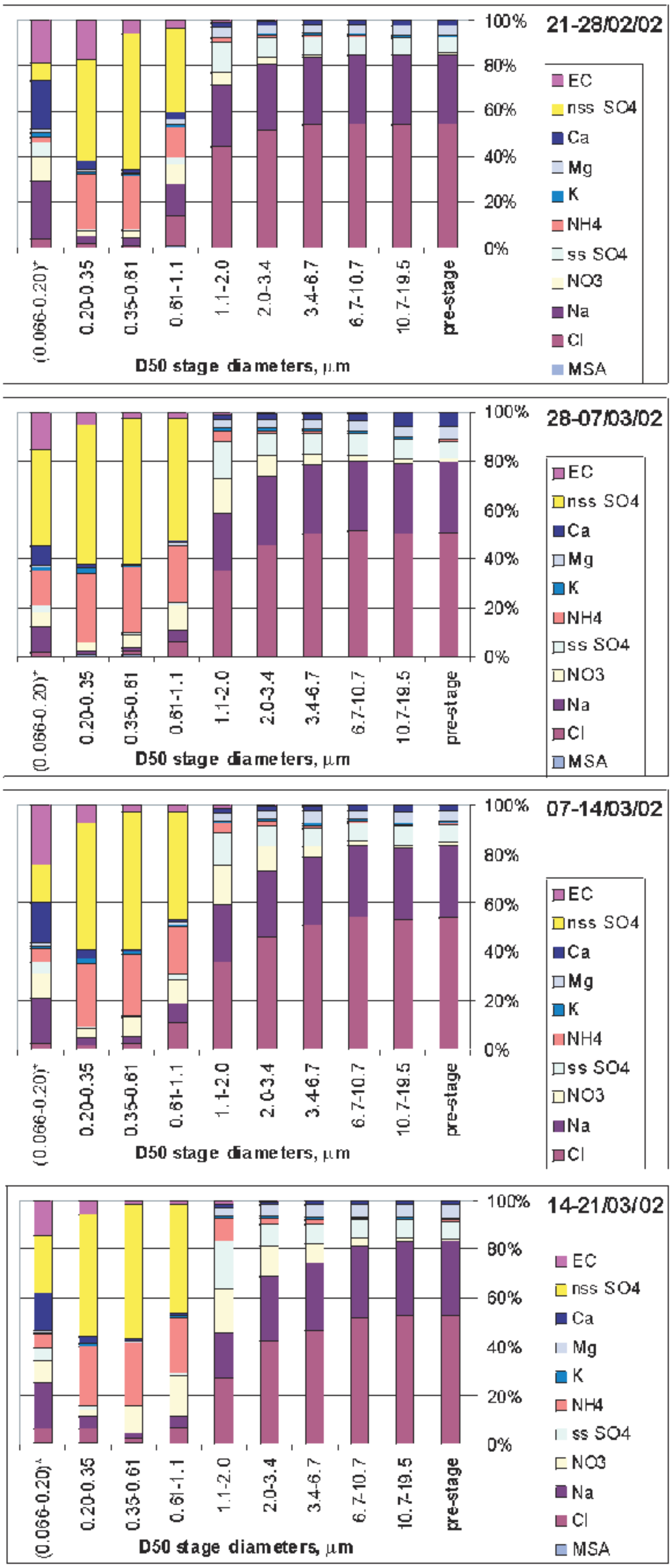


Figure 4.8. Mass fraction of aerosol chemical species as a function of particle size at the coastal site (C).

concentration of all species during an air mass passage over Ireland from west to east during the last week of February 2002. The nss SO_4^{2-} concentration increase was modest (from 0.27 to 0.32 µg/m^3); however, the NO_3^- concentration increased about two-fold (from 0.081 to 0.183 µg/m^3) and the NH_4^+ concentration increased three-fold (from 0.064 to 0.181 µg/m^3). Note that the NO_3^- and NH_4^+ concentrations were similar at the coastal and urban sites while nss SO_4^{2-} concentrations were different at the coastal and urban sites. Such a pattern implies that gaseous precursors to NO_3^- and NH_4^+ are spread across the country, where the agriculture industry is the most likely candidate of NH_3 emissions (the precursor of NH_4^+), while vehicles dominate NO_x emissions (precursor of NO_3^-). SO_2 emissions across the country contributed to the nss SO_4^{2-} during air mass transport across Ireland. However, imported sulphate was high, relative to the imported fractions of nitrate and ammonium, while urban emissions contributed to its increase at the urban site. This suggests that gas-to-particle conversion of sulphur was quite rapid, occurring during the short time period of air mass residence in the city (about 2 h in this case). It was, however, not the case for NO_3^-, despite substantial urban NO_2 concentrations. The difference probably stems from the fact that conversion of SO_2 into SO_4^{2-} can occur rapidly in the aqueous phase (Seinfeld and Pandis, 1998), while NO_2 is mainly produced from primary NO emissions via photochemical reactions before being further converted into NO_3^-.

EC concentration increased little during air mass transport over Ireland, but urban emission concentrations increased about a factor of 5 due to primary emissions. However, OC exhibited quite a different pattern with a larger increase in OC concentration during transport over land (between the rural site (D) and the coastal site (C) in Fig. 4.9) and a smaller difference when comparing the coastal site (Site C) and the urban site (Site B). This finding clearly demonstrates that various emission sources over land contribute to the OC concentration increase. However, not all emissions over land are of anthropogenic origin, as some emissions can be of a biogenic origin, for example, from organic soils (Gelencsér *et al.*, 2002). In fact, Fig. 4.9 implies that during winter most of the OC in rural atmosphere could indeed be of biogenic origin, as EC concentration increases about two-fold during air mass transport over land (from 0.29 to 0.48 µg/m^3), while OC concentration increases about five times (0.32 to 1.69 µg/m^3) during air mass transport (rural and coastal sites). At the same time, urban emissions had limited influence on OC content in urban aerosol, because the short air mass residence time over the city is normally not long enough for secondary processes to take effect and only primary OC emissions will have contributed to the small increase. However, extreme primary emissions, such as at the Dublin kerbside site (A), are capable of increasing OC concentration substantially.

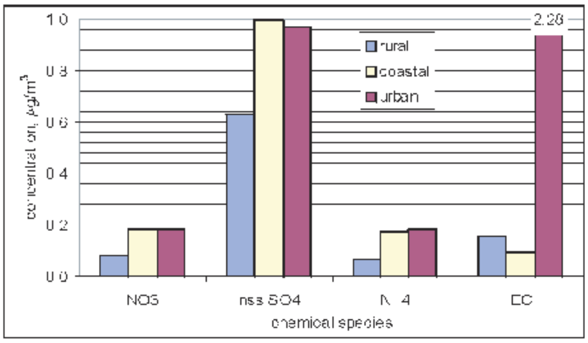


Figure 4.9. Increase of chemical species concentration during a west–east air mass passage over Ireland.

The difference in the increase of different concentrations at the different sites gives an insight into the strength of pollution sources. In summary, it can be seen, that NH_3 emissions (agriculture) are probably the strongest source, followed by NO_x (mobile emission sources) and SO_2 (stationary pollution sources). Elemental carbon comes directly from fossil fuel burning, and it showed the largest increase in concentration between the sites. Finally, it is not clear why EC concentration decreased at the coastal site. Despite low solubility of EC and its low affinity to water, it is possible that washout from the atmosphere during about a 7-h passage of the air mass (high precipitation rates occurred during that week) may have caused a reduction in EC concentration, even though the air mass transit time was rather short.

A gravimetric/chemical mass balance and chemical ion balance method was used to test how complete the chemical analysis was. When both methods are combined it allows a search for non-identified candidate chemical species. The gravimetric/chemical mass balance method is a comparison of gravimetrically measured mass versus the sum of masses of analysed chemical species. The difference between them is the

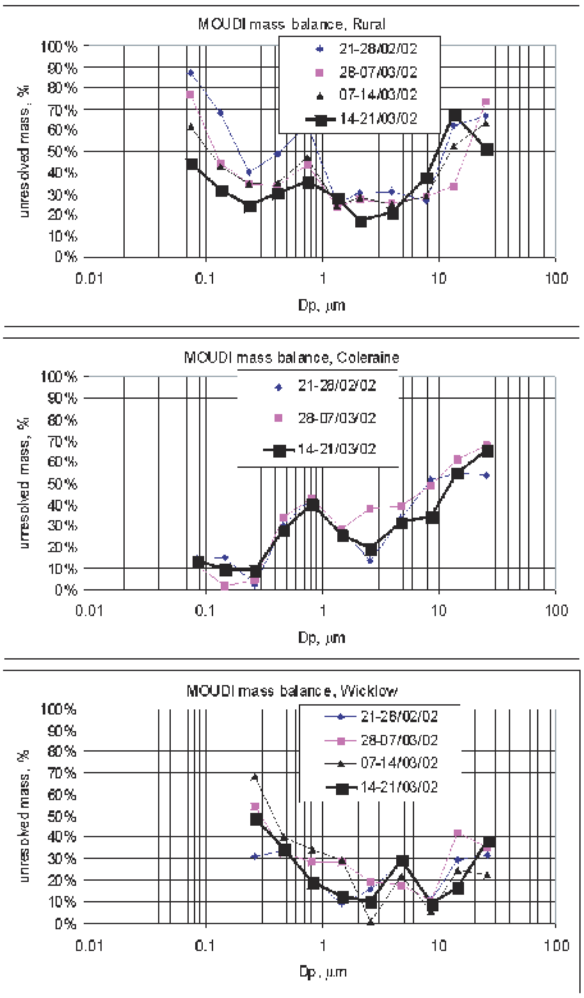


Figure 4.10. Gravimetric mass distributions at the rural, city and coastal sites.

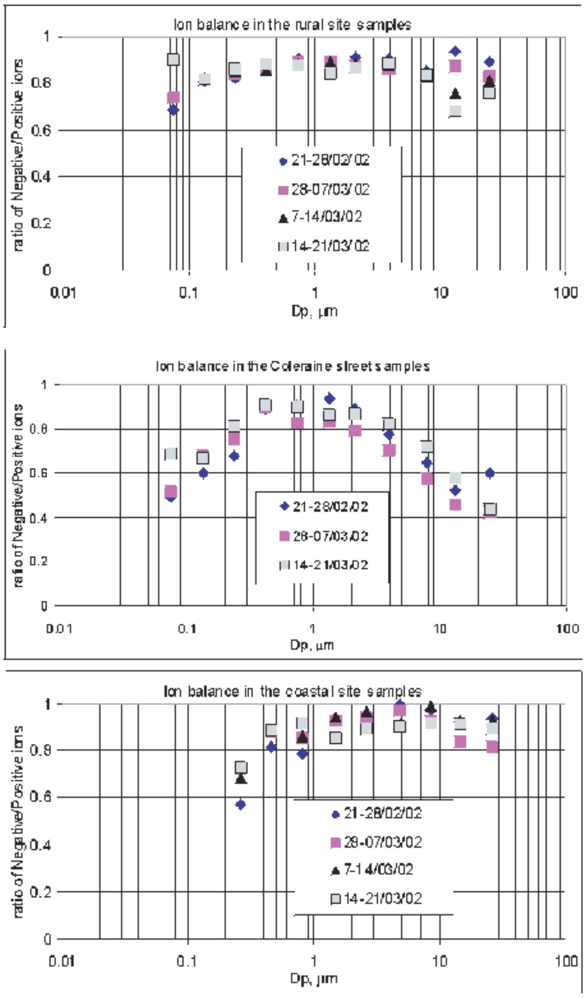


Figure 4.11. Chemical ion balance at the rural, city and coastal sites.

unresolved mass. Figure 4.10 presents gravimetric mass balance at the three sites. Overall, the best balance was achieved at the Coleraine Street site; the worst was at the rural site, where unresolved mass accounted for up to 90% for certain particle sizes. All major chemical components, representing major pollutants, were analysed at all sites. However, as the Coleraine Street site was the most polluted one, main pollutants such as EC accounted for the major mass fraction, thus improving the mass balance. At the relatively clean rural site, mass deficiency was very significant. It is thought that the majority of the missing mass in the fine fraction could be attributed to the non-analysed OC, which is present in significant amounts in all air masses. Organic carbon can be produced by primary as well as secondary processes, and therefore is present at all sites. In summary, organic emissions contributing to unresolved mass could be of biogenic origin, either from marine sources (O'Dowd *et al*., 2004) or from continental soils (Gelencsér *et al*., 2002). Some organic emissions could also be due to anthropogenic sources.

The ion balance method, which is the ratio of positive and negative ions, can give further insight into missing chemical species. Figure 4.11 shows chemical ion balance at the three sites. Deficiency in negative ions across small particle sizes confirms that non-analysed organic acids could be responsible for the missing mass. There was also missing mass across large particle sizes. In this case, the mass balance and ion balance method suggest that the missing candidate species could be crust material, particularly silicates and carbonates, providing large sources of negative ions. Note that at the coastal site there was little missing mass across large particle sizes and there was rather good ion balance due to the

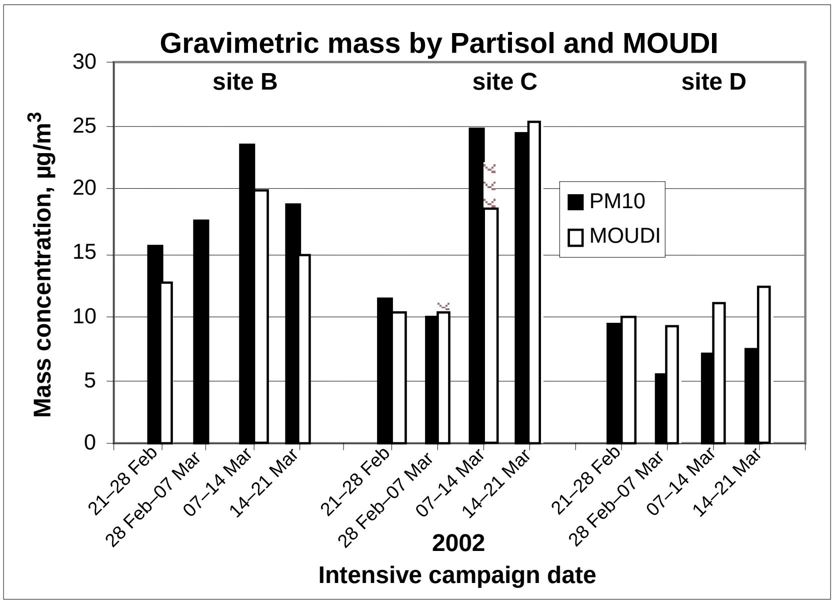


Figure 4.12. Comparison of PM_{10} gravimetric mass sampled by a dichotomous Partisol sampler and a MOUDI impactor.

dominant contribution of sea salt. It should be pointed out that some of the missing mass is likely to be attributed to water, because impactor samples were conditioned and measured at about 40% relative humidity and some water may have been left in the samples before weighting them. However, the contribution of water cannot be dominant at 40% relative humidity and the presence of water cannot significantly affect the ion balance.

During the intensive campaign ordinary PM_{10} samples were collected on alternate days as during the rest of the project. Even though MOUDI impactor samples were deployed continuously during 1-week periods, gravimetric PM_{10} mass sampled by a dichotomous sampler can be compared with gravimetric mass sampled by the MOUDI impactor. Therefore, 1-week-long MOUDI samples were compared with the average of three individual daily Partisol samples over the same week. The comparison is presented in Fig. 4.12. There was fairly reasonable agreement (generally better than about 25%) between the values, despite the fact that the corresponding samples did not represent exactly the same sampling days. The largest disagreement (up to 50% difference) was found at the rural site. It is fair to say that concentrations at the rural site were the most sensitive as they were the lowest among the sites, and therefore any slight changes in particle load had significant influence on the average value. However, during the first week of the campaign, which was characterised by a stable westerly air flow, agreement was very good at all three sites.

The work on the intensive campaign measurements is described by Ceburnis *et al.* (2006).

5 PM_{10} Episodes Study and Air Mass Back-Trajectory Analyses

Urban sites are most likely to exceed the PM_{10} standard limit 24-hour mean value of 50 µg/m^3, particularly at heavily trafficked locations. Closer examination of selected days when PM_{10} exceeded the standard limit has been conducted considering particle physical and chemical properties, and meteorology. Air mass back trajectories were obtained using the British Atmospheric Data Centre (BADC) trajectory service to aid in interpretation of the data.

5.1 Relative Importance of Fine and Coarse Particles and their Chemical Composition during PM_{10} Episodes

Figure 5.1 shows the proportions of fine and coarse particles contributing to the total concentrations of PM_{10} on days when PM_{10} mass exceeded 50 µg/m^3. At urban sites A, B and E, PM_{10} episodes were mostly dominated by the fine fraction, which contributes 62% (range: 30–89%) of the PM_{10} mass on average at Site A, 74% (range: 63–89%) at site B and 67% (range: 43–83%) at Site E. The coarse fraction was predominant only on a few occasions (5 days) at Site A, but its contribution is not negligible, making up about one-third of the total mass, largely due to resuspension of dusts by heavy traffic, as evidenced by high concentrations of calcium (Fig. 5.2). Sea salt may make a large contribution at this site (A) (11/12/02) but on very rare occasions. In comparison, Site E is less influenced by dust resuspension because of a lower traffic volume and the higher position above the ground of the sampling inlet; however, there were also 2 days (12/12/01 and 18/09/02) when over 50% of PM_{10} mass was from coarse particles, which mainly comprised resuspended dusts, sea salt and nitrate. Similarly, Site B experienced less traffic activity than Site A, and during almost all PM_{10} episodes the total mass consisted of more than two-thirds of fine particles. There were only 5 days at Site C that PM_{10} exceeded the EU limit, but on 2 days the coarse fraction was predominant, contributing about 75% and 78%, almost purely due to sea salt. The only day recorded when PM_{10} was over the standard limit at Site D showed an 80% contribution from fine particles.

5.2 Use of Air Mass Back Trajectories in Analysis of PM_{10} Episodes

Meteorological data (wind speed, wind direction, ambient temperature, pressure and relative humidity) were downloaded from the Partisol instruments at Sites A, B and C with only poor data capture (about 30%). Wind data are only available for the period June 2002 to December 2002 at Site E and from October 2001 to December 2002 at Site D. These were not used due to the short run of data (although a reasonably high data capture was obtained at Site D). Instead, 5-day air mass back trajectories were obtained using the BADC trajectory service, and used to identify the likely influences of different air mass/aerosol origins, whether local, regional, national, European or North Atlantic. In the following section, different air mass origins are illustrated, together with analysis of the 24-h particle mass and chemical component mass for selected days characterised by the presence of both polluted and clean air masses.

Example 1

On 15 August 2001 the air mass followed an Atlantic trajectory, crossing south-east Ireland before reaching the sites, with no signs of a European influence (Fig. 5.3a). The local wind direction was consistent with the trajectory at around 205°. High PM_{10} mass (88 µg/m^3) was recorded at Site A, comprising about 60% from the coarse fraction largely due to high levels of resuspended materials indicated by an elevated calcium concentration of about 9 µg/m^3. The EC concentration was also high on this day, again indicating a local traffic source of emissions. Low secondary aerosol mass was measured. In comparison, Site B exhibited much lower PM_{10} mass concentration (16 µg/m^3), although also composed of a higher proportion of coarse particles. A similar profile was found as at Site A, with higher calcium and EC, and lower secondary component levels. On this day local sources predominated in an air mass originating over the Atlantic.

Example 2

The highest PM_{10} concentrations measured over the whole sampling period occurred on 12 December 2001 at Site A (161 µg/m^3) and at Site B (106 µg/m^3) (Fig. 5.3b).

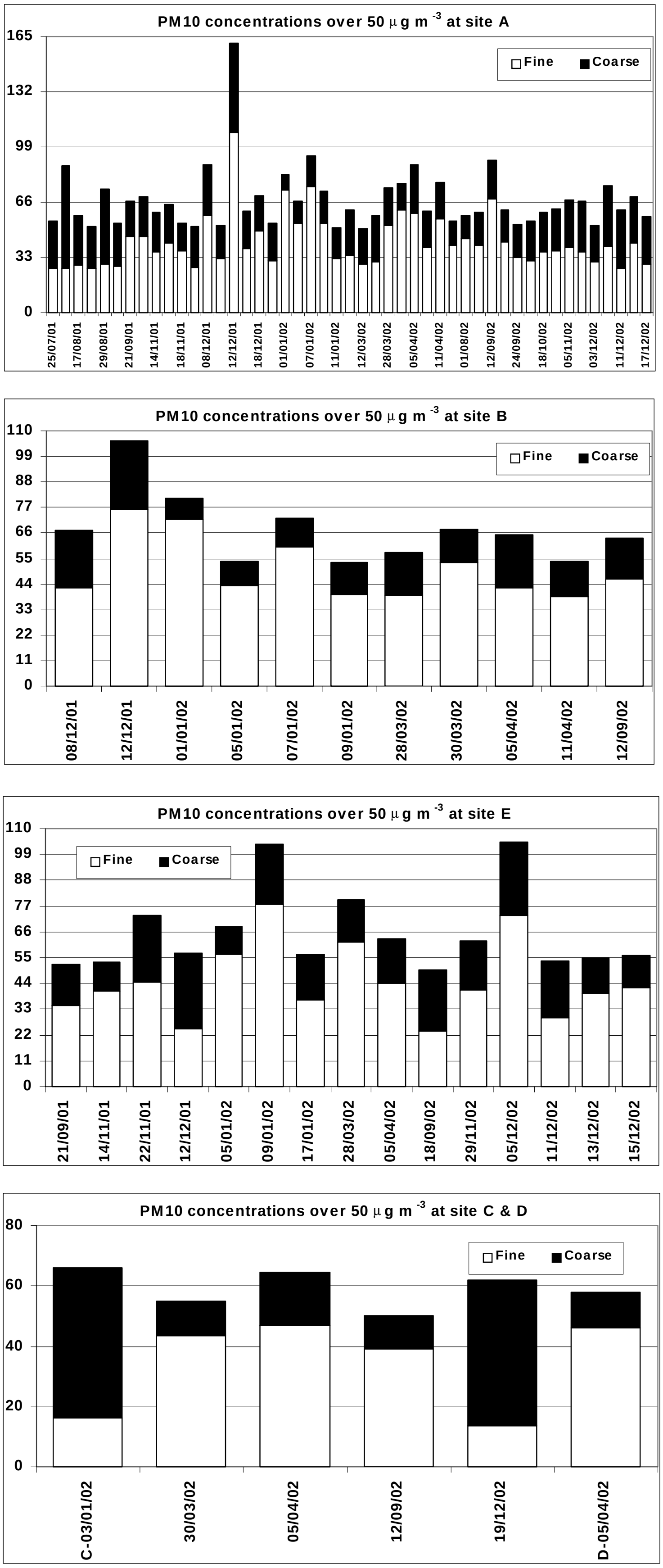


Figure 5.1. Daily fine and coarse mass concentrations when PM_{10} >50 µg/m^3.

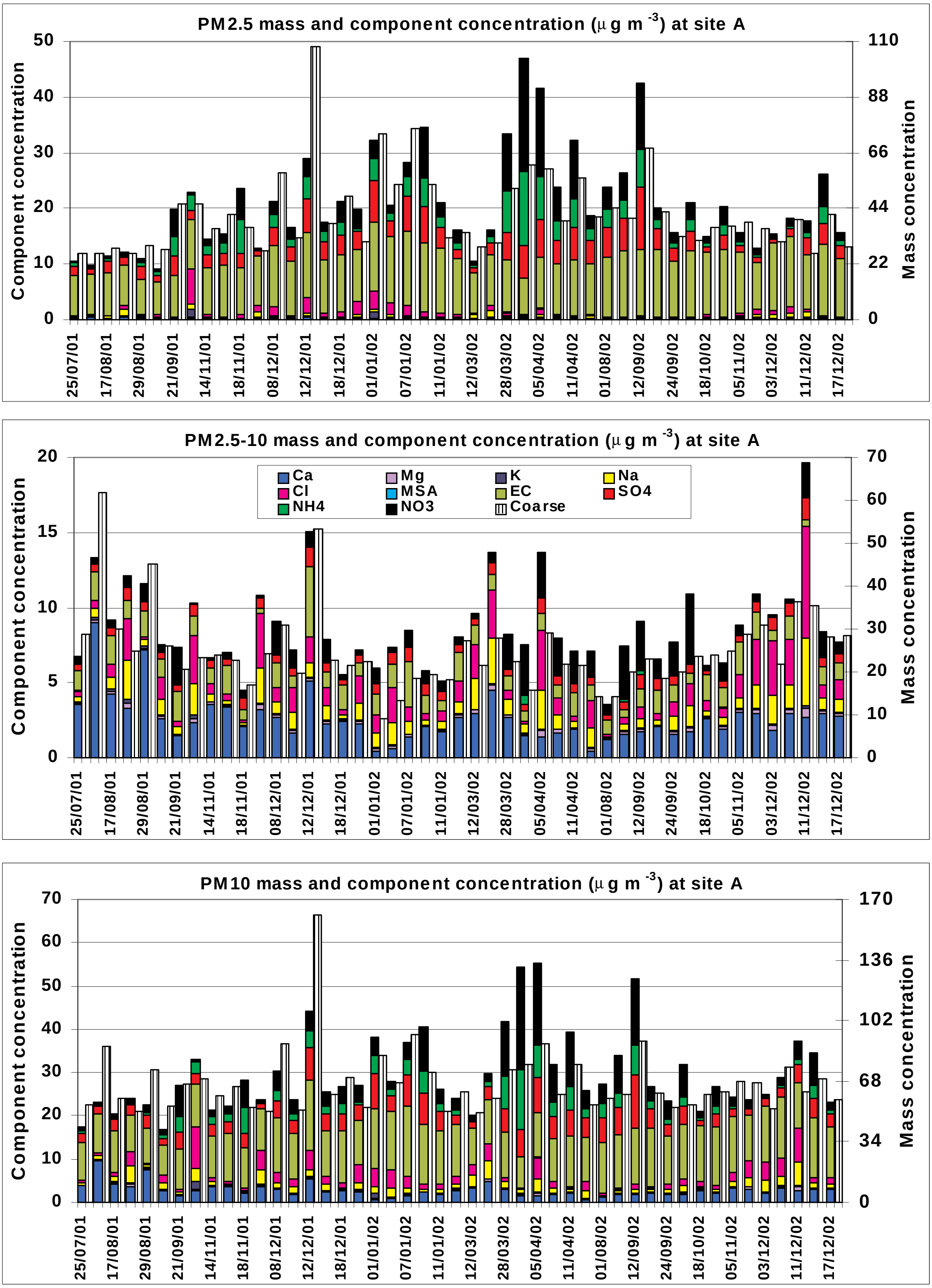
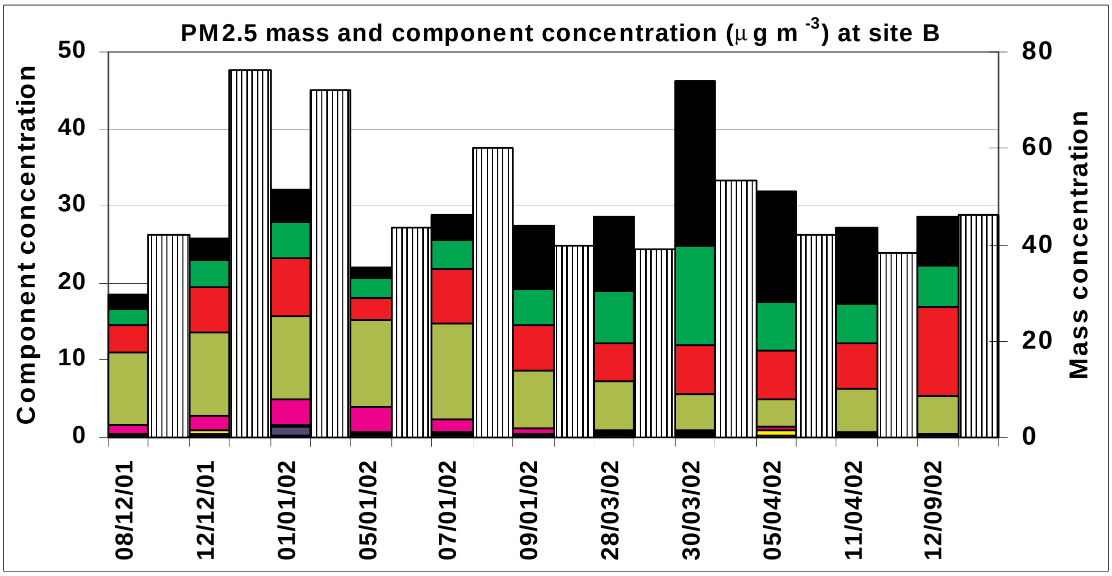
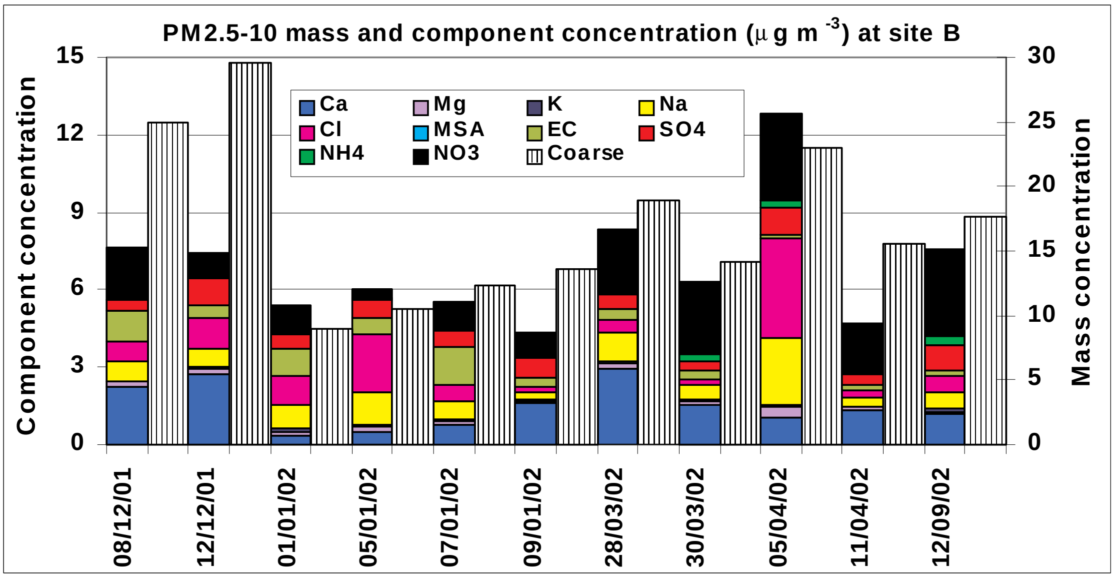
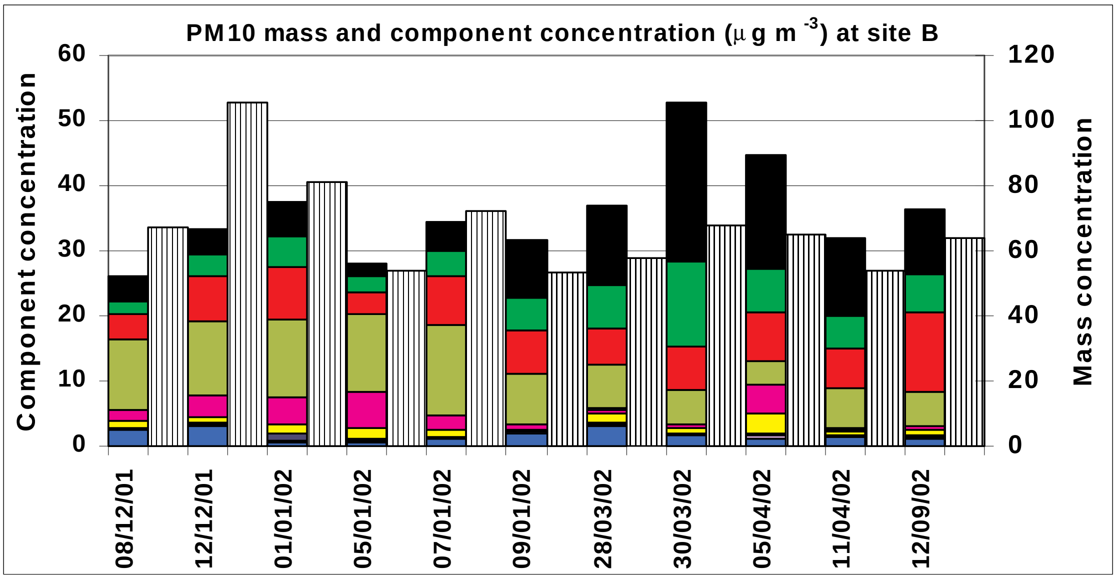


Figure 5.2. Daily PM mass and component concentrations on PM_{10} episodes.







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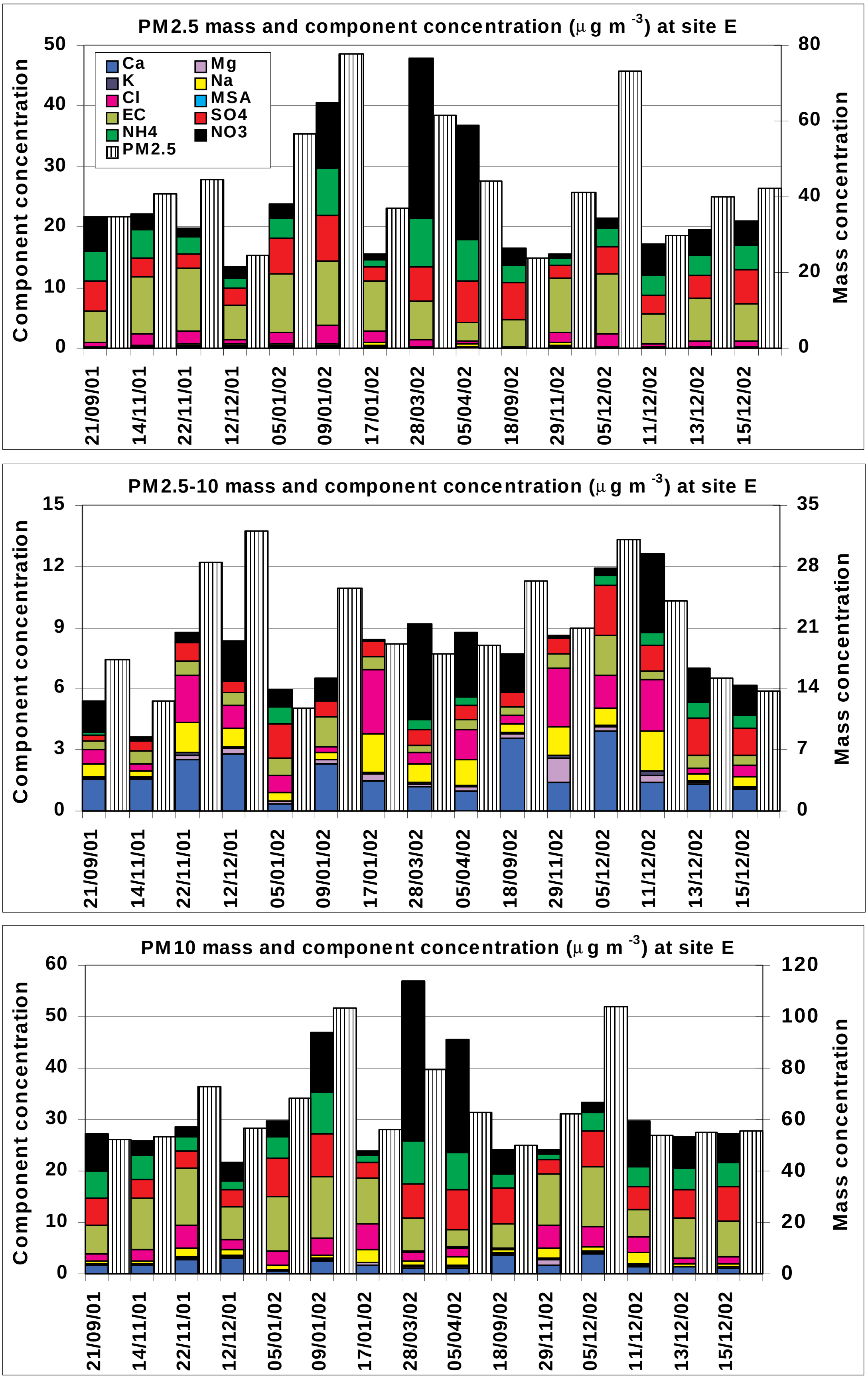

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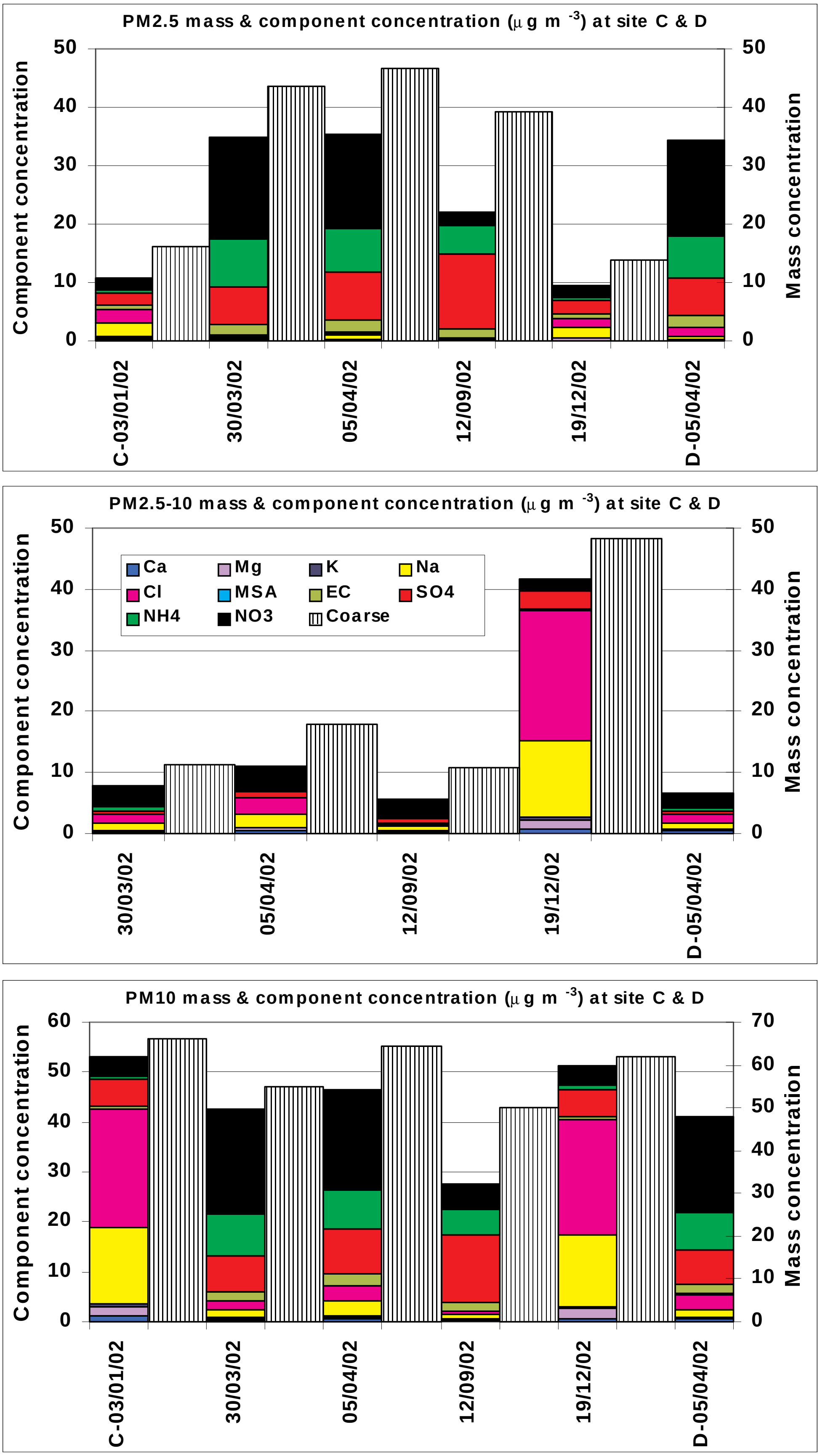

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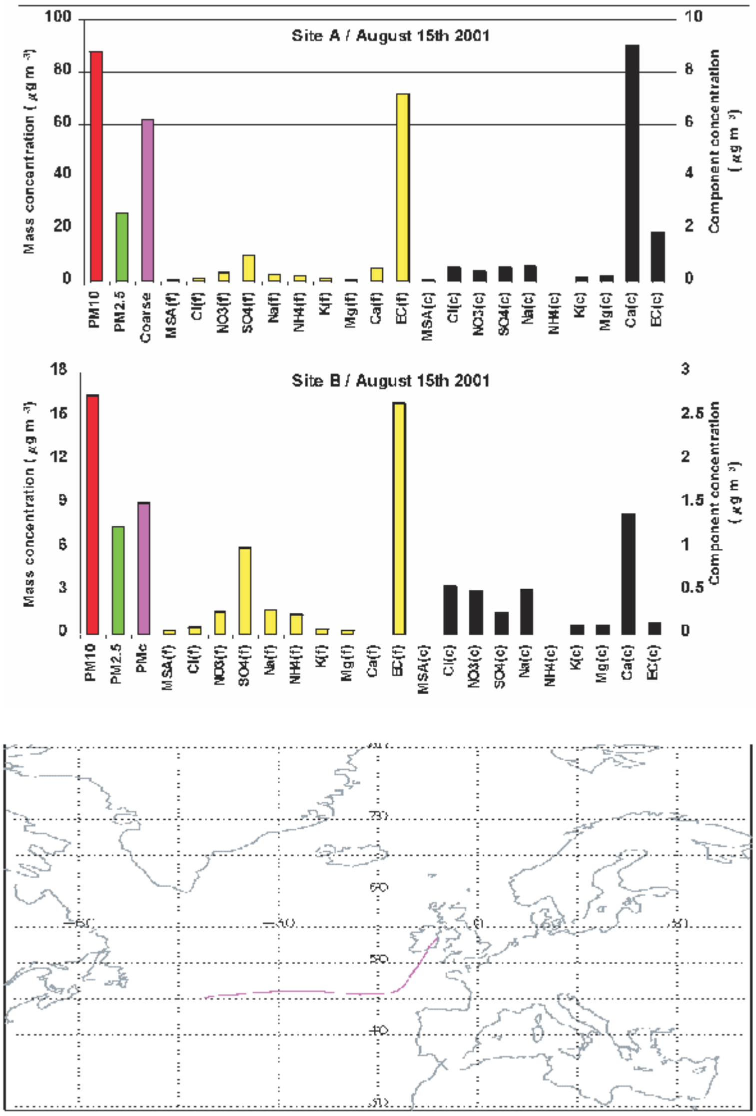


Figure 5.3a. PM and component levels and air mass back trajectory on 15 August 2001.

The air mass originated from the Atlantic, and circled around crossing Scotland and then the Midlands of the UK before arriving at the Dublin sites from the east. A similar back trajectory was observed for Site E except that the air masses travelled across the southern part of England before reaching the site, where the PM_{10} level was also elevated (57 µg/m^3) but only about one-half and one-third of the values at Sites B and A, respectively. This day featured both local and regional sources, showing high levels of EC and dust materials at urban sites, and increased concentrations of secondary components relative to Example 1.

Example 3

On 5 April 2002, a slow-moving air mass brought an accumulation of European and UK pollutants to the sites, where PM levels were consistently elevated (Fig. 5.3c). PM_{10} concentrations at all sites were similar and exceeded the standard limit due to consistently high concentrations of secondary aerosol containing sulphate, nitrate and ammonium. The local source was less important relative to the long-range transported aerosols, although its influence was still apparent at urban locations, particularly at the Dublin roadside site. The local wind speeds were low, at about 0.4, 3.3 and 2.2 m/s at Sites B, C and D, showing easterly direction at Sites C and D but westerly direction at Site B (this site was probably affected by local turbulence induced by high buildings and moving traffic, so that wind direction data may be unreliable). Clearly this is a fine-fraction dominated pollution episode, with the fine mass about

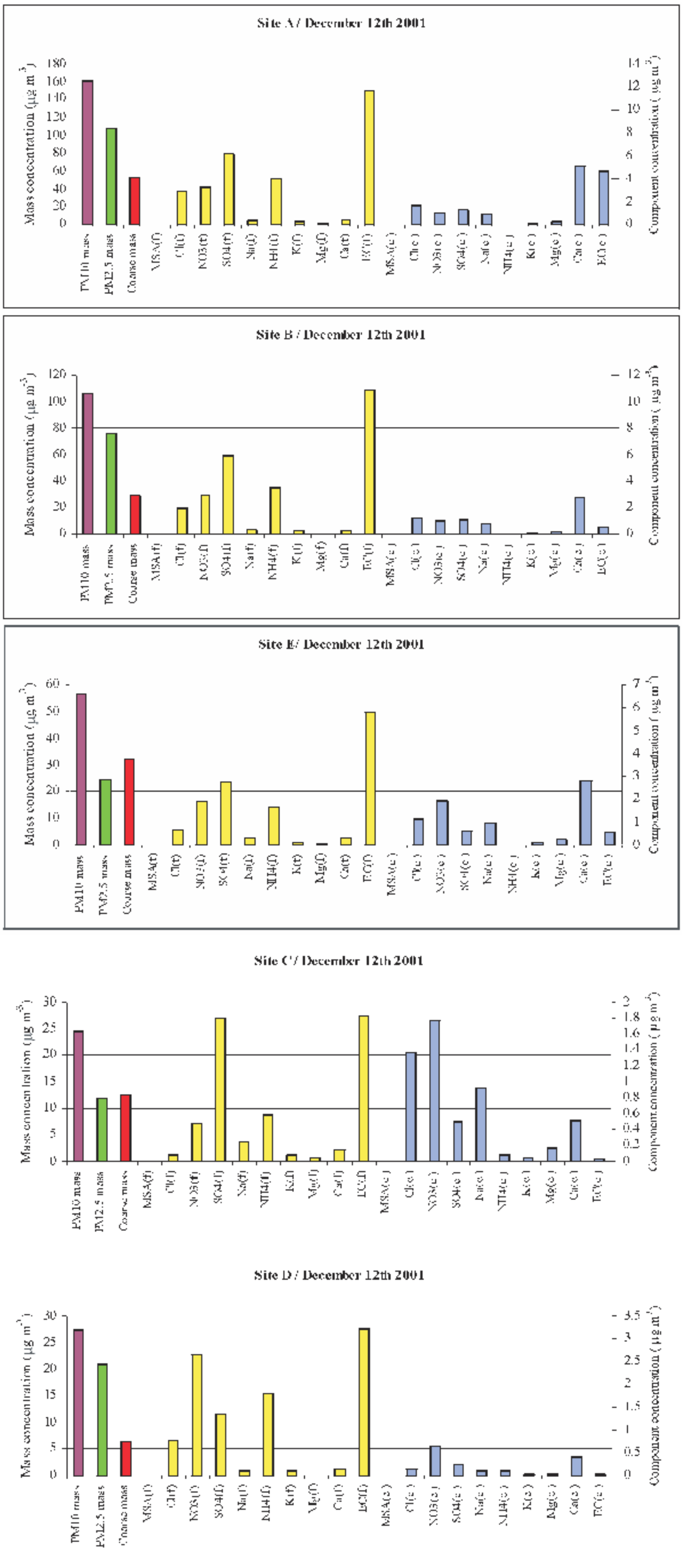


Figure 5.3b. PM levels and air mass back trajectory on 12 December 2001.

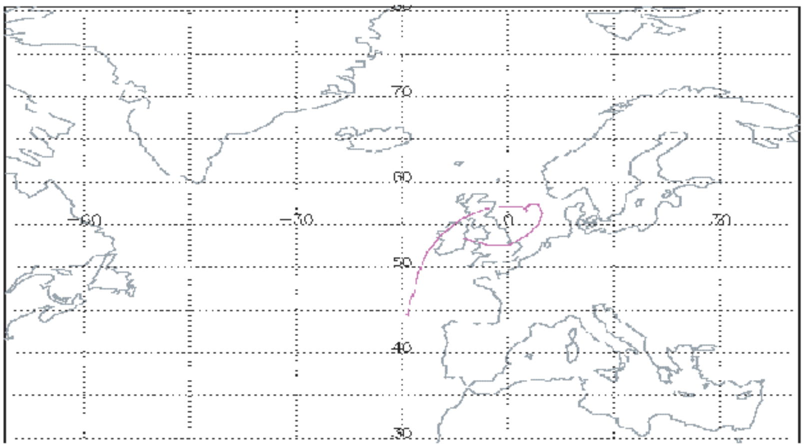


Figure 5.3b. ***Contd.***

twice or more than twice the coarse mass at the urban sites and three or more than three times coarse levels at the non-urban sites.

Example 4

Similar to Example 3 another slow-moving air mass occurred on 9 January 2002. Pollution levels were elevated at all urban sites (no data were recorded at the non-urban sites) (Fig. 5.3d). Very similar profiles were found between sites, showing similar high levels of secondary material, primary combustion emissions and traffic-induced resuspended dusts. It is noticed that the Cork site exhibited higher PM_{10} and $PM_{2.5}$ concentrations than did the Dublin roadside site due to higher levels of secondary particles in air masses originating over France and the UK. In addition, fine fraction chloride was also high at Site E, at about four to five times the levels at Sites A and B, perhaps due to a local combustion source (such as fireworks, peat burning or other unidentified processes).

Example 5

By contrast, 7 September 2001 experienced a clean and fast westerly airflow (Fig. 5.3e) with low levels of PM mass at all sites. Higher proportions of coarse particles at most of the sites were attributed to higher contributions of sea salt. Site A showed similar levels of fine and coarse particles due to both sea salt and vehicular emissions.

Different aerosol concentrations and composition characterise air masses having different origins and which experience different meteorological conditions during transport. High levels of PM_{10} and $PM_{2.5}$ at urban sites can be associated with local, non-local or both sources (Examples 1, 2 and 4) for different air mass origins, whilst at non-urban sites (Example 3) elevated PM_{10} episodes are more likely to be due to external sources, such as the presence of air masses having European or UK origins. PM_{10} often contains a higher contribution from fine particles when there is an influence of easterly or south-easterly air masses (Examples 2–4), but higher proportions of the coarse fraction with a westerly air mass (Examples 1 and 5).

5.3 Mean Concentration Estimates for PM Mass and Chemical Components for Different Air Mass Origins

In order to estimate the contributions of local, regional, national, European and North Atlantic sources of PM_{10}, air mass trajectories obtained for every measurement day were used to categorise the sampled air mass as one of seven types:

i. North Sea/Irish Sea (NS/IS). Arriving from northern sectors after traversing the North Sea and/or the Irish Sea, with additional input from coastal regions of Ireland and the UK.

ii. Northern European (NE). Polluted air masses originating over northern Europe, Scandinavia, Russia or Baltic regions, usually traversing the UK.

iii. Southern European (SE). Polluted air masses originating from southern European and North African sectors.

iv. Mixed (M). Difficult to assign category, mixed maritime/continental type.

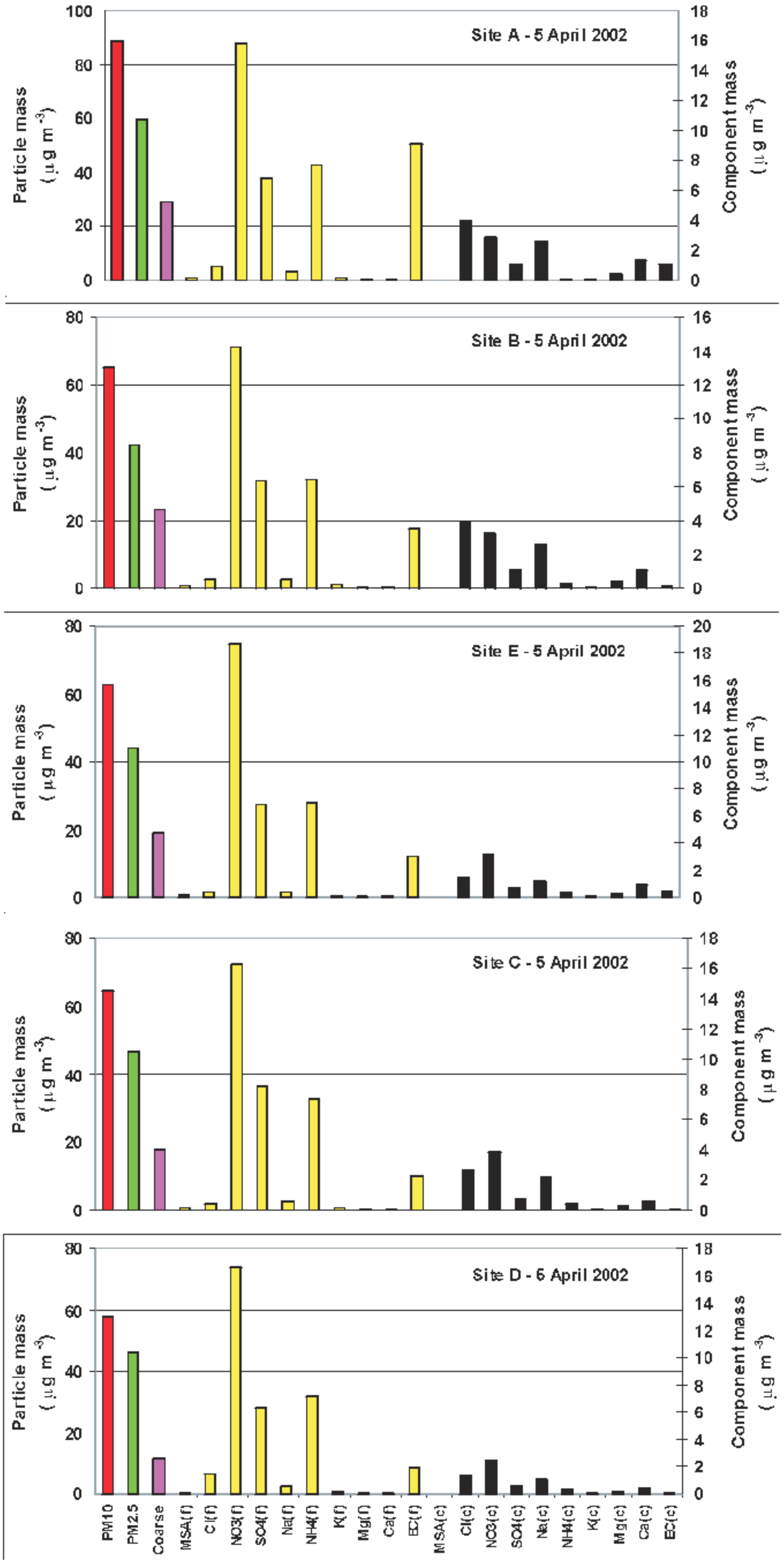


Figure 5.3c. PM levels and air mass back trajectory on 5 April 2002.

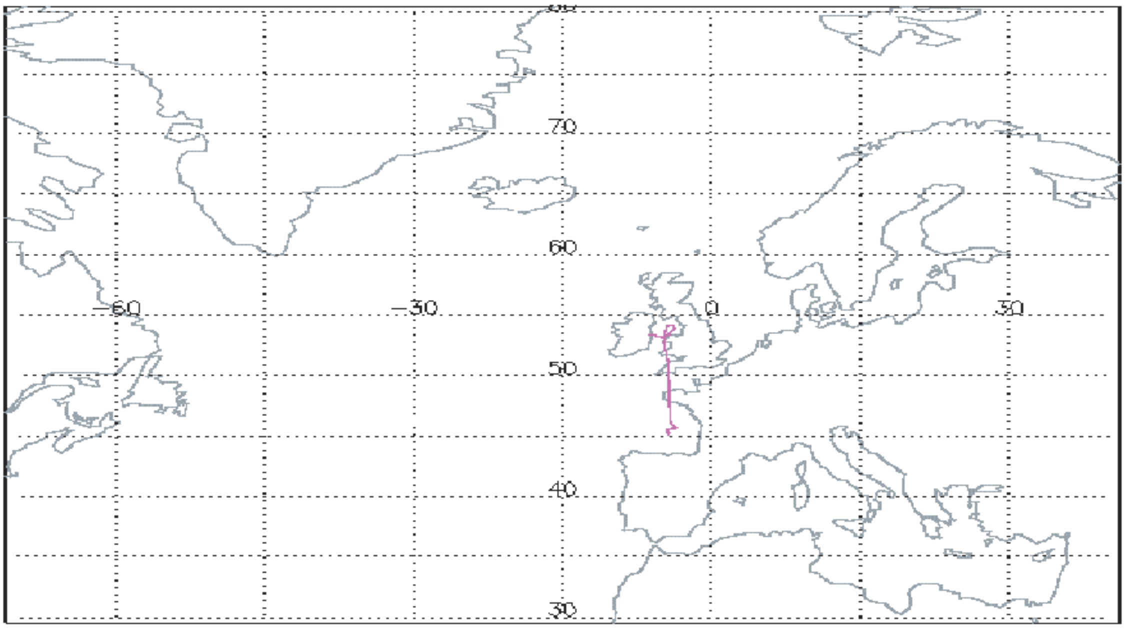


Figure 5.3c. ***Contd.***

v. South Atlantic (SA). Clean maritime air masses with no continental contact for at least 5 days before reaching the Irish coast.

vi. Mid-Atlantic (MA). Normally fast-moving air masses, could originate from eastern USA.

vii. North Atlantic (NA). Clean air masses from North Atlantic or polar regions, with no continental contact for at least 5 days.

The averaged concentrations of PM mass and their chemical components for each air mass origin were calculated using both the measured and the modelled results. For modelled results refer to Section 6.2.2.4. Results from measured data are illustrated in Fig. 5.4.

In general terms, a similarity can be seen within two main trajectory-type subgroups, either those experiencing significant continental contact (NS/IS, NE, SE), or those from maritime sectors (SA, MA, NA), with type M being intermediate in nature. These data provide an opportunity to consider the distinction in magnitude of sources native to Ireland and those which are ‘imported’. Within both categories exist the dominant anthropogenic sources as well as smaller contributions from natural sources. During periods characterised by the presence of continental air masses (these are the periods during which exceedances of European guideline limits tend to occur), at Site A $PM_{2.5}$ particle mass approximately doubles, compared to periods during which Atlantic air masses prevail. Considering individual chemical species, the largest increments are seen in concentrations of secondary aerosol components (sulphate, nitrate and ammonium), and to a lesser extent EC. Similar levels of sea salt species (sodium and chloride), as well as of calcium, are seen irrespective of trajectory type. At Site B the relative increase of $PM_{2.5}$ mass in continental air masses is higher, around 2.5 times the concentration in Atlantic air masses. Here the relative contribution from secondary species is higher, as a result of lower local (vehicular) emissions of EC, while the influence of carbon present in long-range transported continental air masses is proportionately greater. Site E shows generally similar features as Site B, with $PM_{2.5}$ levels in continental air around 2.5–3 times those in Atlantic air; however, here mean $PM_{2.5}$ concentration in SE type air masses was lower than in types NS/IS or NE. It is also seen that sea salt levels were higher in Atlantic air masses, although the differences are not large. At Sites C and D, $PM_{2.5}$ mass was around two times and three times higher, respectively, in continental air than in Atlantic air, the lower value for Site C being due to the masking effect of higher sea salt levels at this coastal location.

The mass of the coarse ($PM_{2.5–10}$) fraction was more constant between different air mass types, due to similar concentrations of the dominant species in this size range (sea salt and calcium). In this case, mass varies according

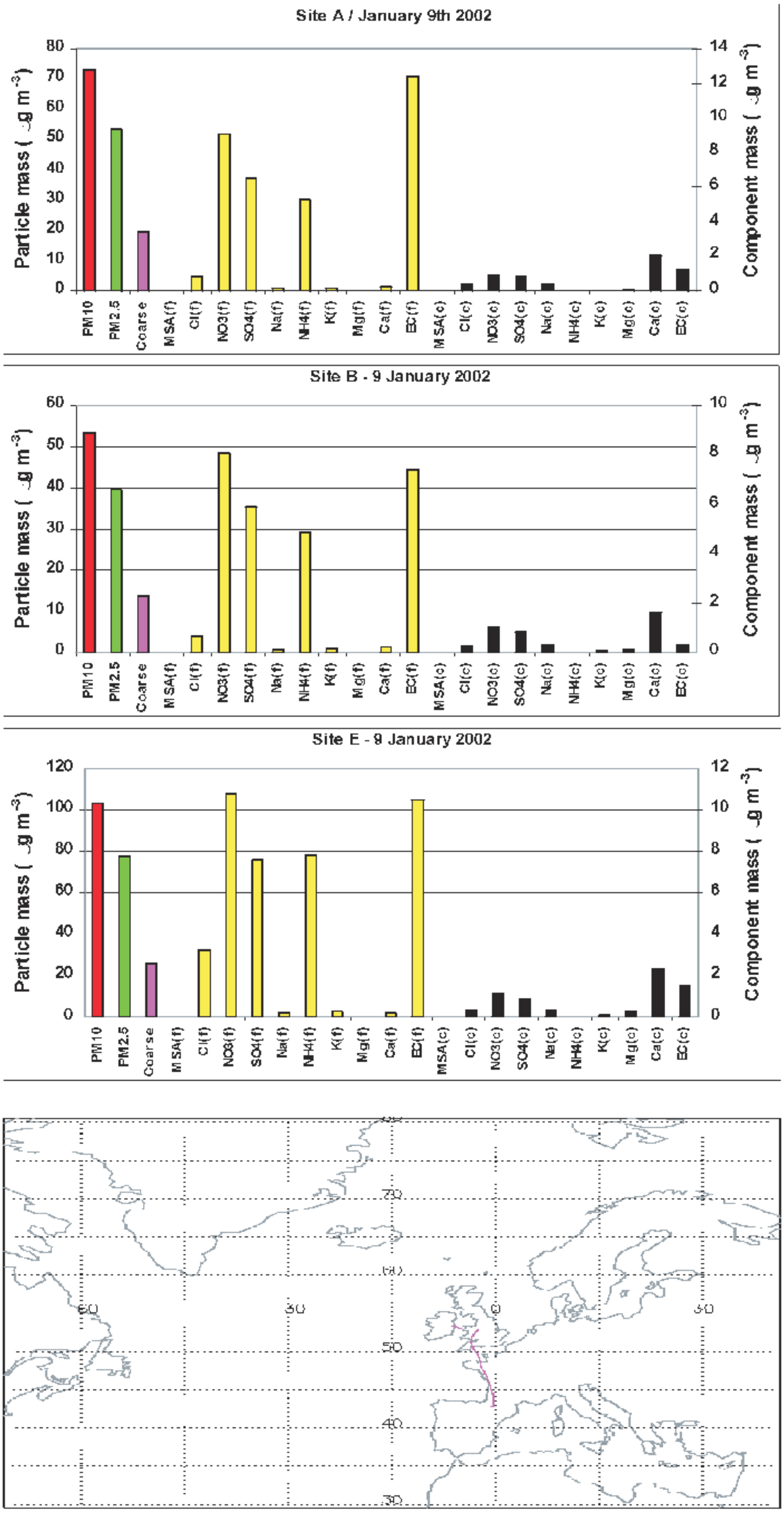
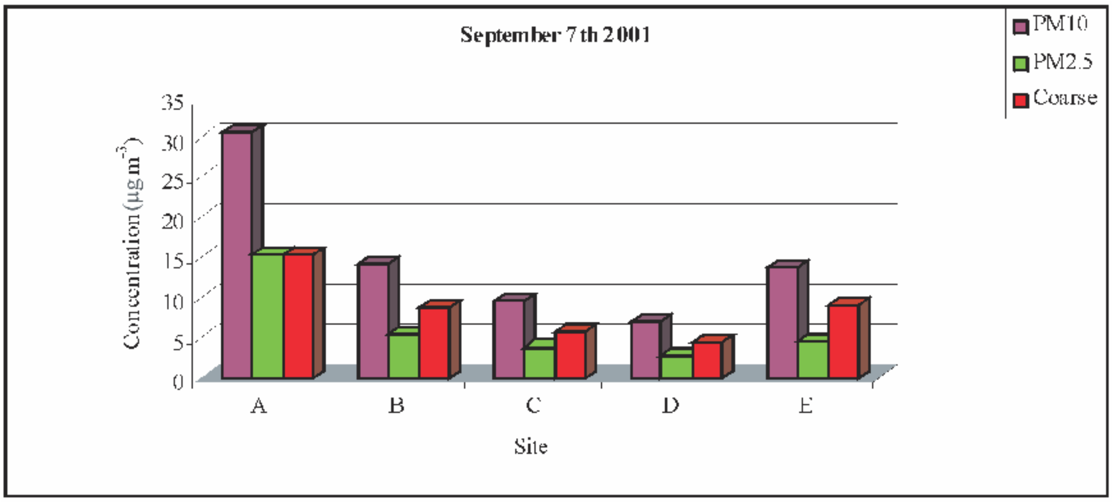


Figure 5.3d. PM levels and air mass back trajectory on 9 January 2002.



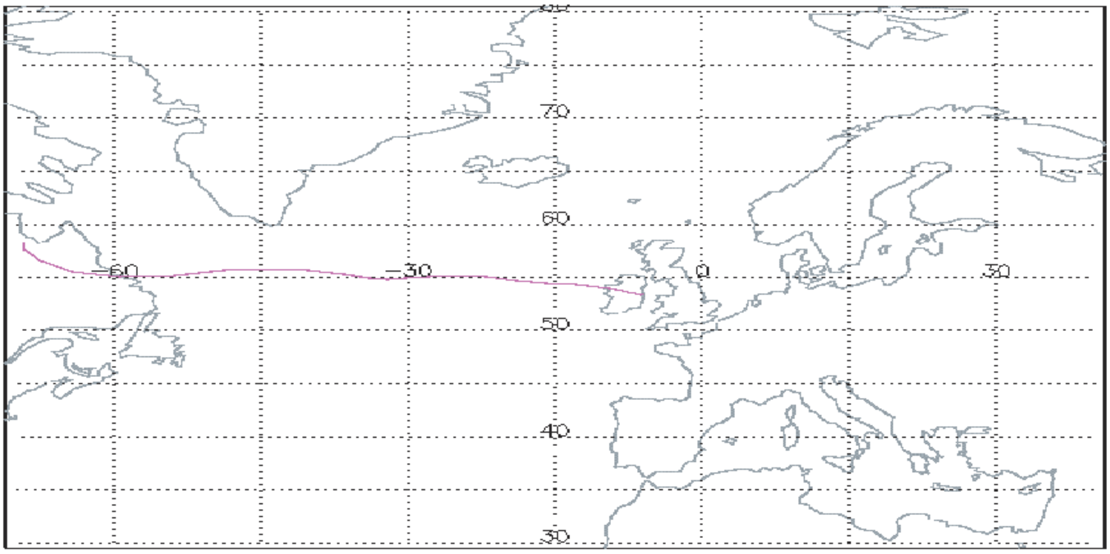


Figure 5.3e. PM levels and air mass back trajectory on 7 September 2001.

to meteorological conditions, with wind speed in particular influencing the rate of release of particles from the surface (whether oceanic or terrestrial). Nevertheless it is interesting to note that, although the absolute values are not large, production of nitrate within coarse particles was much higher within continental type air masses than in Atlantic air, with data for Site C indicative of an association with sea salt, suggestive of heterogeneous formation on sea salt aerosols. Elemental carbon was only a significant contribution to coarse particle mass at Site A, where it was clearly traffic related.

Since the association of coarse particle mass with individual sectors was much weaker than that of $PM_{2.5}$, the combined influences of the two fractions within PM_{10} results in lower differences between Atlantic and continental sectors for PM_{10} than for $PM_{2.5}$. Average increments in continental air (relative to Atlantic air) at Sites A, B, C, D and E were in the region of ×1.6, ×2, ×1.8, ×2.5 and ×1.5, respectively.

The continental air increments described above are derived from mean values determined for each trajectory type. The proportion of the aerosol mass deriving from long-range transport of continental pollutant aerosols is likely to rise in line with fine particle concentrations, so that on the most polluted days, when limit guideline values are more likely to be exceeded, the contribution from long-range transport may be significantly higher.

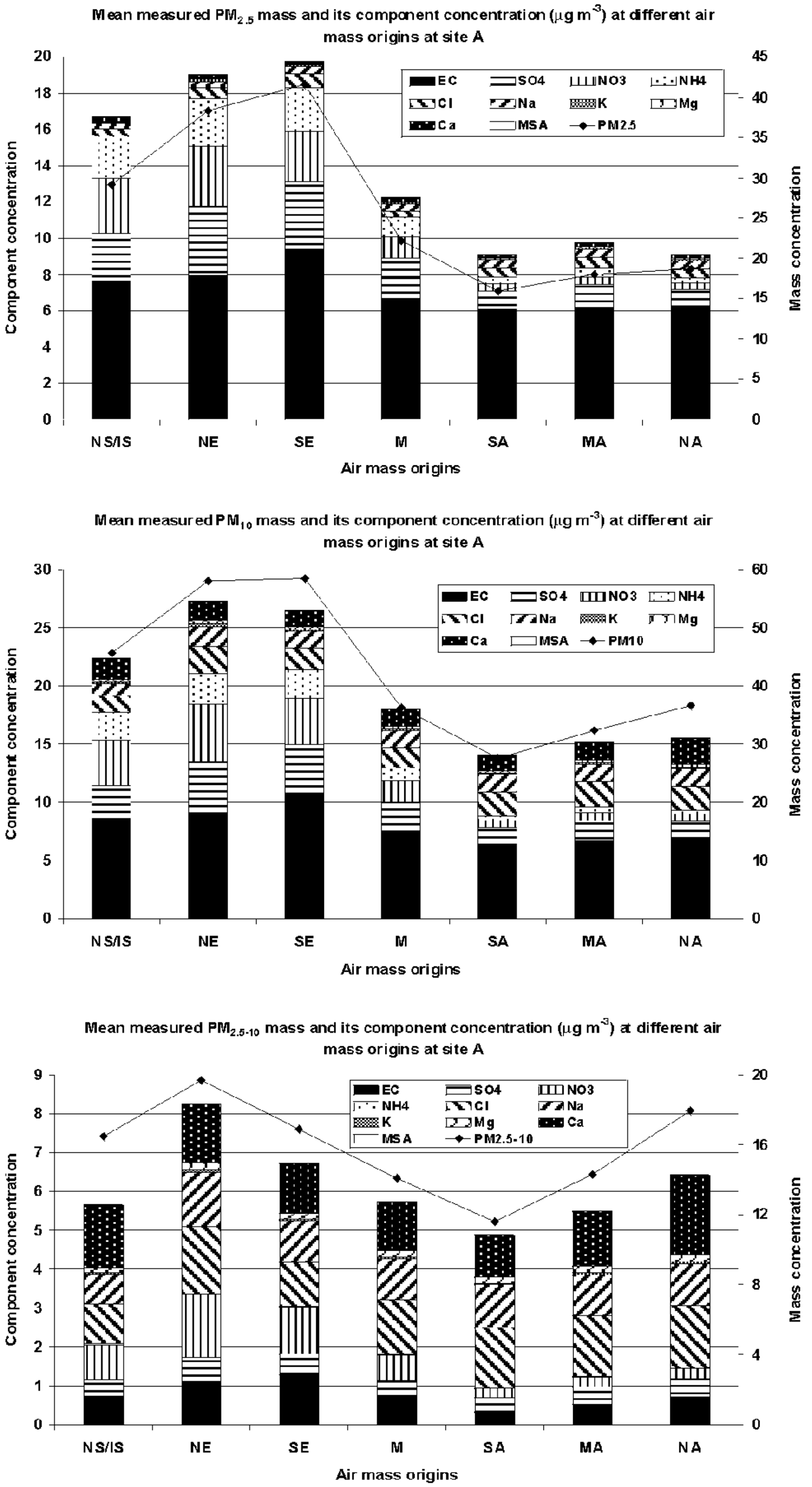
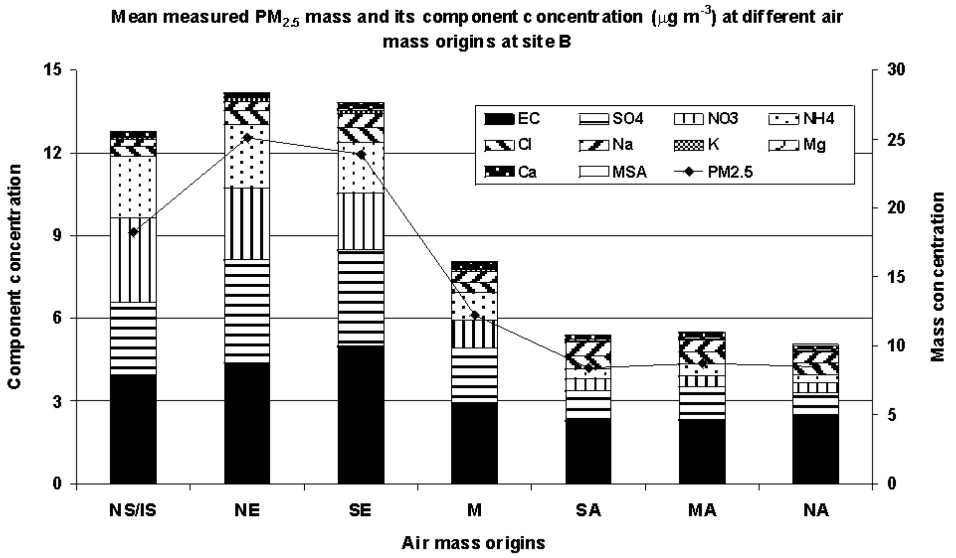
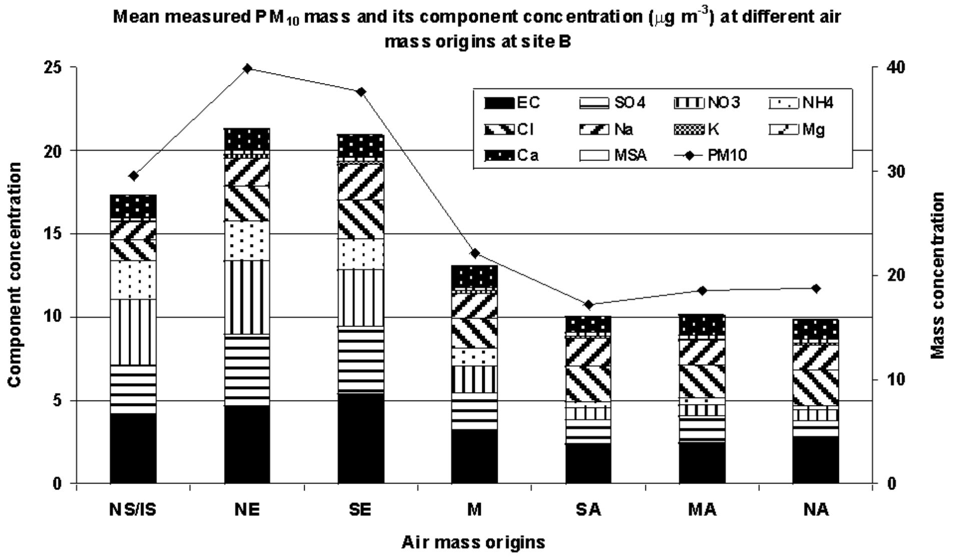


Figure 5.4. Particle mass and chemical component concentrations according to site, size fraction and air mass origin.





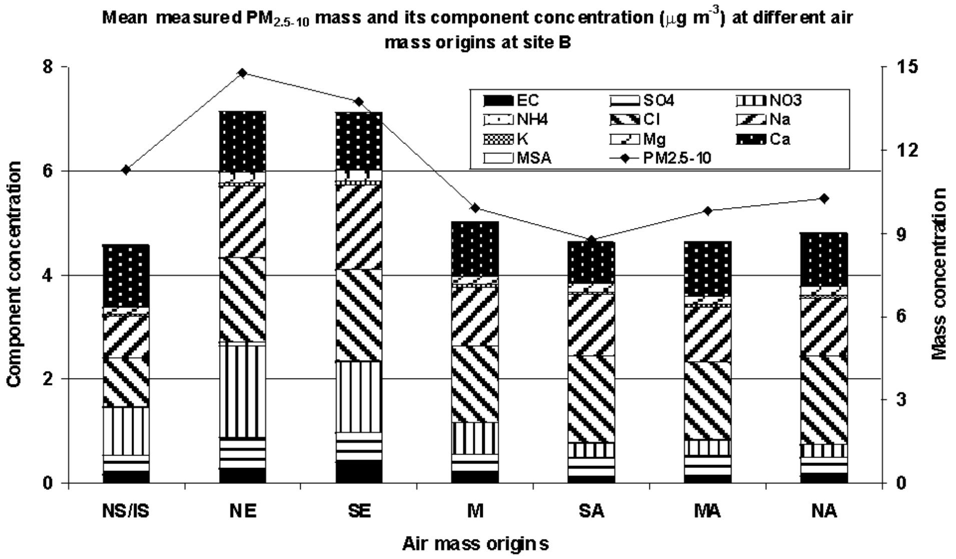
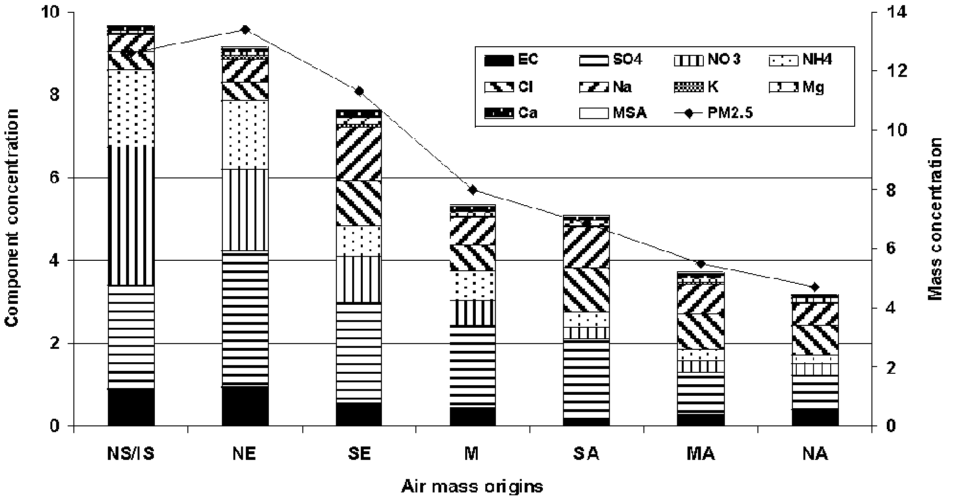
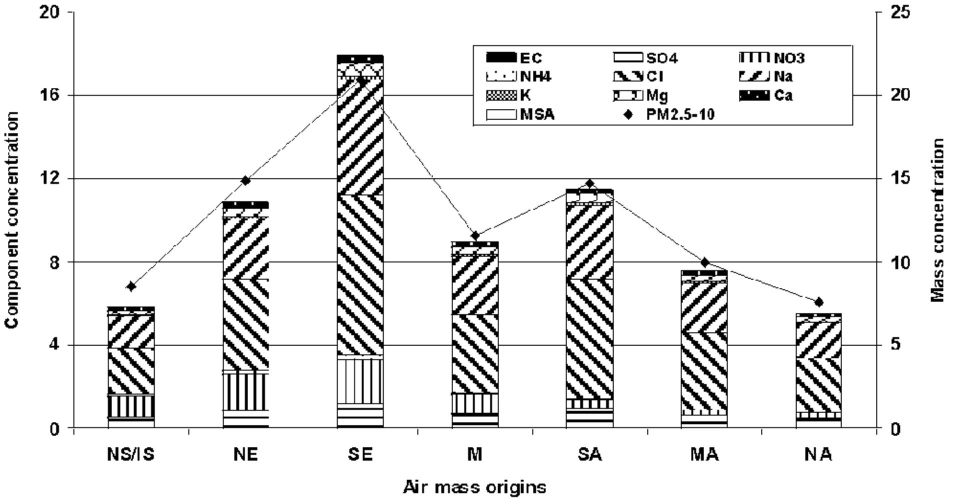


Figure 5.4. ***Contd.***

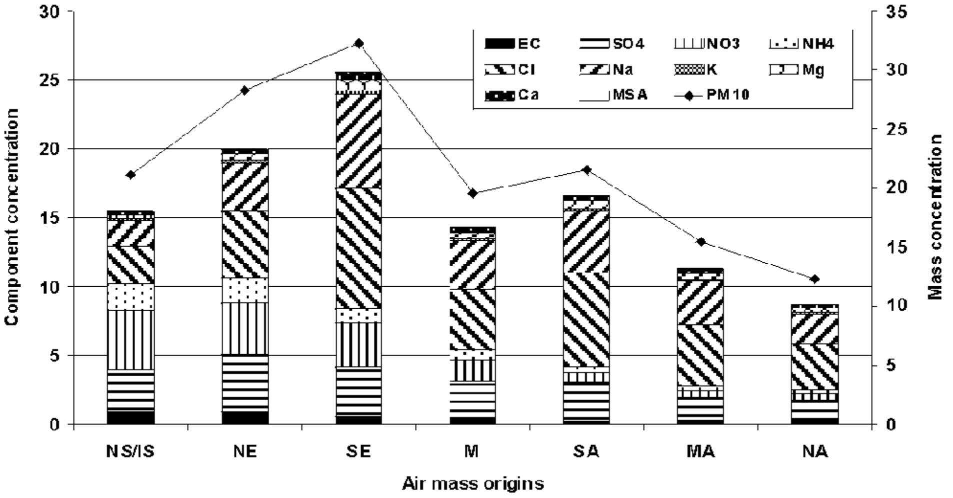
Mean measured $PM_{2.5}$ mass and its component concentration ($\mu g\ m^{-3}$) at different air mass origins at site C



Mean measured $PM_{2.5-10}$ mass and its component concentration ($\mu g\ m^{-3}$) at different air mass origins at site C



Mean measured PM_{10} mass and its component concentration ($\mu g\ m^{-3}$) at different air mass origins at site C



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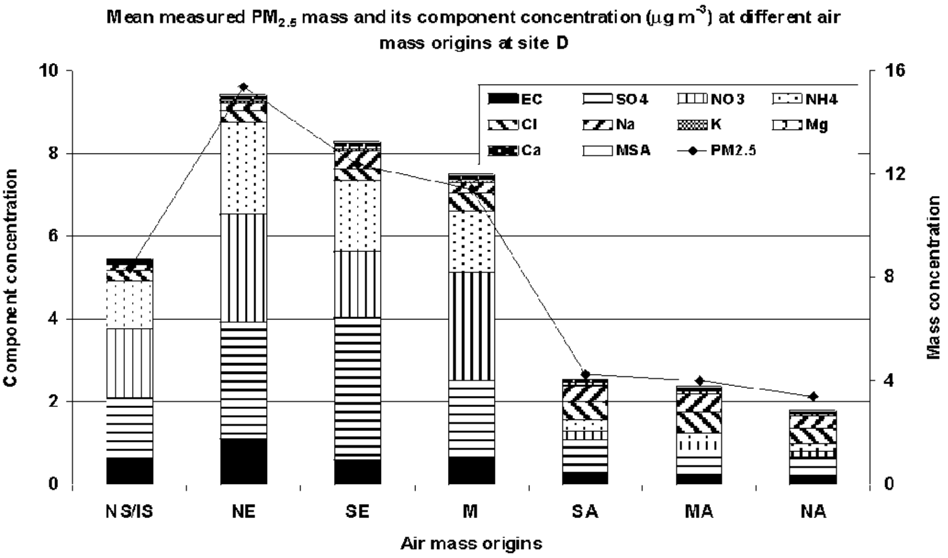
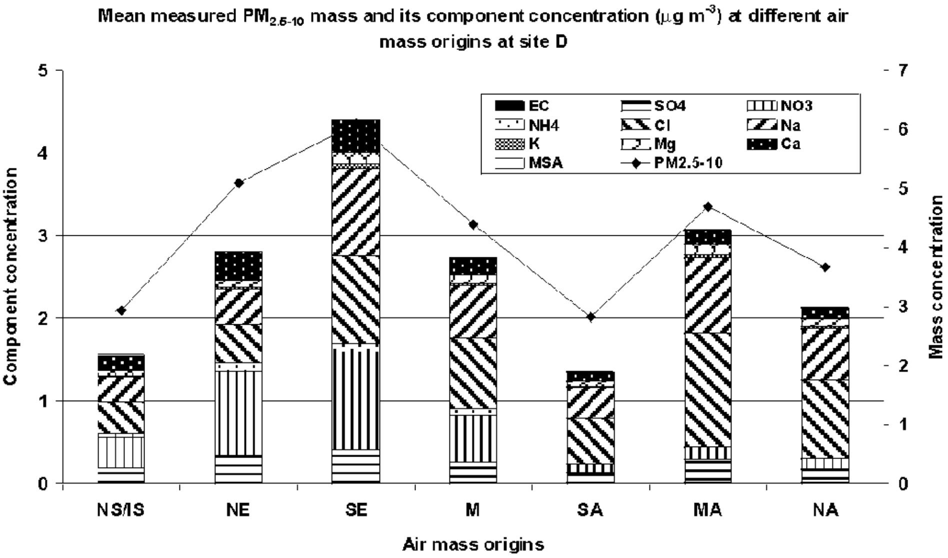




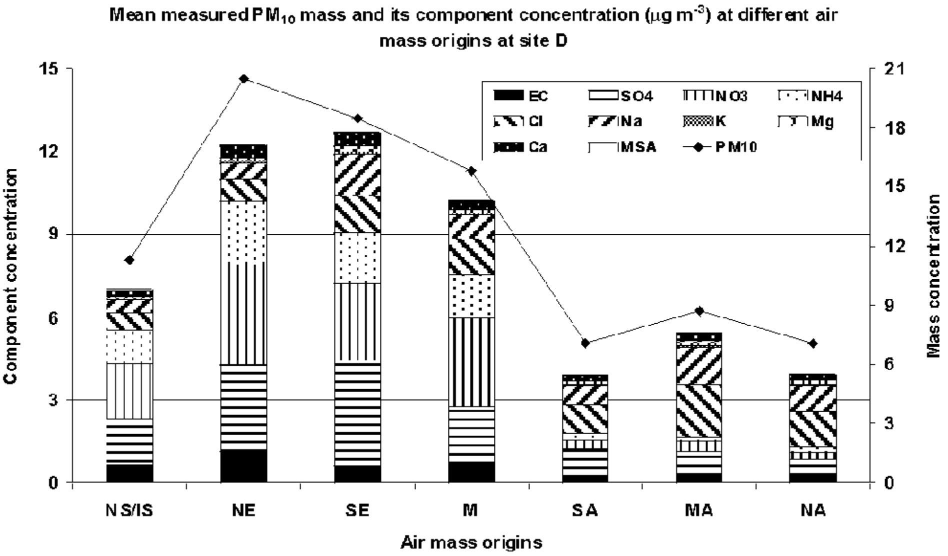
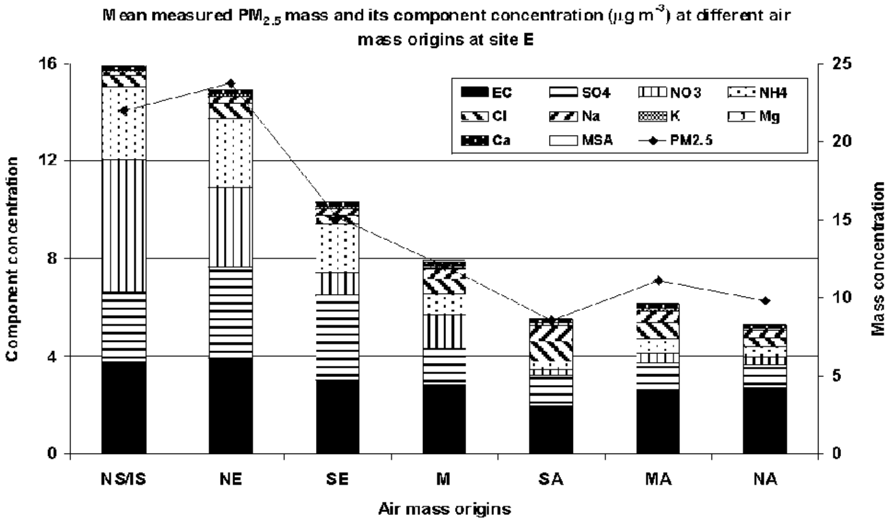
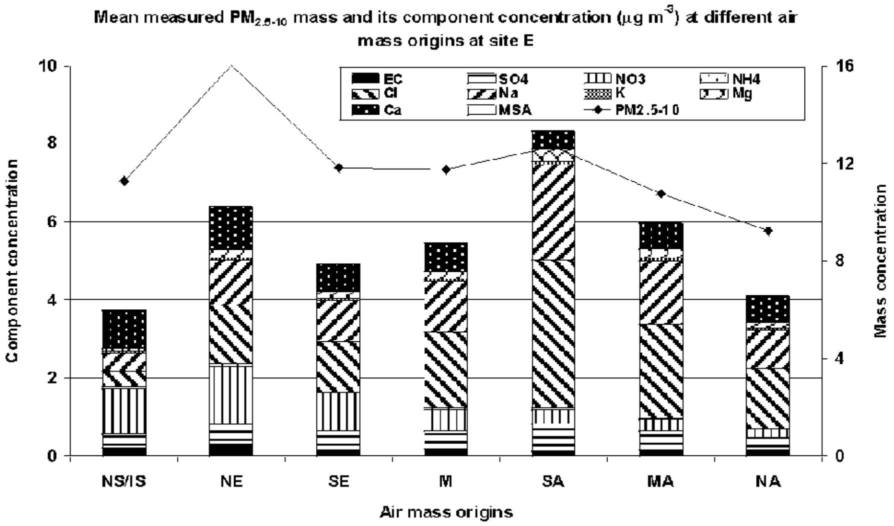


Figure 5.4. ***Contd.***





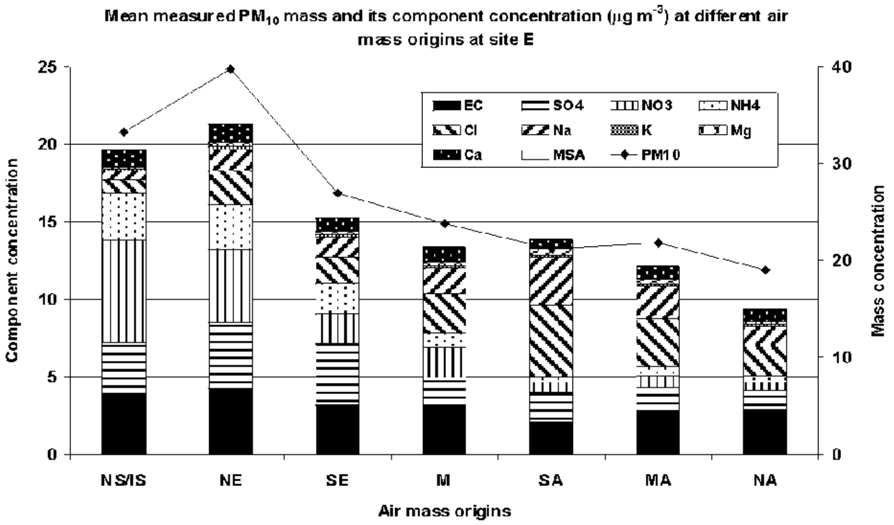


Figure 5.4. ***Contd.***

6 Source Apportionment of Aerosol PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$

6.1 PM Source Apportionment Using the Chemical Reconstruction Method

6.1.1 Mass closure analysis using measured chemical components

Mass closure analysis was conducted by comparing the aerosol gravimetric mass and its measured chemical components, shown in Fig. 6.1. The measured components explain a large portion, in the range 38–76%, of the PM mass, so that chemical component reconstruction may be usefully employed to evaluate the aerosol chemical composition and/or pollution sources, based on the assumption that suitable source/component markers are employed (discussed in Section 6.1.2). Apart from the other (unmeasured) component, the major chemical make-up of $PM_{2.5}$ at urban sites comprises EC, sulphate, nitrate and ammonium. A lesser contribution arises from sea salt and very little from calcium, potassium, magnesium and MSA. The largest proportion in coarse particles at urban sites is sea salt, followed by calcium, nitrate and sulphate. At the coastal and rural sites, fine particles mainly consist of secondary material (SO_4^{2-}, NO_3^- and NH_4^+) and sea salt, with much less EC in comparison with the urban sites. Coarse particles consist of mostly sea salt (55% at C and 35% at D) with additional contributions from NO_3^- and SO_4^{2-}. Similarly different chemical make-up was observed for PM_{10} between urban and non-urban sites, with higher proportions of EC at the urban sites and sea salt at the non-urban sites.

6.1.2 Mass closure analysis using reconstructed chemical components

Chemical reconstruction was performed for both fine and coarse fractions at all sites using appropriate chemical component marker measurements. Five major source categories were considered, including primary marine aerosol, secondary inorganic materials, primary anthropogenic EC, primary and secondary organic materials and resuspended materials.

i. Primary marine aerosol (sea salt). Sea salt was calculated as 2.54 × Na^+, assuming that all Na^+ was in the form of NaCl. Cl^- was not used here as its depletion at all sites was observed, especially in summer time with average PM_{10} ratios (Cl^-/Na^+) of 0.97–1.54 (sea water: $Cl^-/Na^+ = 1.8$).

ii. Secondary inorganic materials ($(NH_4)_2SO_4$ + NH_4NO_3). This component includes ammonium nitrate (NH_4NO_3) and ammonium sulphate ($(NH_4)_2SO_4$), and is calculated as 1.29 × NO_3^- +

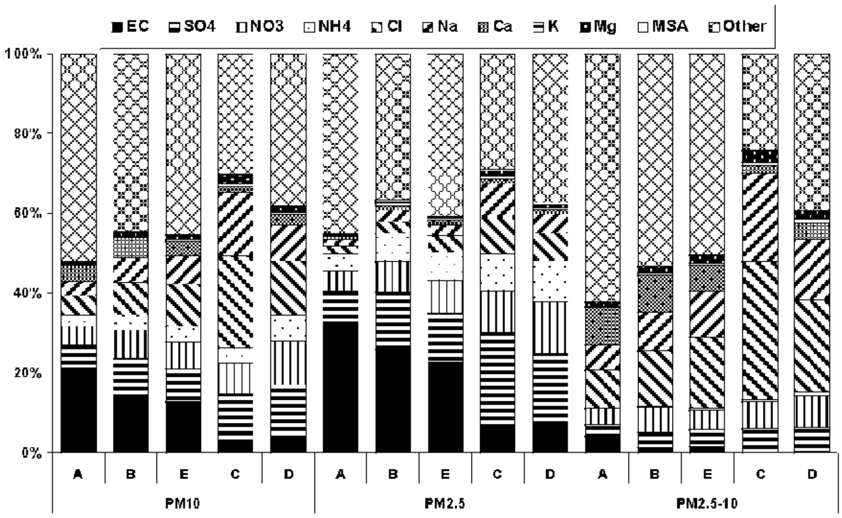


Figure 6.1. Measured relative chemical composition at five sites in Ireland.

1.38 × nss SO_4^{2-} (nss SO_4^{2-}: non-sea-salt sulphate, obtained using a sea salt SO_4^{2-}/Na ratio of 0.25). Some NO_3^- may be present in the form of $NaNO_3$ due to the reaction HNO_3 (g) + NaCl = $NaNO_3$ + HCl (g) (Harrison *et al*., 1994; Bardouki *et al*., 2003), therefore underestimation may occur if a majority of NO_3^- were to be $NaNO_3$; however, the error is expected to be small.

iii. Primary anthropogenic EC. Elemental carbon is essentially a primary pollutant arising directly from combustion sources. It is in elemental form and its mass does not need to be increased.

iv. Primary and secondary organic materials (Organics). Organic carbon has both primary and secondary origins (Bowman *et al*., 1997). Road transport is a major source of primary carbonaceous aerosol in European countries, particularly in urban areas (Hamilton and Mansfield, 1991; Castro *et al*., 1999). Secondary OC may be formed through gas to particle conversion of VOCs locally or during long-range transportation (Pandis *et al*., 1992). In order to incorporate the mass of other elements (such as H and O) which constitute organic compounds, a factor of 1.4 was applied to OC, although other workers have used different values, e.g. 1.6 (Turpin and Lim, 2001) and 1.7 (Bardouki *et al*., 2003).

v. Resuspended materials (Resusp). Non-sea-salt calcium (nss Ca^{2-}), obtained using a sea salt ratio Ca^{2+}/Na^+ = 0.038, was used as a marker for resuspended dusts, assuming that it is present in the same ratio as found in gypsum ($Ca_2SO_4 \cdot 2H_2O$), and calculated as 4.3 nss Ca^{2+}. Roadside increment of calcium has been found in the Ireland atmosphere primarily due to resuspension of dust. A study from the UK suggested that calcium may arise from the use of calcium soaps in automotive lubrication (Harrison *et al*., 2003a); however, this component must be very small since another study also from the UK did not observe any significant roadside increment of calcium (Harrison *et al*., 2003b). Under- or overestimation may occur using the single marker of calcium.

vi. Unexplained materials (Other). The excess mass, which is not included in the chemical reconstruction.

Comparison was made between the reconstructed chemical component masses and the gravimetric masses using a linear correlation (Fig. 6.2 and Table 6.1). Very strong correlations measured as R^2 values ranging from 0.82 to 0.96 were obtained for all fractions (PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$) at all sites, indicating that a reasonable reconstruction method has been applied with a high percentage of variance explained. Slopes (0.75–0.94) from the regression equation show that the gravimetric masses were largely explained by the constructed chemical source components, although small intercepts close to zero (–1.11 to 1.19) were observed.

The average contributions (%) to the PM masses at the five sites are shown in Fig. 6.3. The total contributions from the reconstructed chemical source components to the measured fine particle mass are about 88%, 93%, 90%, 84% and 79% for Sites A, B, E, C and D, respectively. The smaller proportions of the modelled results from the non-urban sites (C and D) are reasonable due to underestimation of the organic compound contribution, which is calculated based on the EC measurements and the OC/EC ratios during intensive periods. Water contents associated with hygroscopic aerosols, such as $(NH_4)_2SO_4$ and NH_4NO_3, may also contribute to the other component. Approximately 79%, 81%, 72%, 75% and 72% of the gravimetric coarse particle masses at the five sites (A, B, E, C and D, respectively) were accounted for by the reconstructed chemical components. The larger percentage of the other (unexplained) components is associated most likely with underestimation of resuspended materials at the urban sites, and both underestimation of organics and of water content at the non-urban sites. Higher contributions were also found for PM_{10} at urban (86%, 88% and 80% – A, B, E) than non-urban (78% and 76% – C, D) areas.

Mass closure analysis has become an accepted tool for aerosol diagnostics. Such analysis can be performed using ambient measurements alone or chemical reconstruction based on a small number of chemical marker measurements. The former generally requires intensive analysis if a majority proportion of aerosol mass is to be covered. The latter may be used to estimate the majority of particle mass using chemical marker measurements, assuming that all chemical components considered account for significant percentages of the mass measured. In this study, smaller percentages of the PM mass were explained (38–76%) (Fig. 6.1) using the former method, although other workers have found higher contributions (75–90%), but based on much more extensive analyses (Chan *et al*., 1997; Kim *et al*., 2000).

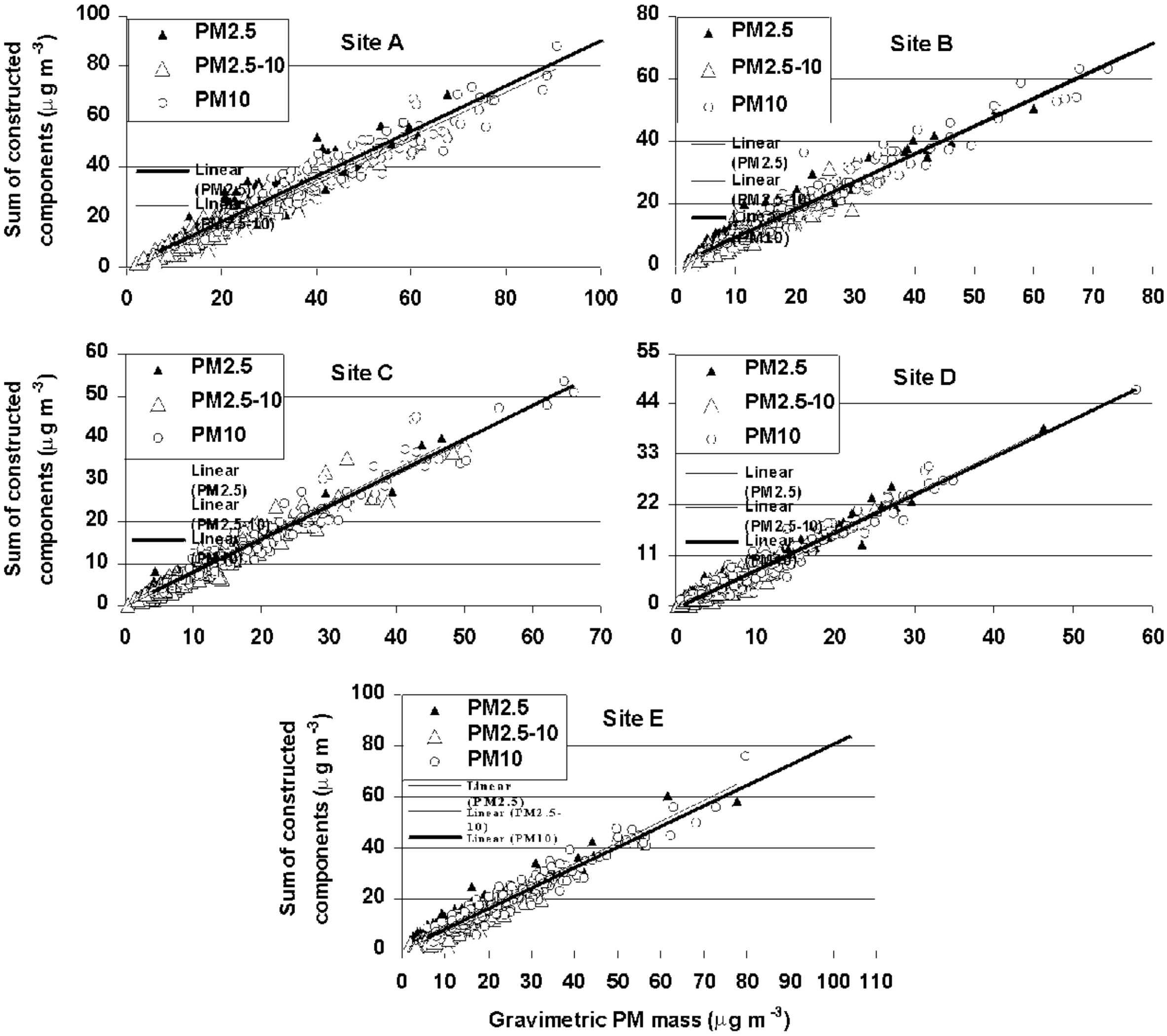


Figure 6.2. Correlation between reconstructed chemical component and gravimetric masses.

Table 6.1. Results of regression for gravimetric mass and reconstructed mass.

	PM_{10}			$PM_{2.5}$			$PM_{2.5–10}$		
Sites	**Correlation**	**R^2**	**N**	**Correlation**	**R^2**	**N**	**Correlation**	**R^2**	**N**
	Reconstructed mass (y) upon gravimetric mass (x)								
A	y = 0.88x – 0.56	0.92	260	y = 0.90x + 0.46	0.86	260	y = 0.85 – 1.11	0.90	264
B	y = 0.89x + 0.25	0.93	259	y = 0.89x + 1.00	0.93	259	y = 0.88 – 0.70	0.84	261
E	y = 0.80x + 0.48	0.93	257	y = 0.82x + 1.19	0.93	258	y = 0.72 + 0.03	0.85	258
C	y = 0.80x – 0.18	0.95	230	y = 0.81x + 0.26	0.95	231	y = 0.70 – 0.41	0.94	231
D	y = 0.83x – 0.67	0.94	260	y = 0.83x – 0.22	0.96	262	y = 0.73 – 0.01	0.82	260

With the reconstruction method, however, about 72–93% of the aerosol mass could be explained in the present study (Fig. 6.3).

Results in Fig. 6.3 indicate that, in urban areas, the major components contributing to fine particles (up to 79–84% of the total mass) are organic compounds (30–33%), EC (23–33%), ammonium sulphate and ammonium nitrate (17–29%), whilst in the coarse fraction resuspended material (27–41%) and sea salt (17–30%) are predominant (up to 56–66% of the total mass). In comparison, at the rural and the coastal sites, $PM_{2.5}$

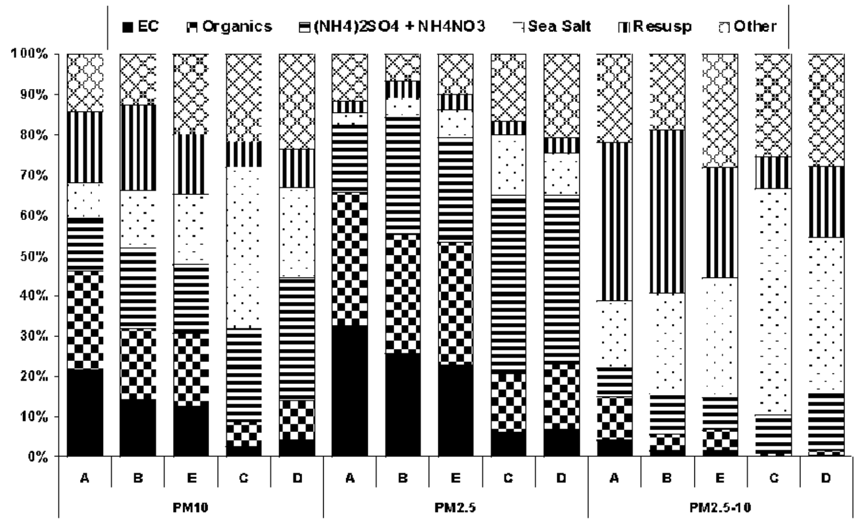


Figure 6.3. Reconstructed relative chemical composition at five sites in Ireland.

mainly consists of ammonium sulphate and ammonium nitrate (42% and 44%) and organic materials (16% and 14%), whereas sea salt is the largest contributor (39% at rural and 56% at coastal) to coarse particles. Similarly, urban site PM_{10} consists of a larger fraction of carbonaceous aerosols (46.1% at A, 31.7% at B and 30.5% at E) and a significant proportion of resuspended materials (17.7%, 21.2% and 14.7%), due to the influence of road traffic. On the other hand, sea salt and secondary components are predominant at non-urban sites.

As mentioned above the unexplained materials, accounting for about 7–28% of the aerosol mass, most likely relate to resuspended materials at the urban sites and organic materials at the other sites. Water content may also contribute to the unexplained fraction, particularly where there is a large amount of hygroscopic material such as NaCl (e.g. at the coastal site), sulphate and nitrate (Speer *et al.*, 2003). The largest uncertainties arise from the resuspended and organic components, which rely on the water-soluble calcium and the EC measurements.

6.2 PM Source Apportionment Using a Statistical Modelling Approach

In addition to the chemical reconstruction method, statistical modelling was also used to estimate the contributions of the major sources to the PM mass. Initially the project was designed to use a modified regression model based on two previous works carried out in the UK by Stedman (1997) and Turnbull and Harrison (2000). Stedman (1997) used a regression model to identify major PM_{10} component concentrations as a secondary inorganic component using sulphate as source marker, a primary combustion fraction with source marker black smoke, and a constant/other component mainly containing coarse marine aerosol and resuspended terrestrial dusts. The extended model of Turnbull and Harrison (2000) included an extra component, sea salt, using sodium chloride as an indicator derived from chloride. These models may be expressed as follows:

$$PM_{10} = a\,(SO_4^{2-}) + b\,(\text{black smoke}) + \text{Constant}$$

$$PM_{10} = a\,(\text{black smoke}) + b\,(NH_4NO_3 + (NH_4)_2SO_4) + c\,(NaCl) + \text{Constant}$$

where *a*, *b* and *c* are regression coefficients. Both sulphate and nitrate were used as source markers for the secondary inorganic component in the later model where ammonium salts were calculated from nitrate and sulphate.

The modified model for the current project includes the addition of two more components, i.e. resuspended dusts and secondary marine aerosols. Considering that source components used in the model can vary significantly at different monitoring sites and for different aerosol fractions, the suitability of this model was checked by consideration of the source categories through a Factor Analysis (FA) using the chemical composition data. A Multiple Linear Regression model (MLR) was then followed using the source marker elements/compounds as independent and the total particle mass concentrations as dependent variables to calculate each source contribution to the PM mass. The software used was SPSS for Windows version 12.0. This procedure was applied separately to all sites for all particle fractions as PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$. As expected, different relative contributions from each source type and different source strengths have been observed.

6.2.1 Factor analysis

The chemical composition data used for factor analysis include the ionic species chloride, nitrate, sulphate, MSA, sodium, ammonium, potassium, magnesium and calcium, plus EC. In order to determine the secondary sulphate (nss SO_4^{2-}), sodium was used to correct for sea-salt sulphate based on a sea salt composition with an SO_4^{2-}/Na^+ ratio of 0.25. Similarly, non-sea-salt calcium (nss Ca^{2+}), potassium (nss K^+) and magnesium (nss Mg^{2+}) were obtained using a sea-salt Ca^{2+}/Na^+ ratio of 0.038, K^+/Na^+ ratio of 0.037 and Mg^{2+}/Na^+ ratio of 0.12.

Concentrations below the detection limit were replaced with zero. The number of replacements was less than 5–10% for all data sets, which has no discernible effect on the FA results (Morandi *et al.*, 1987).

At the first attempt, it was found that EC tended to interfere with secondary nss SO_4^{2-}, particularly at the urban sites, presumably due to a similar source from long-range transportation. To minimise the interference, the EC concentrations were corrected for urban sites using Site D as a reference site when there is a westerly air mass, and Site C when there is an easterly air mass, assuming that all nss SO_4^{2-} and EC at Sites D and C are attributed to long-range transportation. Therefore, EC concentrations at urban sites were recalculated by excluding a long-range transported component, using the ratios nss SO_4^{2-}/EC at Site D or C. Similarly, interferences were also noticeable between EC and nss Ca^{2+} at urban sites since both components are related to road transport. However, no remedy has been applied in this case, which may influence the outcome of the MLR analysis.

Although statistical modelling is a traditional method and has been used in the study of aerosol source apportionment since the early 1970s, the procedure is not simple and straightforward. Prior to the analysis, all data sets were explored graphically to screen out any extreme outliers and to check their normality since skewed distributions and outliers can affect the results. It was found that most of the data sets possessed a log-normal distribution and ideally symmetrising or log-normal transformations seem to be appropriate. This procedure was not carried out in this study due to resultant difficulties of subsequent interpretation. However, outliers were screened out to make the data fit more closely to a normal distribution, and exclusion of data points was less than 5%.

A principal component factor extraction method was used with orthogonal (Varimax) rotation transformation. Four or five factors (source components) were extracted with eigenvalues over 1, which accounted for 75.8–89.2% of the total variance. Table 6.2 shows the factors identified with associated high loading variables (>0.7 or 0.5–0.7) and the sum of variance explained at all sites for all particle fractions.

The primary combustion source component is always associated with high loadings of EC at all sites and for all fractions, although on a few occasions high loadings of potassium, non-sea-salt sulphate and non-sea-salt calcium were observed. Fine potassium, which would arise from sources such as peat burning or fireworks, can contribute to fine aerosol mass, whereas coarse potassium was associated with sea salt or resuspended dusts indicated by high loadings with sea salt or resuspended dust source components. High loadings of nss Ca^{2+} at urban sites were presumably due to the fact that both EC and nss Ca^{2+} are associated with road traffic, and of nss SO_4^{2-} and NO_3^- at the coastal site were due to a similar source, i.e. long-range transport.

Major loadings for the secondary inorganic source component are shown by nitrate, sulphate and ammonium, except at the rural site where EC also has a contribution presumably since the EC concentrations at Sites C and D were not corrected for excluding a fraction associated with long-range transport.

The sea salt component has high loadings of chloride, sodium, magnesium and sometimes potassium. Interestingly, at Site C, nss Ca^{2+} and nss SO_4^{2-} are also associated with sea salt for the coarse fraction.

Resuspended dusts were characterised by high loadings of nss Ca^{2+} and occasionally potassium and nss SO_4^{2-} at Sites A, B, E and D but not at Site C. High loadings of nss SO_4^{2+} may indicate the presence of calcium sulphate in dust materials.

Table 6.2. Results of factor analysis (source components and associated variables with strong loading – >0.7 or *0.5–0.7).

Sites	Fraction	Primary combustion	Secondary combustion	Sea salt	Resuspended dusts	Secondary marine	Sum of variance (%)
A	PM_{10}	EC	NO_3^-, nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}, K^+	N/A	85.9
	$PM_{2.5}$	EC	NO_3^-, nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}	MSA	88.5
	$PM_{2.5–10}$	EC, *nss Ca^{2+}	NO_3^-, NH_4^+	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}, K^+	N/A	83.0
B	PM_{10}	EC, K^+	NO_3^-, nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}	N/A	81.5
	$PM_{2.5}$	EC, K^+	NO_3^-, nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}	N/A	86.2
	$PM_{2.5–10}$	EC	NO_3^-, *nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}, K^+	nss Ca^{2+}	N/A	85.6
E	PM_{10}	EC	NO_3^-, nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}, *K^+	nss Ca^{2+}, *K^+	N/A	81.5
	$PM_{2.5}$	EC	NO_3^-, nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}, *K^+	N/A	80.0
	$PM_{2.5–10}$	EC, *nss Ca^{2+}	NO_3^-, *nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}, K^+	nss Ca^{2+}, *nss SO_4^{2-}	N/A	75.8
C	PM_{10}	EC, *nss SO_4^{2-}	NO_3^-, nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}, K^+	N/A	MSA	84.7
	$PM_{2.5}$	EC, *NO_3^-	nss SO_4^{2-}, NH_4^+	Cl^-, Na^+, Mg^{2+}	N/A	MSA	80.3
	$PM_{2.5–10}$	EC	NO_3^-, NH_4^+	Cl^-, Na^+, Mg^{2+}, K^+, *nss Ca^{2+}, *nss SO_4^{2-}	N/A	MSA	89.2
D	PM_{10}	EC	NO_3^-, nss SO_4^{2-}, NH_4^+, *EC	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}, K^+	N/A	86.9
	$PM_{2.5}$	EC	NO_3^-, nss SO_4^{2-}, NH_4^+, *EC	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}	N/A	88.5
	$PM_{2.5–10}$	EC	NO_3^-, NH_4^+	Cl^-, Na^+, Mg^{2+}	nss Ca^{2+}, nss SO_4^{2-} , K^+	N/A	81.9

Significant loadings of MSA were only found at the coastal site for the secondary marine component, which is not included in the MLR analysis later due to low and often zero concentrations in autumn and winter seasons.

6.2.2 *MLR analysis*

All five source components identified from the FA procedure were used in the MLR analysis, which utilised a stepwise regression method with the default variable selection criteria P_{enter} ≥0.050 and P_{remove} ≤0.100. Similarly, outliers were checked and removed following a careful screening of the data sets before and after running the regression model by looking at individual paired scatter plots and plots of residuals and diagnostics. Clearly, as Table 6.2 shows, it is reasonable to use EC, nss Ca^{2+} and MSA as source indicators for primary combustion, resuspended dusts and secondary marine materials respectively, although MSA is not included in the final model since its contributions to the aerosol mass were insignificant at most of the sites except at Site C. For testing purposes, ammonium nitrate and/or ammonium sulphate derived from nitrate and sulphate were used as source markers for the secondary inorganic component. The regression models involving sulphate as a marker often result in a negative intercept at urban sites, presumably due to interference between long-range transported fractions of EC and sulphate, therefore ammonium nitrate was chosen for use in the final model at urban sites. At the non-urban sites both nitrate and sulphate were used, but only for the PM_{10} and $PM_{2.5}$ fractions. Ammonium was not suitable as a tracer due to its low concentrations, often below the detection limit, in winter and for the coarse fractions. In the case of sea salt, both chloride and sodium concentrations were well above the detection limit of the chemical measurement, but sodium was used for calculating the amount of sea salt (NaCl) as chloride is liable to a depletion problem as indicated earlier. Magnesium and potassium are not considered as appropriate source markers for sea salt. The overall finalised regression model is expressed as:

$$PM = a\,(EC) + b\,(NH_4NO_3) + c\,(NaCl) + d\,(nss\ Ca) + \text{Constant}$$

where a, b, c and d are regression coefficients, and the constant indicates unexplained/other components.

6.2.2.1 Results of MLR

Table 6.3 shows the model results, regression coefficients, coupled with standardised coefficients β, and the adjusted R^2. The significance values of the *t*-statistics for all regression coefficients are less than 0.05, except at the coastal site, for nss Ca^{2+}, the coefficients are not significant and were excluded from the model.

Reasonable model fits were obtained using the above four predictor variables and a constant variable, giving an average coefficient of determination of $R^2 = 0.87$ (range: 0.77–0.98), indicating that 77–98% of the total variance in the total aerosol mass was accounted for by the model. The EC coefficient *a* is much larger than unity as this marker element represents primary combustion materials covering not only EC but also organic and other related materials. Interestingly, those coefficients were smaller at urban sites (smallest at Site A) than at non-urban sites, indicative of a higher proportion of EC in the carbonaceous particles at urban sites due to a high vehicle exhaust contribution. Furthermore, the coefficients for fine fractions were smaller than for coarse fractions, again reflecting the importance of EC contributing to fine particles.

Similarly, values of coefficient *b* were greater (2.38–3.49) when only ammonium nitrate was used as a secondary source marker at the urban sites, but close to unity (1.14–1.24) when a combined ammonium nitrate and ammonium sulphate source marker was used at non-urban sites. The PM_{10} coefficient of 1.24 at Site C is higher than that (0.83) determined for the Lizard coastal site in the UK, while 1.14 at Site D is close to those obtained (1.01 and 1.36) for the rural Lichfield and Pershore sites in the UK (Turnbull and Harrison, 2000). In the case of coarse particles, the coefficients were lower in comparison with fine particles since ammonium sulphate can compose a large part of the secondary materials mainly in the fine particle mode.

Sea-salt coefficients *c* were generally consistent at all sites and for all fractions and more or less close to unity indicating that this component is mostly composed of sodium chloride and is a significant contributor to aerosol mass in the Ireland atmosphere, which is clearly seen from the estimated sea salt PM_{10} concentrations of 2.9–4.7 µg/m^3 (Table 6.4).

Non-sea-salt calcium was used as a source indicator for resuspended dusts, a source component not included in the previous models of Stedman *et al*. (2001) and Turnbull

Table 6.3. Results of multi-linear regression.

Fractions	Sites	Regression coefficients and beta coefficients (β)				Constant	R^2
		EC ***a*** **(β)**	NH_4NO^3 ***b*** **(β)**	NaCl ***c*** **(β)**	nss Ca ***d*** **(β)**		
PM_{10}	A	2.18 (0.36)	2.38 (0.48)	1.05 (0.15)	6.63 (0.43)	2.34	0.88
	B	2.76 (0.40)	2.47 (0.56)	0.89 (0.24)	4.10 (0.20)	2.49	0.84
	E	2.88 (0.37)	2.68 (0.60)	1.12 (0.36)	6.04 (0.26)	2.40	0.84
	C	4.25 (0.15)	*1.24 (0.56)	1.25 (0.88)	–	1.96	0.95
	D	4.21 (0.33)	*1.14 (0.68)	1.21 (0.41)	4.01 (0.09)	1.36	0.94
$PM_{2.5}$	A	2.23 (0.16)	2.89 (0.64)	0.84 (0.07)	5.14 (0.06)	2.16	0.78
	B	2.35 (0.46)	2.87 (0.60)	0.81 (0.08)	1.44 (0.02)	1.92	0.77
	E	2.81 (0.48)	3.49 (0.63)	1.01 (0.08)	2.87 (0.05)	1.21	0.77
	C	3.11 (0.23)	*1.14 (0.82)	1.20 (0.33)	–	0.44	0.97
	D	3.98 (0.38)	*1.19 (0.69)	1.10 (0.15)	4.03 (0.04)	0.50	0.96
$PM_{2.5–10}$	A	3.70 (0.28)	1.52 (0.23)	1.21 (0.38)	5.51 (0.60)	1.52	0.91
	B	8.46 (0.20)	1.23 (0.25)	1.07 (0.48)	4.14 (0.49)	1.51	0.89
	E	6.24 (0.21)	1.54 (0.20)	1.15 (0.56)	5.57 (0.54)	1.48	0.83
	C	9.90 (0.02)	1.61 (0.18)	1.21 (0.98)	–	1.68	0.98
	D	11.77 (0.07)	1.21 (0.28)	1.26 (0.73)	4.21 (0.23)	0.72	0.81

*NH_4NO_3 + $(NH_4)_2SO_4$ was used as an indicator for the secondary inorganic source.

Table 6.4. Mean modelled component concentrations (µg/m^3) and their relative contributions to PM mass in Ireland.

Fractions	Sites	Primary combustion	Secondary combustion	Sea salt	Resuspended dusts	Other
PM_{10}	A	15.8(42%)	5.4 (14%)	3.4 (9%)	9.8 (26%)	2.9 (8%)
	B	7.0 (32%)	5.1 (23%)	3.1 (14%)	4.3 (20%)	2.6 (12%)
	E	7.1 (30%)	5.1 (21%)	4.7 (20%)	4.7 (20%)	2.3 (10%)
	C	2.0 (11%)	5.0 (27%)	9.5 (51%)	–	2.0 (11%)
	D	1.8 (18%)	3.3 (32%)	2.9 (28%)	0.8 (8%)	1.5 (15%)
$PM_{2.5}$	A	14.5(65%)	4.2 (19%)	0.7 (3%)	0.8 (3%)	2.2 (10%)
	B	5.7 (49%)	3.4 (29%)	0.7 (6%)	0.2 (1%)	1.7 (15%)
	E	6.3 (51%)	3.4 (27%)	0.9 (7%)	0.3 (3%)	1.6 (13%)
	C	1.4 (19%)	3.6 (48%)	1.9 (26%)	–	0.5 (6%)
	D	1.7 (28%)	2.9 (49%)	0.7 (12%)	0.2 (3%)	0.5 (9%)
$PM_{2.5–10}$	A	2.2 (15%)	1.2 (8%)	2.9 (19%)	7.3 (49%)	1.3 (9%)
	B	1.2 (11%)	1.0 (10%)	2.9 (28%)	3.9 (37%)	1.5 (14%)
	E	1.2 (10%)	1.1 (10%)	3.9 (34%)	3.7 (33%)	1.5 (13%)
	C	0.2 (2%)	1.5 (14%)	7.7 (69%)	–	1.7 (15%)
	D	0.2 (4%)	0.6 (13%)	2.1 (49%)	0.6 (15%)	0.8 (19%)

and Harrison (2000), but an important pollution source especially at urban sites. The highest coefficients *d* were observed at the roadside sites, Sites A (5.14–6.63) and E (2.87–6.04), implying the existence of other resuspended materials other than that considered in the chemical reconstruction. Coarse fractions always exhibited higher coefficients than the fine fractions in spite of higher calcium concentrations being observed in the coarse mode. In addition, the coefficients at Sites A and E (except for the fine fraction) are certainly higher than the factor of 4.3 used in the chemical reconstruction above (Yin *et al.*, 2005), suggesting an underestimation for resuspended dust materials in the reconstruction model. However, a similar value of just over 4 was found for other sites including the Dublin centre site (B) and the rural site (D) which may suggest different sources of resuspended dusts which are simply not related to calcium. The conclusion from the calcium coefficients here is that a factor of 5.5 might have been most appropriate in the mass reconstruction, especially at roadside sites.

The constant consists of mainly secondary organics and other materials, which are not explained by the model. In general, this value was higher at urban than at non-urban sites, which suggests that other than secondary organics this component may also contain materials having other urban sources.

6.2.2.2 Mean modelled component concentration estimates

Table 6.4 and Fig. 6.4 show the mean modelled component concentrations and the relative contributions to particulate mass at each site. As expected, the highest estimated mean concentration of primary combustion materials was found at the Dublin roadside site (A: PM_{10} 15.8 µg/m^3), which is more than twice the concentrations at urban centre sites (B and E: PM_{10} 7.0 and 7.1 µg/m^3) and nearly eight times that at the coastal site (C: PM_{10} 2.0 µg/m^3) and the rural site (D: PM_{10} 1.8 µg/m^3). Clearly this component is a major source for the PM_{10} and $PM_{2.5}$ aerosol mass at urban sites with a relative contribution of around 30–42% to PM_{10} and 49–65% to $PM_{2.5.}$

In comparison, the secondary inorganic component exhibited more spatial unity with mean PM_{10} estimates of about 5.0–5.4 µg/m^3 at Sites A, B, E and C, which is lower than that (6.5–7.6 µg/m^3) estimated at UK sites (Turnbull and Harrison, 2000). This component is closely related to the process of long-range transportation from continental Europe, which may explain the lower concentrations found in Ireland than in the UK due to a dilution effect through travelling on to the Ireland sites. These estimates from Ireland are higher than those (2.8–4.8 µg/m^3) found in the UK from Stedman's model, in which sulphate was used as a source marker, which likely caused source overlap in the model. Secondary materials are also a

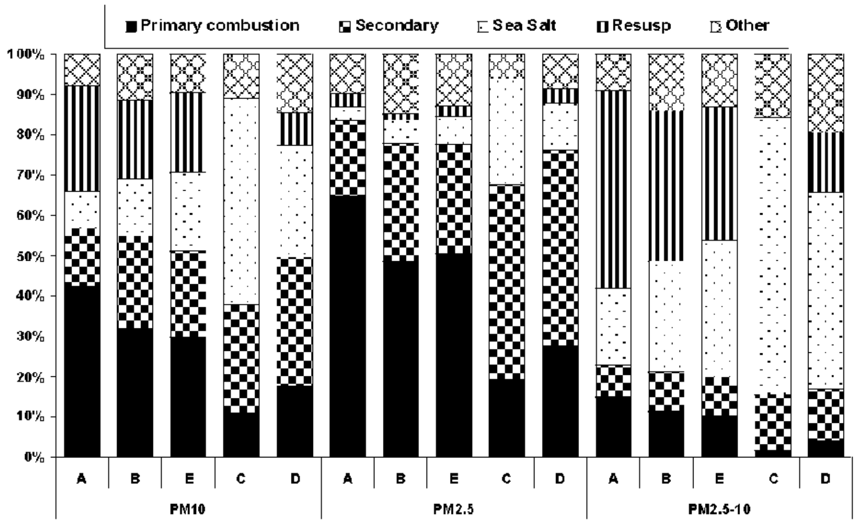


Figure 6.4. Modelled relative chemical composition at five sites in Ireland.

major contributor to the aerosol mass, representing about 14–32% of PM_{10} and 19–49% of $PM_{2.5}$.

Sea salt, mostly present in the coarse fraction, was produced mainly from the marine environment, although another source from de-icing salt exists particularly in urban areas in winter. Therefore the coastal site (C) exhibited the highest concentrations (9.5 $\mu g/m^3$ and 7.7 $\mu g/m^3$ for PM_{10} and $PM_{2.5–10}$, respectively) and the highest contributions of 51% and 69% to the PM_{10} and $PM_{2.5–10}$ mass. The lowest concentration appeared at the central rural site (D: 2.9 $\mu g/m^3$ and 2.1 $\mu g/m^3$ for PM_{10} and $PM_{2.5–10}$, respectively) compared with other inland sites (A, B and E) which are closer to the coast. As a result, sea salt is a more important aerosol source component in Ireland than in the UK atmosphere, where the inland concentrations are only around 1.5–1.9 $\mu g/m^3$ (APEG, 1999).

Similar to primary combustion materials, resuspended dust is a localised source component, exhibiting the highest mean estimates at the urban roadside site (A: PM_{10} 9.8 $\mu g/m^3$; $PM_{2.5–10}$ 7.3 $\mu g/m^3$). Concentrations at the urban centre sites (B and E) were about half of the values at Site A, whilst the non-urban site (D) had the lowest values below 1 $\mu g/m^3$. This component is closely related to human activities, mainly road transportation and sometimes building or road construction (Harrison *et al.*, 2001), and its contribution to the aerosol mass is not negligible at urban sites particularly for coarse particles and hence for the PM_{10} mass.

The ‘other’ component contributing about 6–19% to the aerosol mass has higher values at urban than at non-urban sites, especially for fine particles indicative of the existence of other urban emissions. In the case of the coarse fraction, similar values were found at the urban sites with higher values at the coastal site and lower values at the rural site.

6.2.2.3 Comparison between modelled and measured particle mass

Comparison between modelled and gravimetric PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$ mass was made by a single regression plot, and the results are shown in Fig. 6.5 and Table 6.5. A strong correlation was found between the two data sets showing high correlation coefficients (R^2) in the range 0.75–0.97. The best correlation appeared for both fine and coarse particles at Site C, where aerosol mass is dominated by sea salt and secondary components, with higher slopes of 0.96, 0.94 and 0.97 and smaller intercepts of 0.73, 0.41 and 0.38 for PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$, respectively. It is noticed that, except at Site D where a perfect model fit was obtained for the fine fraction with a slope equal to 1 and an intercept close to 0 (–0.05), all slopes are less than unity with a positive intercept, indicating that an overestimation at lower particle mass and an underestimation at higher particle mass occurred by using the MLR model. This is most apparent at the urban sites, particularly at the Dublin roadside site for PM_{10} and $PM_{2.5}$, which exhibited lower slopes and higher intercepts. It is anticipated that the model underestimation is likely due to prediction of the primary combustion component with a source marker EC for fine particles and

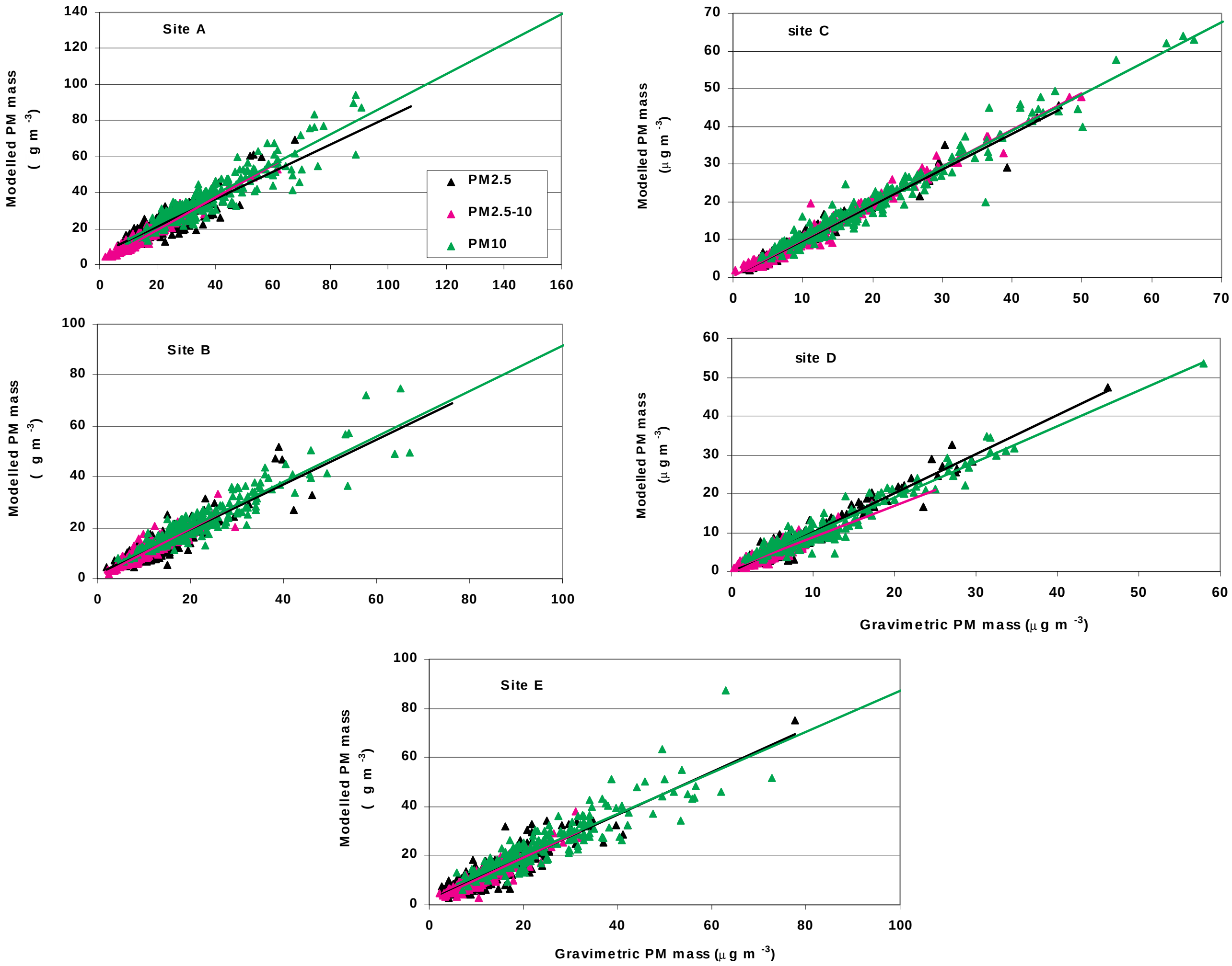


Figure 6.5. Comparison between modelled and measured PM masses.

Table 6.5. Results of regression for modelled mass and gravimetric mass (modelled mass *y* upon gravimetric mass *x*).

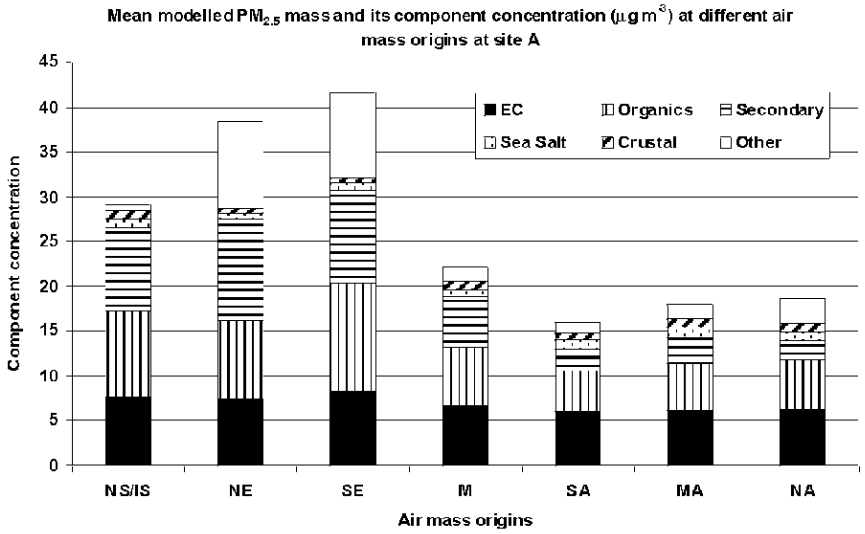
Sites	PM_{10}			$PM_{2.5}$			$PM_{2.5–10}$		
	Correlation	R^2	N	Correlation	R^2	N	Correlation	R^2	N
A	$y = 0.83x + 5.55$	0.85	260	$y = 0.76x + 5.78$	0.75	255	$y = 0.90x + 1.51$	0.93	264
B	$y = 0.89x + 2.50$	0.87	256	$y = 0.88x + 1.70$	0.79	255	$y = 0.95x + 0.56$	0.83	261
E	$y = 0.83x + 3.77$	0.84	255	$y = 0.87x + 1.75$	0.83	251	$y = 0.89x + 1.17$	0.85	258
C	$y = 0.96x + 0.73$	0.96	231	$y = 0.94x + 0.41$	0.96	230	$y = 0.97x + 0.38$	0.97	230
D	$y = 0.92x + 0.71$	0.94	260	$y = 1.00x – 0.05$	0.96	260	$y = 0.80x + 0.77$	0.82	257

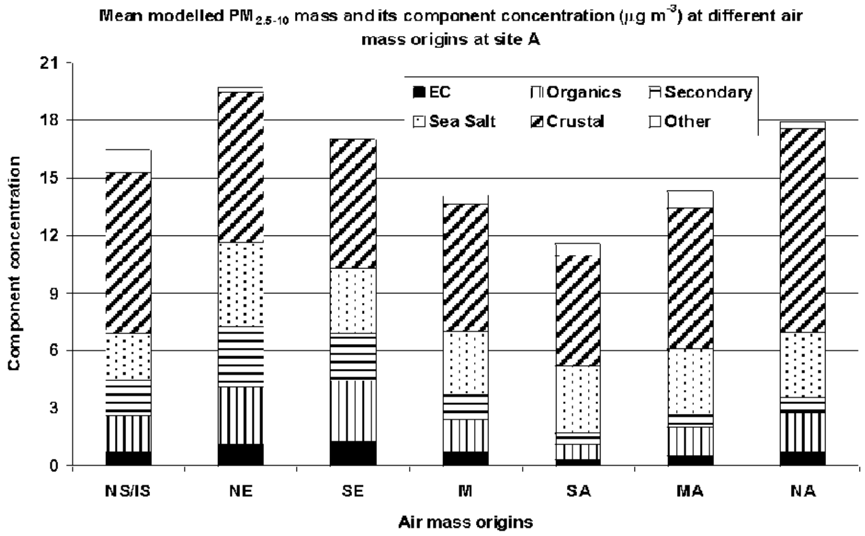
both the primary combustion and resuspended materials with calcium as a source indicator for coarse particles. However, it is unresolved as to why an overestimation should be obtained at the lower PM mass.

6.2.2.4 Mean modelled particulate mass and composition according to air mass origin

Subsets of modelled data segregated according to air mass type were generated as in Section 5.3, and are illustrated in Fig. 6.6.

General features are as previously described (Section 5.3). Higher $PM_{2.5}$ mass concentrations in continentally influenced air masses were in large part attributable to increased contributions of secondary material, which showed a three-fold increase at Dublin sites in continental air masses relative to Atlantic air, and corresponding four- to five-fold increases in Cork and up to six-fold at Site D.





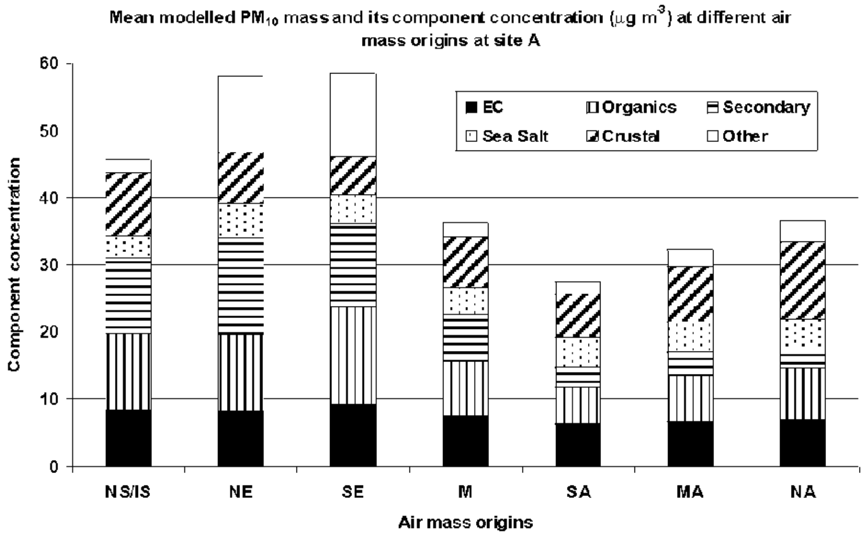


Figure 6.6. Modelled particle mass and component concentrations according to site, size fraction and air mass origin.

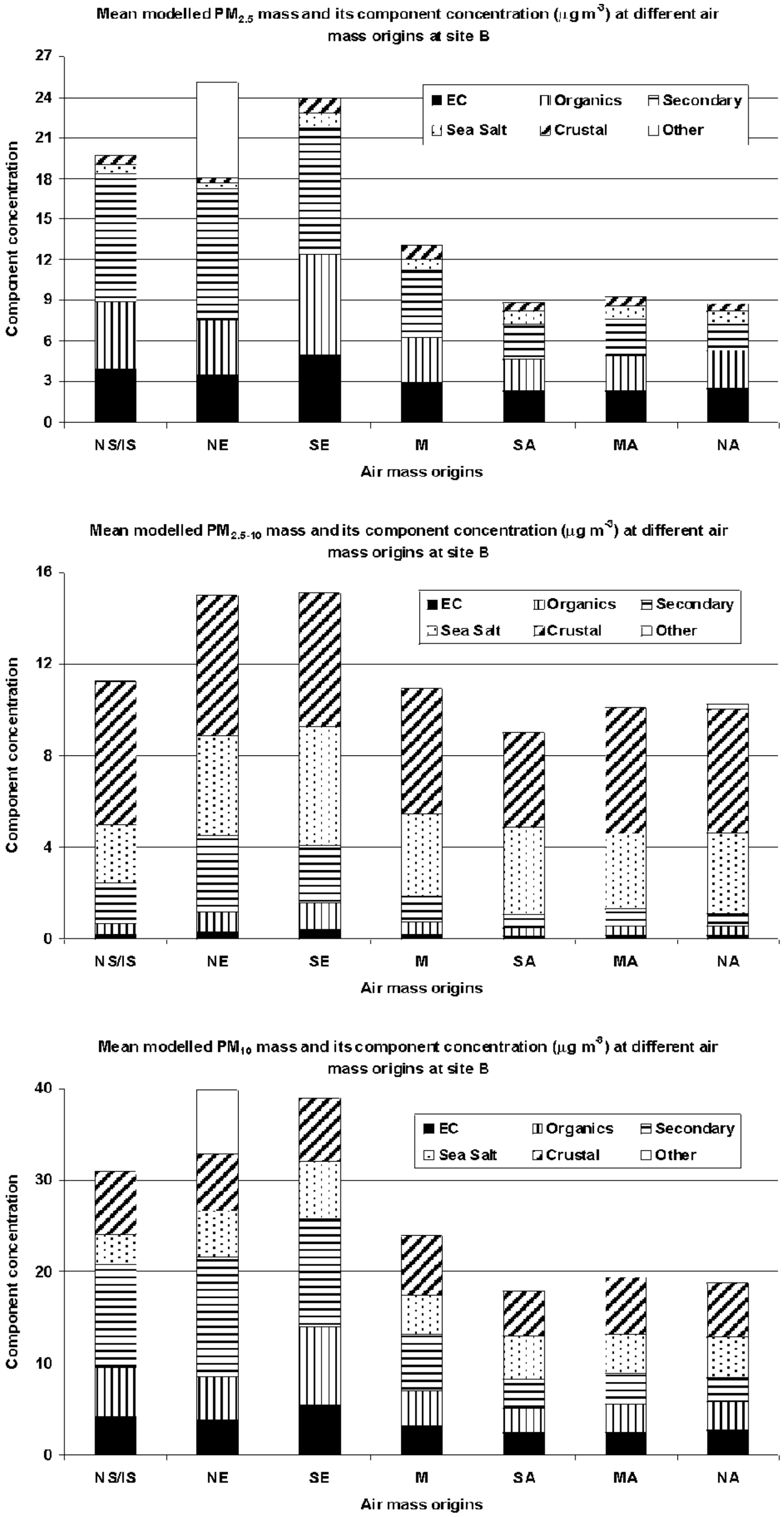
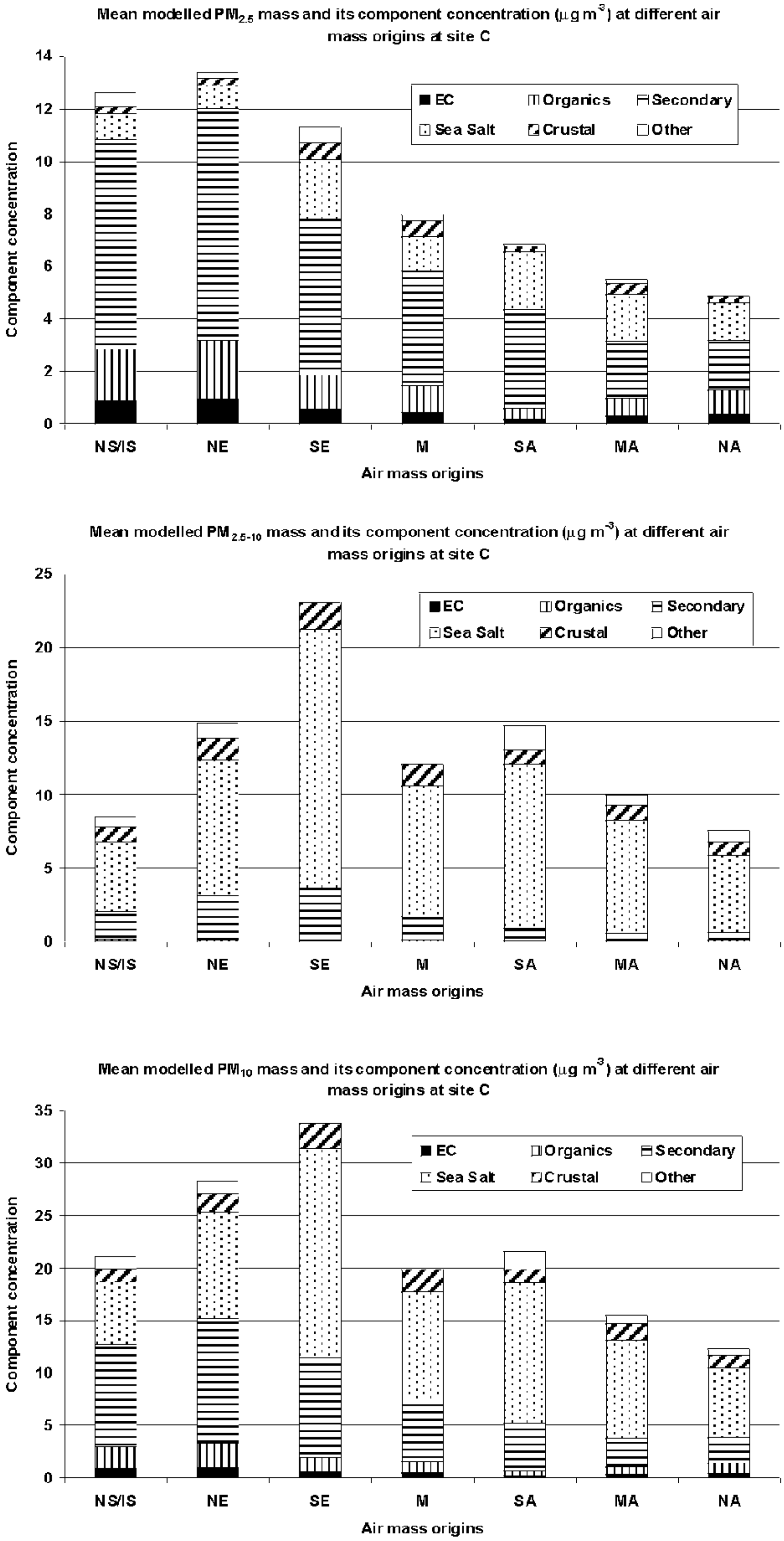


Figure 6.6. ***Contd.***



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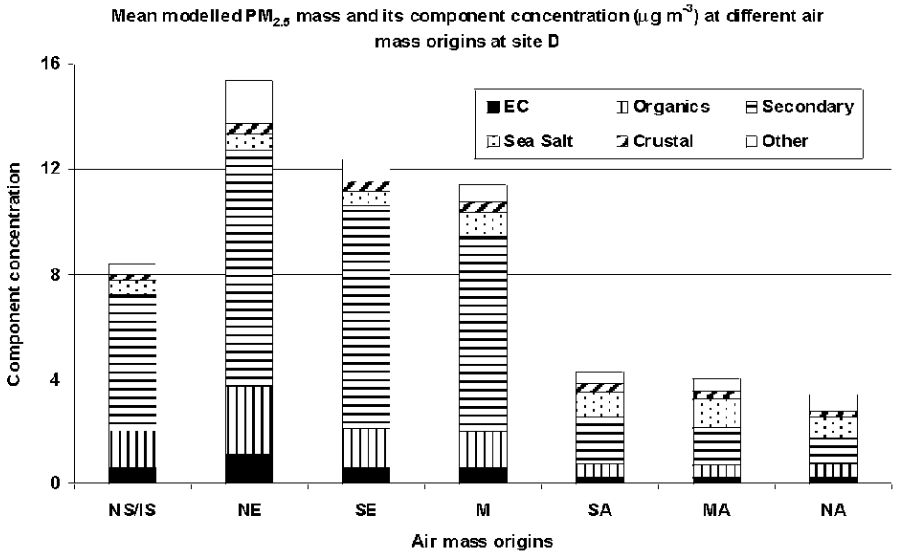

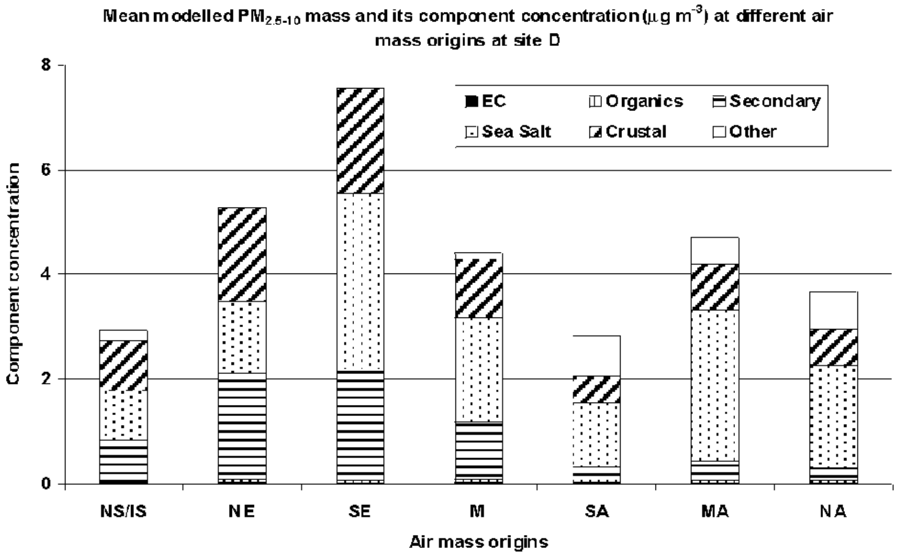

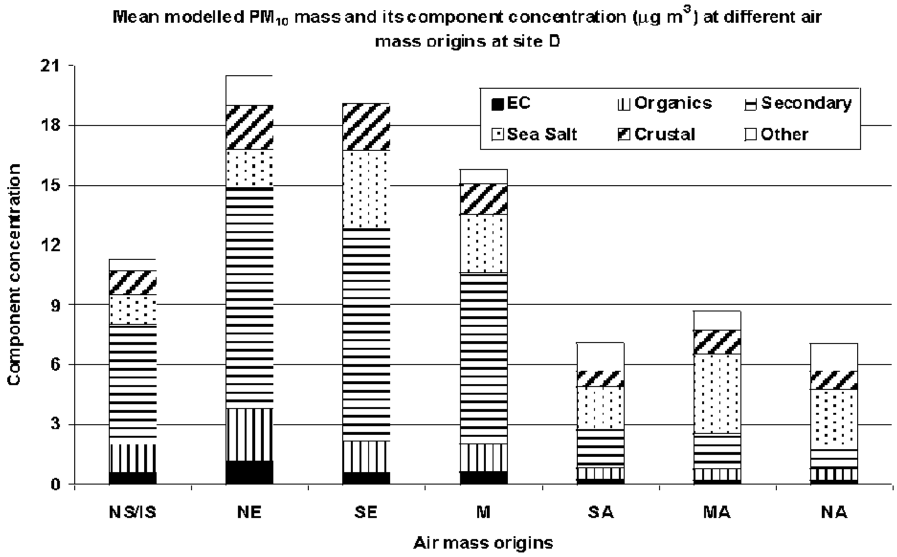

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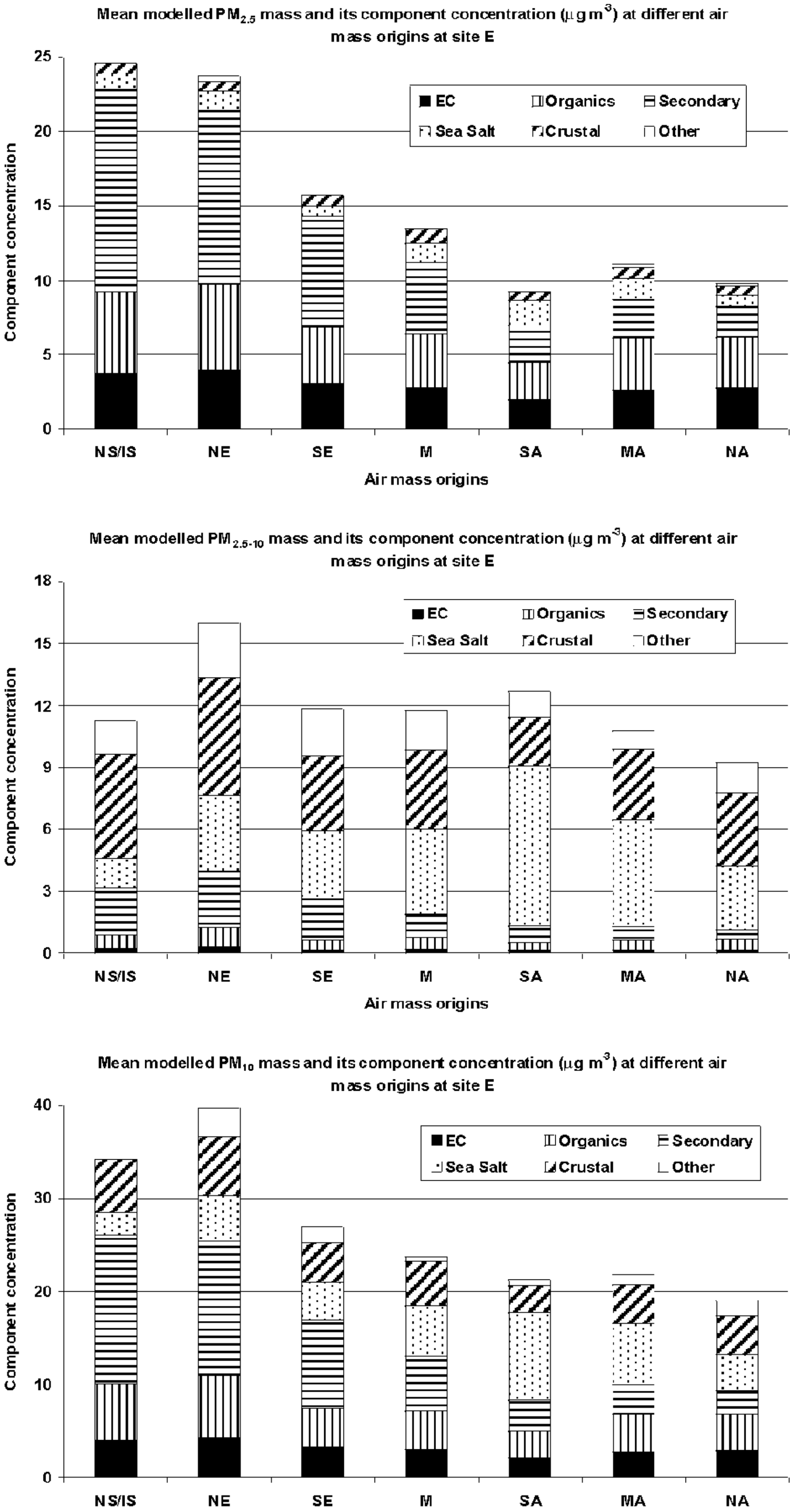


Figure 6.6. ***Contd.***

The OC fraction was also present at higher levels in continental air masses; in the absence of local sources (Site D is the best example) these air masses contained three to five times as much fine fraction organic material as the Atlantic air masses. At the Dublin urban sites, OC levels in continental air masses were around twice those in Atlantic air, while the difference was somewhat lower in Cork. There is evidence for higher levels of fine (and coarse) mode crustal (resuspended) material during continental type events at Sites C, D and E, but not at the Dublin sites, where differences were probably obscured by the predominance of locally generated dusts. Fine fraction sea salt levels were similar in all air mass types at all sites, with sea salt only contributing a minor fraction of $PM_{2.5}$ at urban locations. However, sea salt was a significant component of PM_{10}, showing no sector association in Dublin but higher levels in Atlantic air in Cork.

6.3 Comparison between Modelled and Reconstructed Component Mass

Comparison was also made between the modelled (Table 6.4) and reconstructed (Table 6.6) component mass. In general, fine mode modelled concentrations of primary combustion components are slightly lower than the sum of reconstructed concentrations for EC and organics, in which secondary organic compounds were included. For coarse fractions, however, except for Site A, the modelled concentrations were higher than reconstructed. As a result, for PM_{10}, urban sites exhibited similar or slightly lower modelled values for primary combustion materials in comparison with the reconstructed results, but non-urban sites showed much higher modelled concentrations of this component, indicating an underestimation for organic compounds in the reconstructed mass. Similar or slightly higher secondary and sea salt component concentrations were modelled compared with those reconstructed. At the coastal site, a much larger value of coarse sea salt (7.7 $\mu g/m^3$) was modelled and hence a higher concentration of PM_{10} (9.5 $\mu g/m^3$), whereas the reconstructed values were 6.3 $\mu g/m^3$ and 7.4 $\mu g/m^3$ for the coarse mode and PM_{10}, respectively. Most interestingly, the Dublin roadside site gave a much greater PM_{10} value for resuspended dusts from modelled results (9.8 $\mu g/m^3$) than from reconstructed results (6.5 $\mu g/m^3$), indicative of an underestimation in the chemical reconstruction using 4.3 × Ca^{2+}. A similar finding occurred at Site E but not at Site B.

In general terms, the PM mass was better explained by the MLR model (81–92%) than by the chemical reconstruction (72–93%) using similar source markers. The major advantage of the regression model is seen

Table 6.6. Mean reconstructed component concentrations ($\mu g/m^3$) and their contributions to PM mass (%) in Ireland.

Fractions	Sites	EC	Organics	Secondary	Sea salt	Resuspended dusts	Other
PM_{10}	A	7.9 (22%)	9.0 (25%)	4.8 (13%)	3.2 (9%)	6.5 (18%)	6.1 (14%)
	B	3.1 (14%)	3.9 (17%)	4.5 (20%)	3.2 (14%)	4.7 (21%)	2.8 (12%)
	E	3.0 (13%)	4.3 (18%)	4.1 (17%)	4.2 (18%)	3.5 (15%)	4.8 (20%)
	C	0.5 (3%)	1.1 (6%)	4.3 (23%)	7.4 (40%)	1.2 (6%)	4.0 (22%)
	D	0.4 (4%)	1.0 (10%)	3.2 (30%)	2.3 (22%)	1.0 (10%)	2.4 (24%)
$PM_{2.5}$	A	7.3 (33%)	7.4 (33%)	3.8 (17%)	0.7 (3%)	0.6 (3%)	2.6 (12%)
	B	3.0 (26%)	3.5 (29%)	3.4 (29%)	0.6 (5%)	0.5 (4%)	0.8 (7%)
	E	2.9 (23%)	3.8 (30%)	3.3 (26%)	0.8 (7%)	0.5 (4%)	1.2 (10%)
	C	0.5 (6%)	1.1 (14%)	3.3 (44%)	1.1 (15%)	0.3 (4%)	1.2 (16%)
	D	0.4 (7%)	1.0 (16%)	2.5 (42%)	0.6 (11%)	0.2 (3%)	1.3 (21%)
$PM_{2.5–10}$	A	0.6 (4%)	1.6 (11%)	1.1 (7%)	2.5 (17%)	5.9 (39%)	3.3 (22%)
	B	0.1 (1%)	0.4 (4%)	1.1 (10%)	2.6 (25%)	4.2 (41%)	1.9 (19%)
	E	0.2 (2%)	0.6 (5%)	0.9 (8%)	3.4 (30%)	3.1 (27%)	3.2 (28%)
	C	0.02(0.2%)	0.1 (1%)	1.1 (9%)	6.3 (56%)	0.9 (8%)	2.8 (25%)
	D	0.01(0.3%)	0.05 (1%)	0.6 (14%)	1.7 (39%)	0.8 (18%)	1.2 (28%)

from the calculation of resuspended dusts, in which different factors were assigned for each site and for different fractions due to a varied dust composition, whilst a fixed factor was used in the chemical reconstruction. Errors in regression models may arise from careless selection of source indicators, skewed distributions, outliers and source overlaps; however such errors have been minimised here. The simplicity of the chemical reconstruction procedure may be more advantageous when source markers and source composition are clear, such as for secondary inorganic and sea salt components.

6.4 Results of the Revised Chemical Reconstruction

It is important to notice that the MLR method accounts for the water associated with the hygroscopic components through the coefficients as seen in Table 6.3, which is probably why MLR analysis accounts for a larger proportion of the mass. Similarly with the resuspended component, a better estimation is achieved with the MLR model. Therefore an improvement of the chemical reconstruction can be made based on the statistical model results in Table 6.3.

In order to allow for bound water (or other matter not measured) for hygroscopic particles such as sodium chloride and ammonium salts, the water (or other material) contents were estimated and added to the sea salt, sulphate and nitrate. For sodium chloride at Site C, the coefficient is 1.25, suggesting that a further 25% of the value should be added to the NaCl mass in the mass reconstruction method. Similarly, for the sum of ammonium nitrate and ammonium sulphate at Sites C and D, the coefficients suggest that about 20–25%, representing bound water (or other material), should be added. As a result, a further 25% of the mass was added to these components. The results for calcium in the coarse particle fraction suggest that a factor of 5.5 might have been most appropriate in the mass reconstruction. In other words, about 22% should have been added to the mass of the resuspended dust to include materials other than gypsum, but associated with this source.

Table 6.7 and Fig. 6.7 show the corrected reconstructed chemical component concentrations and the relative chemical composition. The ‘other’ component concentrations were significantly reduced by about 48–100% after the adjustment for additional material (mainly hygroscopic and resuspended materials). A much better mass closure is seen in Fig. 6.6 with the relative contributions of the ‘other’ component to the aerosol mass dropping from above 10% (7–28%) to below 10% (1–13%).

The annual (2002) average relative chemical composition is shown in Table 6.8 for the three PM categories at all

Table 6.7. Mean corrected reconstructed PM component and total concentrations (µg/m^3) in Ireland.

Fractions	Sites	Total	EC	Organics	Secondary	Sea salt	Resuspended dusts	Other
PM_{10}	A	37.3	7.9	9.0	6.0	4.0	7.9	2.7
	B	22.1	3.1	3.9	5.6	4.0	5.7	–0.2
	E	23.9	3.0	4.3	5.1	5.3	4.3	1.9
	C	18.6	0.5	1.1	5.4	9.3	1.4	0.8
	D	10.4	0.4	1.0	3.9	2.9	1.2	0.9
$PM_{2.5}$	A	22.4	7.3	7.4	4.7	0.9	0.8	1.4
	B	11.7	3.0	3.5	4.3	0.7	0.6	–0.3
	E	12.5	2.9	3.8	4.1	1.1	0.6	0.1
	C	7.4	0.5	1.1	4.1	1.4	0.3	0.1
	D	6.0	0.4	1.0	3.2	0.8	0.3	0.4
$PM_{2.5–10}$	A	14.9	0.6	1.6	1.3	3.1	7.2	1.1
	B	10.4	0.1	0.4	1.3	3.2	5.1	0.1
	E	11.4	0.2	0.6	1.1	4.2	3.8	1.4
	C	11.2	0.0	0.1	1.3	7.8	1.1	0.8
	D	4.3	0.0	0.0	0.8	2.1	0.9	0.5

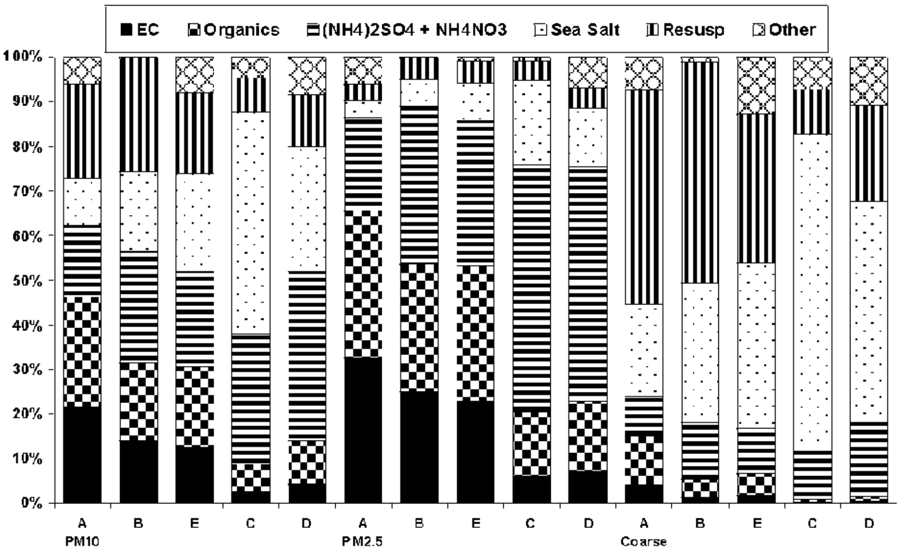


Figure 6.7. Corrected reconstructed relative chemical composition at five sites in Ireland.

Table 6.8. Annual (2002) average relative chemical composition.

	Site (%)	Sea Salt (%)	Primary (EC) (%)	Organics (%)	Secondary inorganic (%)	Crustal (%)	Other (%)
PM_{10}	A	13.0	24.5	23.6	15.3	18.7	5.0
	B	20.5	14.1	16.6	24.8	23.9	0.2
	E	24.6	12.5	17.4	20.3	18.6	6.7
	C	44.6	2.7	9.6	31.7	7.3	4.1
	D	31.3	3.9	12.9	34.1	11.9	5.8
$PM_{2.5}$	A	4.8	39.2	33.8	19.4	3.2	–0.4
	B	7.5	27.1	30.1	36.2	5.4	–6.2
	E	10.6	23.3	29.8	30.3	4.4	1.6
	C	21.7	5.9	20.6	53.8	3.5	–5.5
	D	15.5	6.9	22.9	48.8	6.0	–0.2
$PM_{2.5–10}$	A	23.4	3.2	8.5	10.1	41.2	13.5
	B	31.9	1.0	3.1	13.6	43.6	6.7
	E	38.5	1.6	5.0	9.9	33.7	11.4
	C	59.9	0.2	0.7	16.0	11.1	12.1
	D	47.6	0.4	1.3	18.9	22.0	9.8

sites in terms of the following chemical composition categories: sea salt, primary (EC), organics, secondary organics, crustal (or resuspended matter) and ‘other’ as explained in more detail in Section 6.1.2. Seasonally averaged relative chemical data are shown in Table 6.9.

The remaining ‘other’ component concentrations are highest at Sites A and E for the $PM_{2.5–10}$ fraction, and probably contain both resuspended and organic materials. These resuspended materials must not be covered by the 22% increment as they are not related to calcium and not reflected in the calcium coefficient. In the case of Sites C and D, the ‘other’ component is mainly related to organic material, which is clearly underestimated using the very low EC concentrations for the coarse mode. Similarly, considering the $PM_{2.5}$ and PM_{10}, underestimation may occur for the organic component at non-urban sites and for both organic and resuspended components at urban sites. At Site B only,

Table 6.9. Seasonal average relative chemical composition.

			Sea salt (%)	Primary (EC) (%)	Organics (%)	Secondary inorganic (%)	Crustal (%)	Other (%)
Site A	PM_{10}	Spring	14.6	21.5	20.0	17.3	19.3	7.3
		Summer	7.4	27.7	27.7	13.2	19.8	4.2
		Autumn	10.6	26.2	25.9	15.5	16.9	5.1
		Winter	19.4	22.6	20.8	15.0	18.9	3.3
	$PM_{2.5}$	Spring	4.2	34.7	28.0	22.4	2.8	7.8
		Summer	2.1	43.7	39.0	16.2	3.2	–4.3
		Autumn	3.4	40.1	36.0	18.5	2.6	–0.6
		Winter	9.3	38.3	32.2	20.4	4.2	–4.4
	$PM_{2.5-10}$	Spring	28.3	3.3	8.4	9.6	42.7	7.7
		Summer	14.3	2.6	9.1	8.8	44.9	20.3
		Autumn	19.5	4.0	10.1	13.0	39.8	13.5
		Winter	31.4	3.1	6.4	9.1	37.5	12.5
Site B	PM_{10}	Spring	23.9	12.1	14.4	24.5	25.8	–0.8
		Summer	14.4	13.3	17.8	25.8	26.9	1.8
		Autumn	16.4	17.8	19.4	25.8	21.8	–1.2
		Winter	27.1	13.1	14.7	23.3	21.0	0.8
	$PM_{2.5}$	Spring	7.7	23.5	25.9	36.1	5.5	1.4
		Summer	5.5	27.0	34.0	40.3	5.8	–12.5
		Autumn	5.2	33.6	35.4	33.8	3.9	–12.0
		Winter	11.6	24.3	25.1	34.5	6.3	–1.8
	$PM_{2.5-10}$	Spring	39.7	1.0	3.0	12.3	46.9	–2.9
		Summer	18.8	0.8	2.7	12.2	49.6	15.9
		Autumn	28.1	0.7	2.2	17.7	41.4	9.9
		Winter	41.2	1.6	4.4	12.3	36.5	4.1
Site E	PM_{10}	Spring	26.7	11.5	15.6	25.0	17.7	3.5
		Summer	21.9	12.2	17.3	14.2	25.8	8.6
		Autumn	14.2	15.1	20.9	26.5	18.0	5.3
		Winter	35.6	11.2	15.8	15.5	12.7	9.3
	$PM_{2.5}$	Spring	12.9	21.7	27.5	38.3	4.8	–5.2
		Summer	8.2	24.5	30.9	24.5	6.9	5.1
		Autumn	5.0	26.4	33.9	36.6	2.7	–4.6
		Winter	16.2	20.6	26.9	21.9	3.4	11.0
	$PM_{2.5-10}$	Spring	40.4	1.2	3.6	10.5	32.7	11.5
		Summer	32.3	1.8	6.3	6.0	43.0	10.6
		Autumn	32.5	1.6	5.0	12.6	33.2	15.1
		Winter	48.9	1.8	5.1	10.3	25.7	8.2
Site C	PM_{10}	Spring	45.1	2.5	9.4	30.7	6.1	6.3
		Summer	32.2	2.8	11.9	37.5	9.0	6.5
		Autumn	41.7	3.0	10.4	37.2	6.4	1.3
		Winter	59.5	2.4	6.8	21.5	7.7	2.1
	$PM_{2.5}$	Spring	20.2	5.0	18.6	51.0	2.0	3.1
		Summer	11.8	5.6	23.7	63.7	4.3	–9.2
		Autumn	20.4	6.8	22.7	56.4	3.2	–9.4
		Winter	34.4	6.2	17.3	44.1	4.4	–6.4
	$PM_{2.5-10}$	Spring	63.3	0.3	0.9	16.2	9.9	9.4
		Summer	48.1	0.2	0.8	15.6	13.5	21.7
		Autumn	54.9	0.2	0.7	21.9	11.0	11.3
		Winter	73.3	0.1	0.4	10.3	9.9	6.0
Site D	PM_{10}	Spring	33.3	3.2	11.6	32.1	9.9	9.9
		Summer	33.9	2.6	10.9	32.9	14.6	5.1
		Autumn	26.2	4.9	15.4	36.6	11.4	5.5
		Winter	31.7	5.0	13.9	34.9	11.6	2.8
	$PM_{2.5}$	Spring	16.8	5.6	20.0	45.6	4.2	7.9
		Summer	15.3	5.0	21.1	53.6	7.5	–2.6
		Autumn	13.6	8.8	27.2	48.7	5.2	–3.4
		Winter	16.5	8.4	23.5	47.2	7.1	–2.8
	$PM_{2.5-10}$	Spring	52.3	0.3	1.2	15.7	20.6	9.7
		Summer	49.9	0.3	1.1	15.7	22.6	10.4
		Autumn	40.9	0.3	0.8	24.7	21.9	11.3
		Winter	47.1	0.7	1.9	19.5	23.1	7.8

the fine and the total mass were overestimated by 3% and 1%, respectively.

Based on the improved reconstruction method, a much higher proportion, about 87–100%, of the aerosol mass can be accounted for, compared with the uncorrected reconstruction and the statistical methods, which explain about 72–93% and 81–92%, respectively. It is clear that using the results of the MLR analysis, the chemical reconstruction can be improved well beyond the regression model. Furthermore, it would be possible to obtain a 100% or close to a 100% chemical reconstruction for all particle size fractions at all sites if we were to make a direct measurement of the elemental and OC contents instead of an indirect measurement and estimation, and to use both water-soluble and insoluble calcium (the latter was not measured as daily data) rather than only the soluble content.

Contribution of local source components to PM total gravimetric mass was estimated by comparing Sites A, B, E and C with D, assuming that all particles at Site D are long-range or regionally transported. The contribution of local source components to PM and the total mass contribution from local sources (sum of each component) are shown in Table 6.10 for the three PM particle categories over the whole measurement period of 18 months. The first column is the total contribution of local sources to the total PM mass. For example, the contribution of local sea salt at Site E is 7.9% to PM_{10} mass, and total contribution of all local sources to PM_{10} mass is 56.6%. Therefore the non-local sources will be 43.4%, which includes sea salt, EC, organics, secondary, crustal and other matter.

Table 6.10. Contribution of local sources to PM.

	Sites (%)	Mass (%)	Sea salt (%)	Primary (EC) (%)	Organics (%)	Secondary inorganic (%)	Crustal (%)	Other (%)
PM_{10}	A	72.3	2.4	20.2	20.9	4.8	14.8	9.2
	B	53.1	3.8	12.3	11.0	6.0	16.7	3.3
	E	56.6	7.9	10.8	12.0	3.9	10.6	11.5
	C	44.2	27.4	0.2	1.0	6.4	0.9	8.2
$PM_{2.5}$	A	73.0	0.5	31.0	27.8	6.0	1.8	5.9
	B	49.7	0.0	22.1	17.8	7.6	2.2	0.0
	E	51.8	1.7	19.6	19.4	5.8	2.1	3.3
	C	19.8	6.5	0.5	2.4	9.9	0.5	0.0
$PM_{2.5–10}$	A	71.1	5.3	4.0	10.5	3.1	34.3	13.8
	B	58.3	8.8	1.3	3.6	4.3	33.2	7.0
	E	62.0	14.9	1.6	4.5	2.8	20.7	17.5
	C	61.3	41.2	0.0	0.1	4.1	1.2	14.7

7 Metals

7.1 Sources of Trace Metals

Calcium (Ca)

Calcium is mainly crustal in origin and is associated with rocks and soils that enter the atmosphere mainly from resuspension of surface dusts. It is usually found in higher concentrations in the coarse fraction (Harrison and Jones, 1995; Horvath *et al*., 1996; Harrison *et al*., 2003a).

Manganese (Mn)

Manganese can have both crustal and anthropogenic origins (Harrison *et al*., 2003a). It can occur in both the coarse and fine fractions. The coarse fraction results from erosion of soils (Harrison and Jones, 1995), and the fine fraction can result from higher temperature combustion of manganese-rich fuel enhancers or smelting (Spokes *et al*., 2001), but also from incineration and modern coal-fired power plants (Horvath *et al*., 1996).

Iron (Fe)

Iron is found in both the coarse and fine fractions. In the coarse fraction, iron is mainly crustal in origin and is soil derived (Horvath *et al*., 1996; Harrison *et al*., 2003a). In the fine fraction, it can originate from industry and power plants (Horvath *et al*., 1996). Exhaust emissions from both gasoline and diesel fuelled road vehicles contain variable quantities of iron (Allen *et al*., 2001).

Nickel (Ni)

Sources of nickel are mainly anthropogenic in origin. It is emitted during coal and oil combustion (Horvath *et al*., 1996). Fine fraction nickel is also an excellent indicator of residual fuel (heavy oil) burning (Borbely-Kiss *et al*., 1999).

Zinc (Zn)

Zinc is primarily anthropogenic in origin (Spokes *et al*., 2001). It is emitted during coal combustion, steel production/treatment and refuse burning (Horvath *et al*., 1996). Rubber tyre abrasion can also be a source of zinc (Allen *et al*., 2001).

Magnesium (Mg)

Magnesium is found mostly in the coarse fraction. Its natural source is dominant and it is present in sea spray (Harrison and Jones, 1995).

Lead (Pb)

Lead is mostly anthropogenic in origin, resulting from the high-temperature combustion of leaded fuels in vehicle engines. It is predominantly found in fine aerosols <1 µm in diameter (Spokes *et al*., 2001). Although traffic is one of the major sources of lead, others also include paints and emissions from incinerators and coal-fired power plants (Horvath *et al*., 1996).

Chromium (Cr)

Chromium is an anthropogenically released metal. Combustion of fossil fuels is a large contributor of Cr (Allen *et al*., 2001).

Vanadium (V)

Combustion of fossil fuels is the principal anthropogenic source of vanadium (Allen *et al*., 2001). It is a tracer for residual oil burning, e.g. large power plants, but it is also emitted by coal-fired power plants (Horvath *et al*., 1996). One natural, although very minor, source of vanadium could be sea spray (Cohen *et al*., 2002).

Cadmium (Cd)

Again, cadmium is mostly anthropogenically produced. Industrial metallurgical processes produce large amounts of Cd (Allen *et al*., 2001).

Copper (Cu)

Copper can have anthropogenic and crustal sources. Combustion of fossil fuels produces copper (Allen *et al*., 2001), and it is also linked with traffic (Borbely-Kiss *et al*., 1999). Copper is also contained in emissions from biomass combustion (Allen *et al*., 2001).

In conclusion, airborne particulate matter derives from a wide variety of sources. The major sources in urban areas are road traffic emission, secondary particles deriving mainly from marine aerosols and resuspension of soils and road dusts. Elements with higher concentrations in the coarse fraction are Fe, Ca and Mg and are crustal in origin. For most of the toxic trace metals (Pb, Cd, Zn, Ni and Cu) anthropogenic inputs are more important than natural sources such as continental dust, volcanic dust and gas, sea spray and biogenic particles.

7.2 Monthly Variation in Metal Concentration

The mean monthly concentrations of Ca, Mn, Fe, Ni, Zn, Mg, Pb, Cr, V, Cd and Cu detected in PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$ over the period from July 2001 to December 2002 are presented in Figs 7.1–7.11. In general, the highest concentrations were found at the urban roadside site (A, College Street, Dublin) and the lowest concentrations at the rural site (D, Co. Galway). Site C (coastal site, Co. Wicklow) shows the highest average concentrations of Mg. None of the results are particularly surprising given the sources of many of the metals (Section 7.1).

7.3 Seasonal Trends in Trace Metal Concentrations during July 2001–December 2002

The concentrations of the metals in the fine and coarse fractions are also presented as seasonal mean values in Table 7.1: autumn (September–November), winter (December–February), spring (March–May) and summer (June–August).

Calcium (Ca)

Calcium was predominantly found in the $PM_{2.5–10}$ fraction with Site A having the highest concentration in nearly all cases. Site B had the next highest concentrations followed by Site E, whilst the levels at Sites C and D were lower than at the urban sites. There is no significant seasonal variation in calcium concentrations. The results are consistent with the general finding that resuspension of surface material caused by automobiles is the major source of calcium.

Manganese (Mn)

Manganese was predominantly found in the $PM_{2.5–10}$ fraction with the highest mean concentrations for the urban sites. The rural and coastal sites had very low concentrations. There was no obvious seasonal variation in Mn concentrations in either the fine or coarse fractions.

Iron (Fe)

Iron was mainly found in the coarse fraction at the urban sites with the highest concentrations again found at Site A. In contrast, there was little difference between the concentrations observed in the fine and coarse fractions measured at the coastal and rural sites. There did not appear to be any real seasonal variation for iron in either the fine or the coarse fraction for any of the sites.

Nickel (Ni)

Nickel concentrations were higher at the urban sites. The concentrations were low and there was little difference between the levels in the fine and coarse fractions at all sites. In most cases, slightly higher concentrations were present in the winter months, possibly due to heavy oil burning.

Zinc (Zn)

Zinc concentrations were higher at the urban sites. Interestingly, the levels were slightly higher in the fine fraction than the coarse fraction. However, there did not appear to be any significant seasonal variation in the concentrations.

Magnesium (Mg)

Magnesium was predominantly found in the coarse fraction and was highest at the coastal site (C). The results are consistent with sea spray being the major source of magnesium. Concentrations were lowest in the summer months, as the calmer weather conditions produced less sea spray.

Lead (Pb)

There was little difference between the levels of lead in the fine and coarse fractions at all sites. A clear seasonal trend is observed for Pb with concentrations in the coarse and fine fractions noticeably higher during the autumn and winter months.

Chromium (Cr)

Chromium concentrations were slightly higher at the urban sites. There was little difference between the levels of Cr in the fine and coarse fractions at all sites. There was no apparent seasonal variation in chromium concentrations.

Vanadium (V)

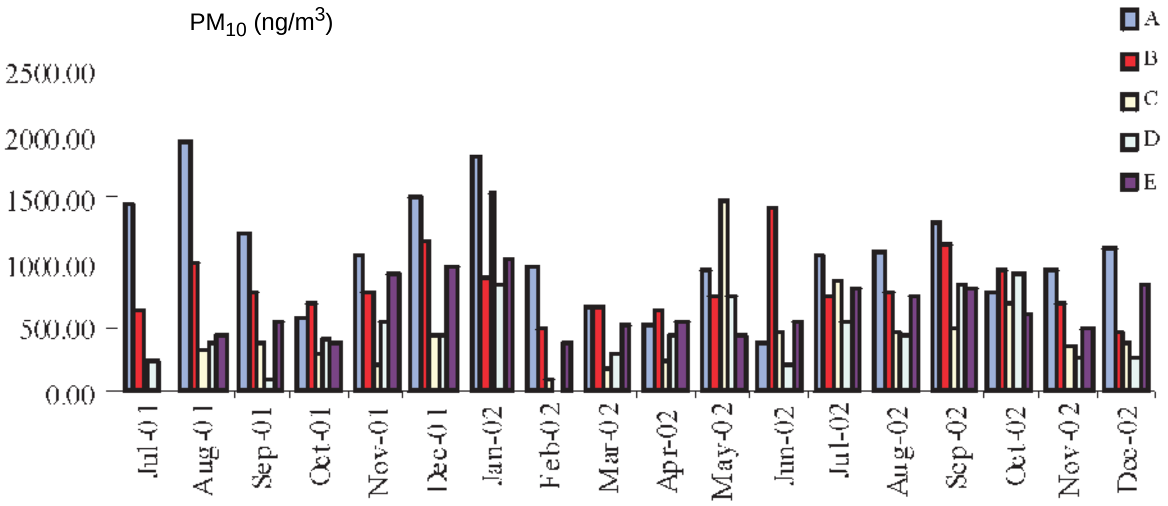
Vanadium concentrations were generally higher during the winter months at the urban sites. Very low levels of V were detected at Sites C and D.

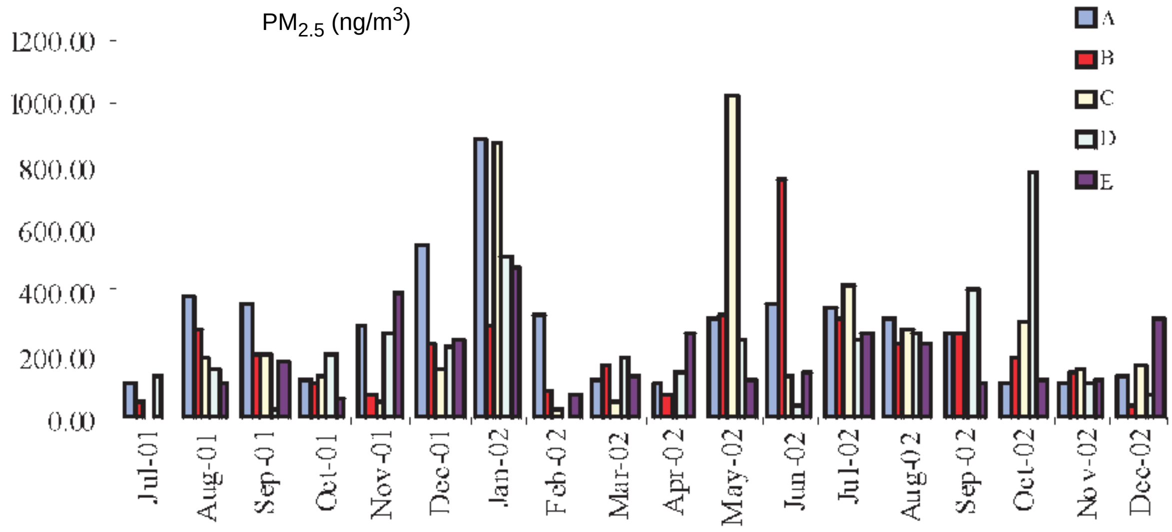
Cadmium (Cd)

Cadmium concentrations were low at all sites and show no seasonal variation.

Copper (Cu)

Copper concentrations were much higher at the urban sites. It was predominantly found in the coarse fraction and was highest at Site A. For the coastal and rural sites, there was little difference between the levels in the fine and coarse fractions. No seasonal variation in the concentrations of copper is observed.





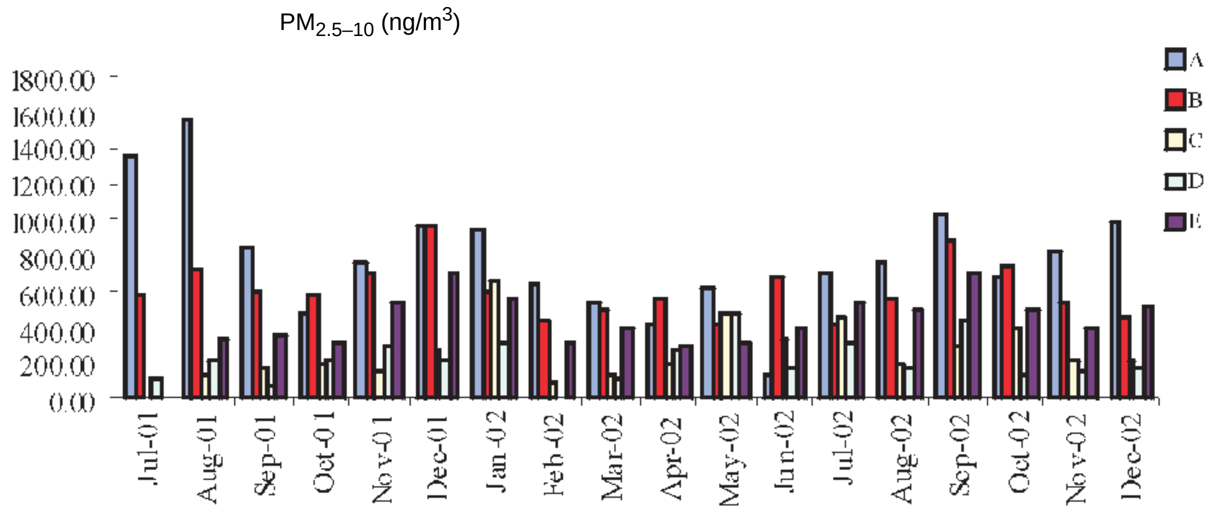


Figure 7.1. Monthly variation of calcium concentration in Ireland, July 2001–December 2002.

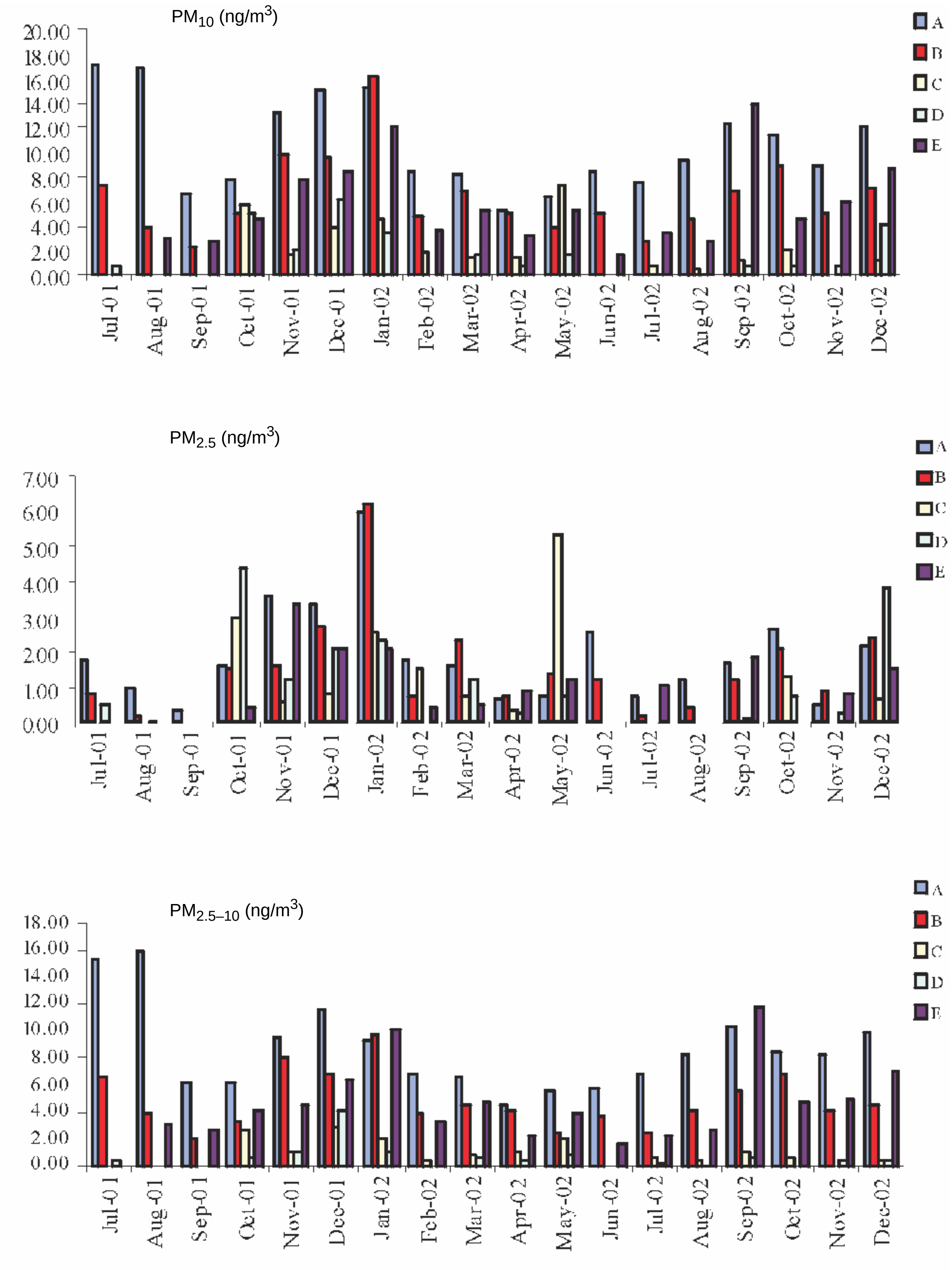


Figure 7.2. Monthly variation of manganese concentration in Ireland, July 2001–December 2002.

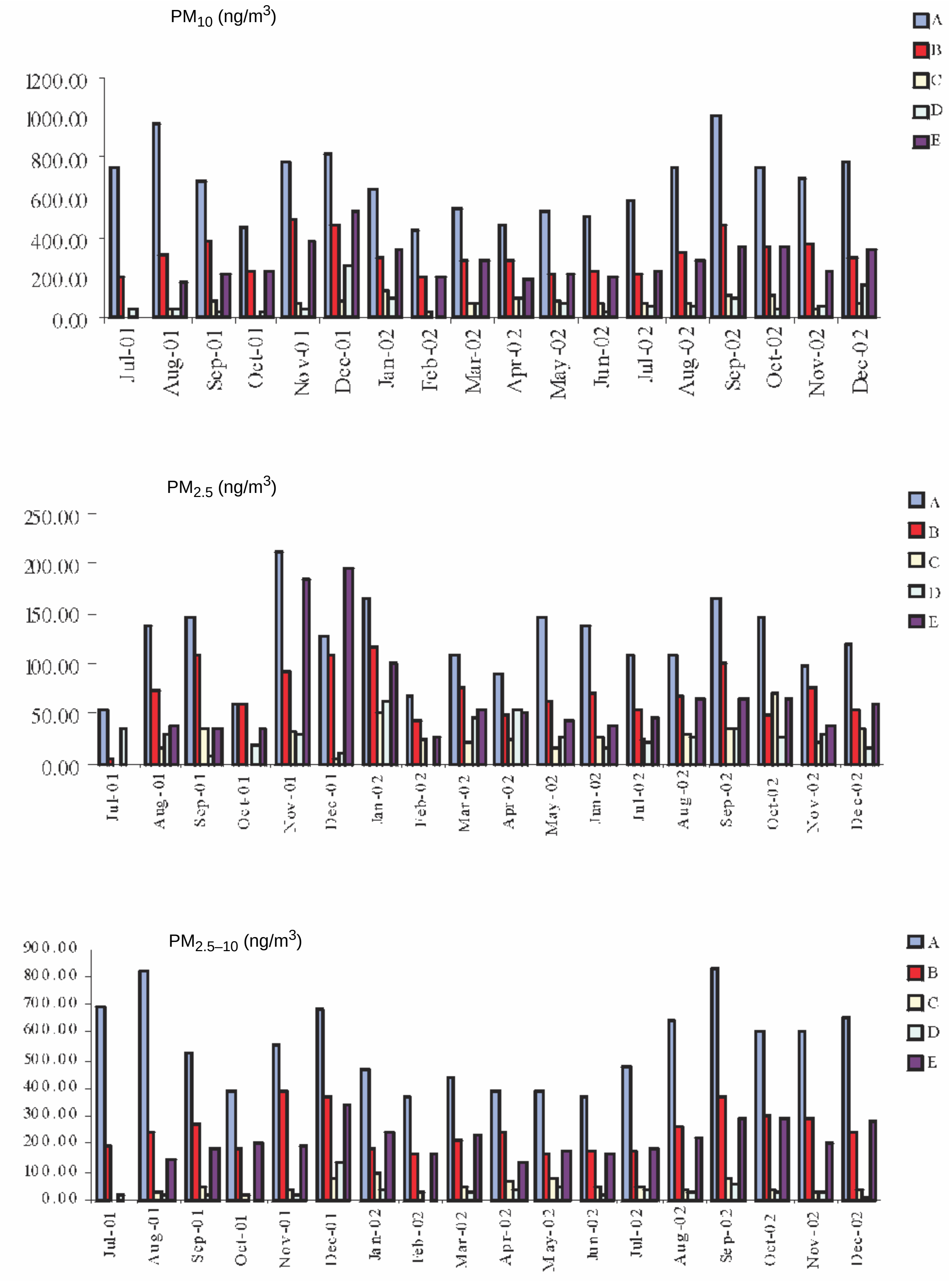


Figure 7.3. Monthly variation of iron concentration in Ireland, July 2001–December 2002.

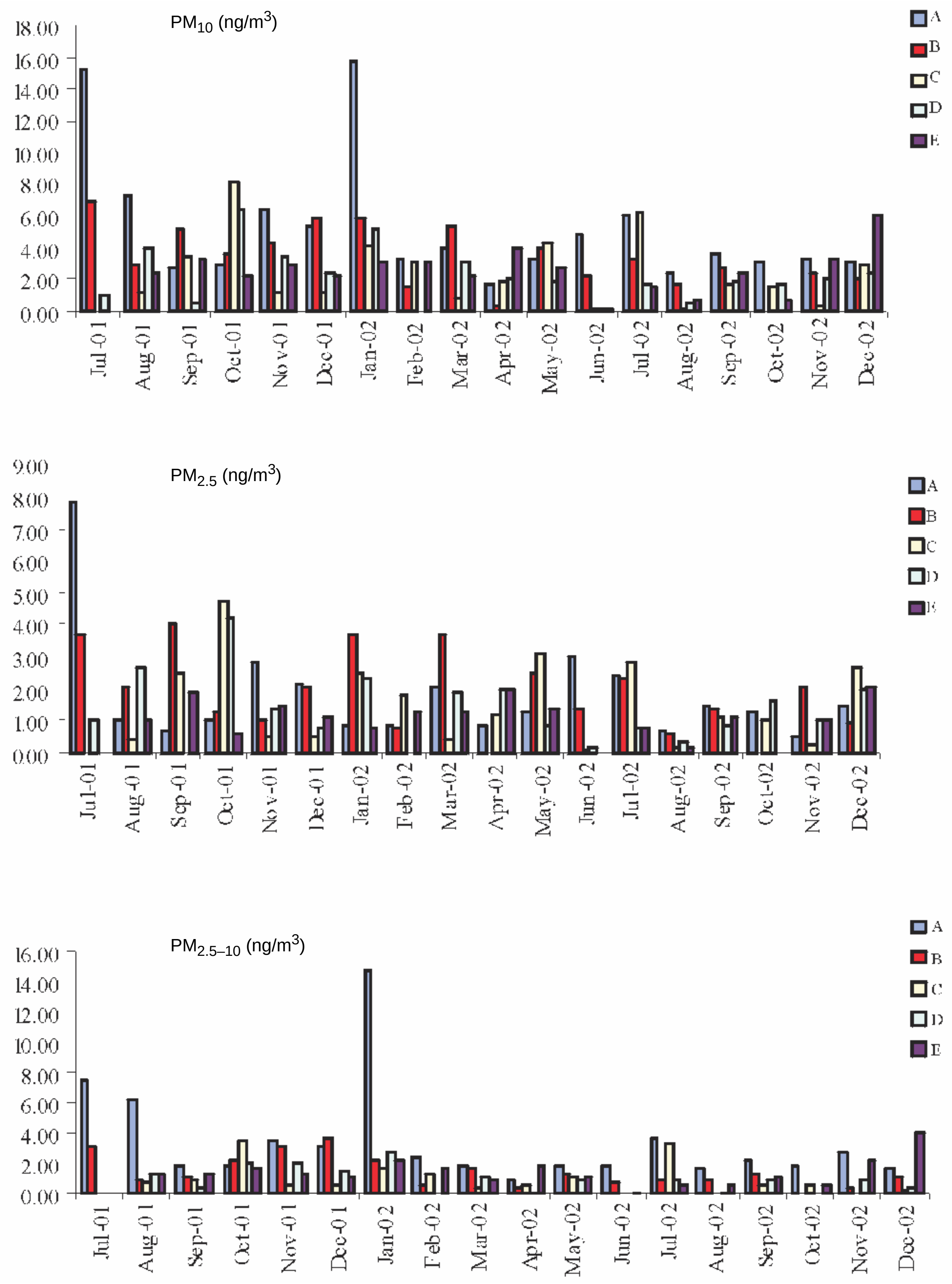


Figure 7.4. Monthly variation of nickel concentration in Ireland, July 2001–December 2002.

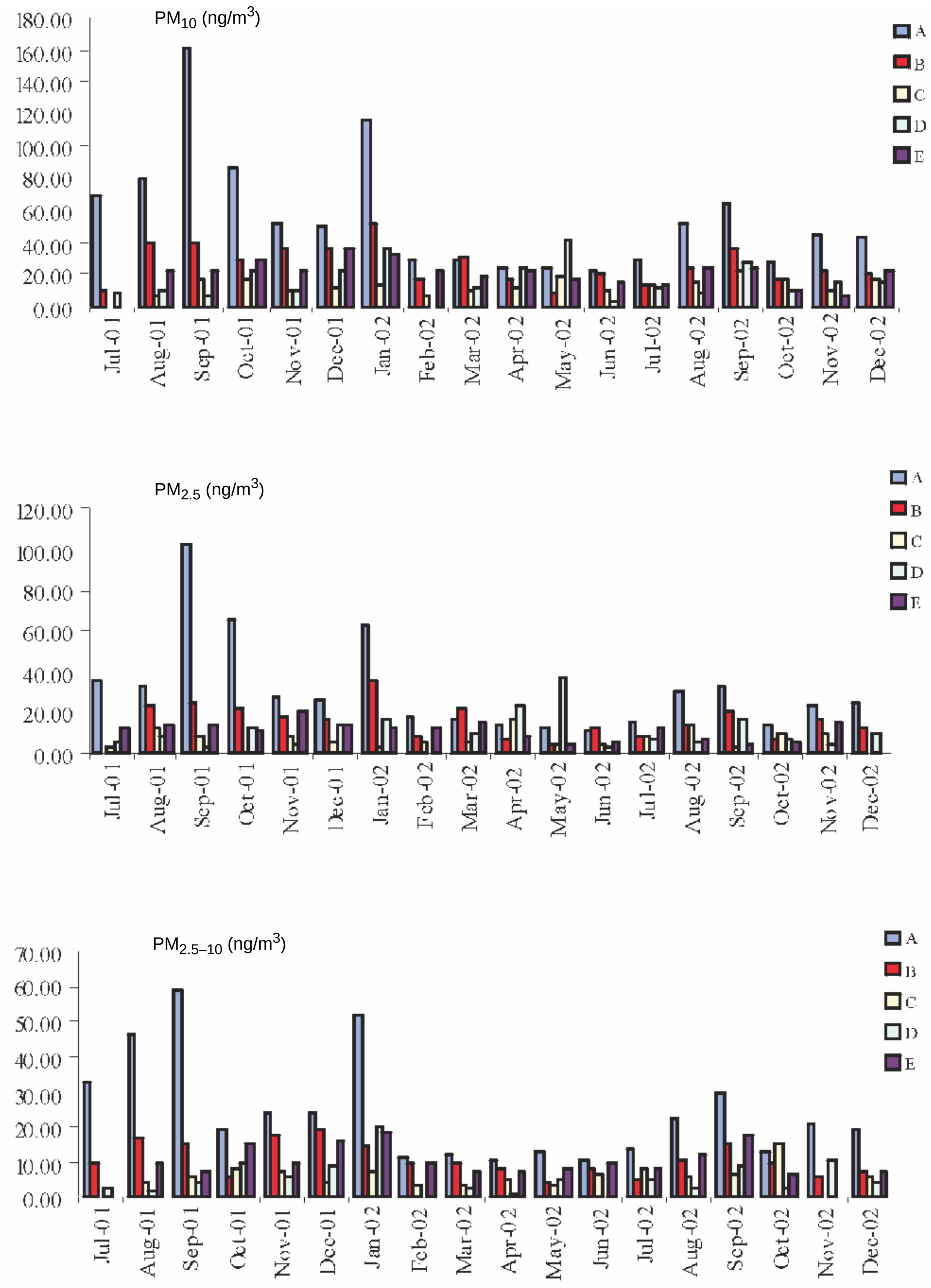


Figure 7.5. Monthly variation of zinc concentration in Ireland, July 2001–December 2002.

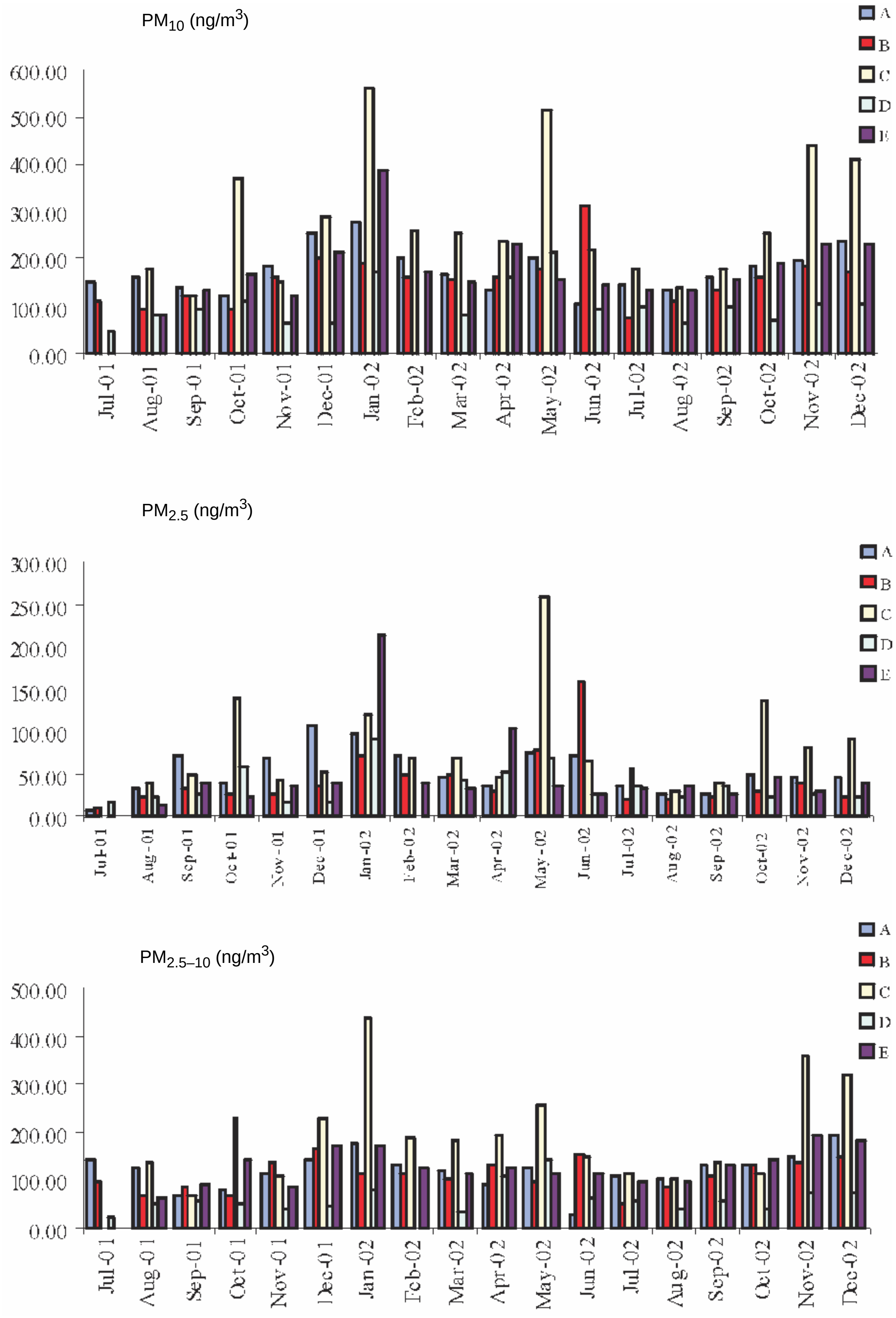
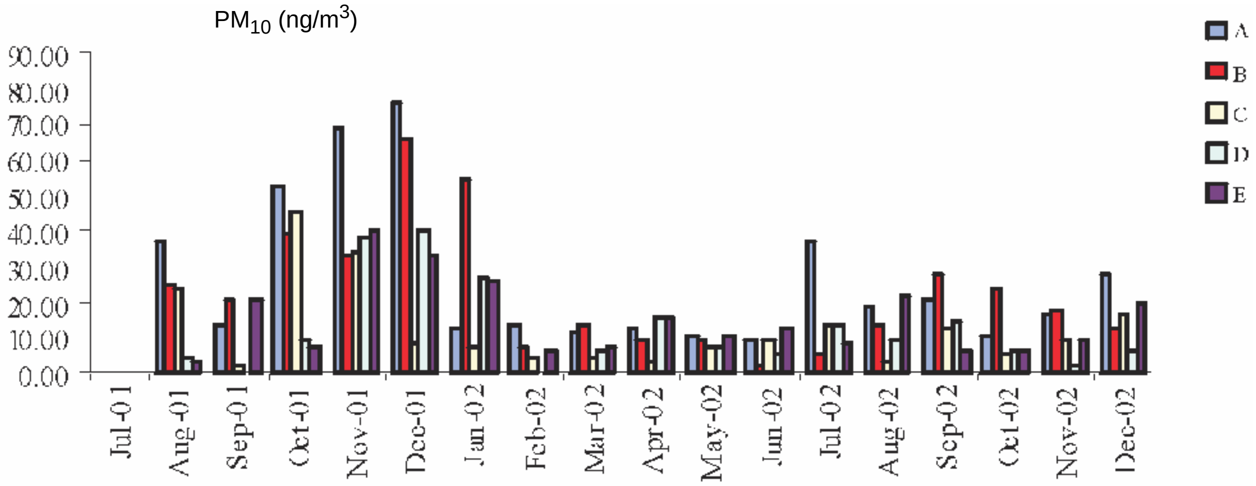
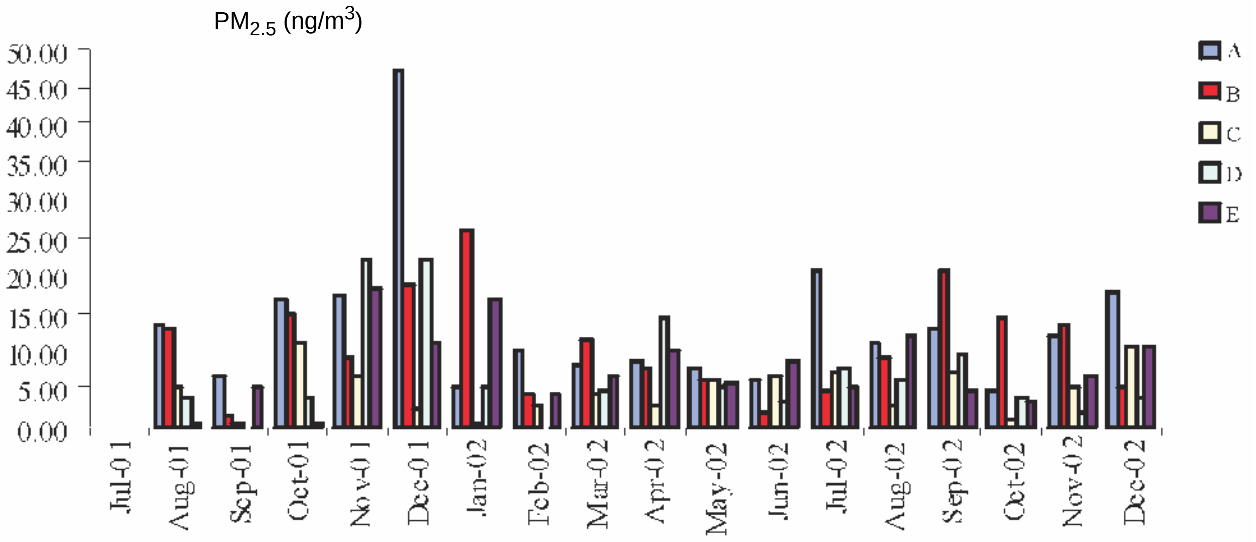


Figure 7.6. Monthly variation of magnesium concentration in Ireland, July 2001–December 2002.





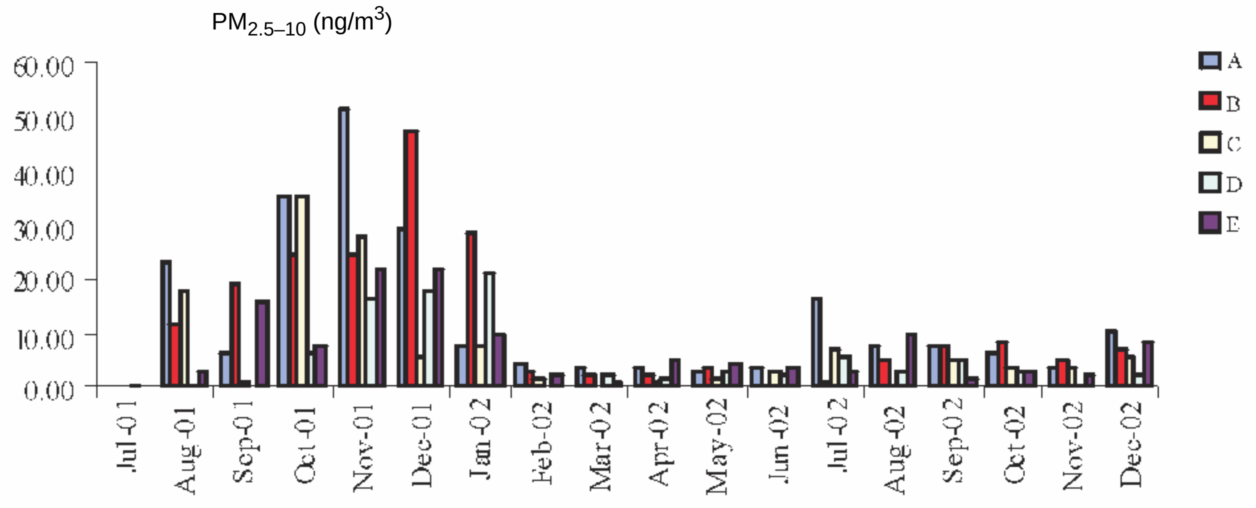


Figure 7.7. Monthly variation of lead concentration in Ireland, July 2001–December 2002.

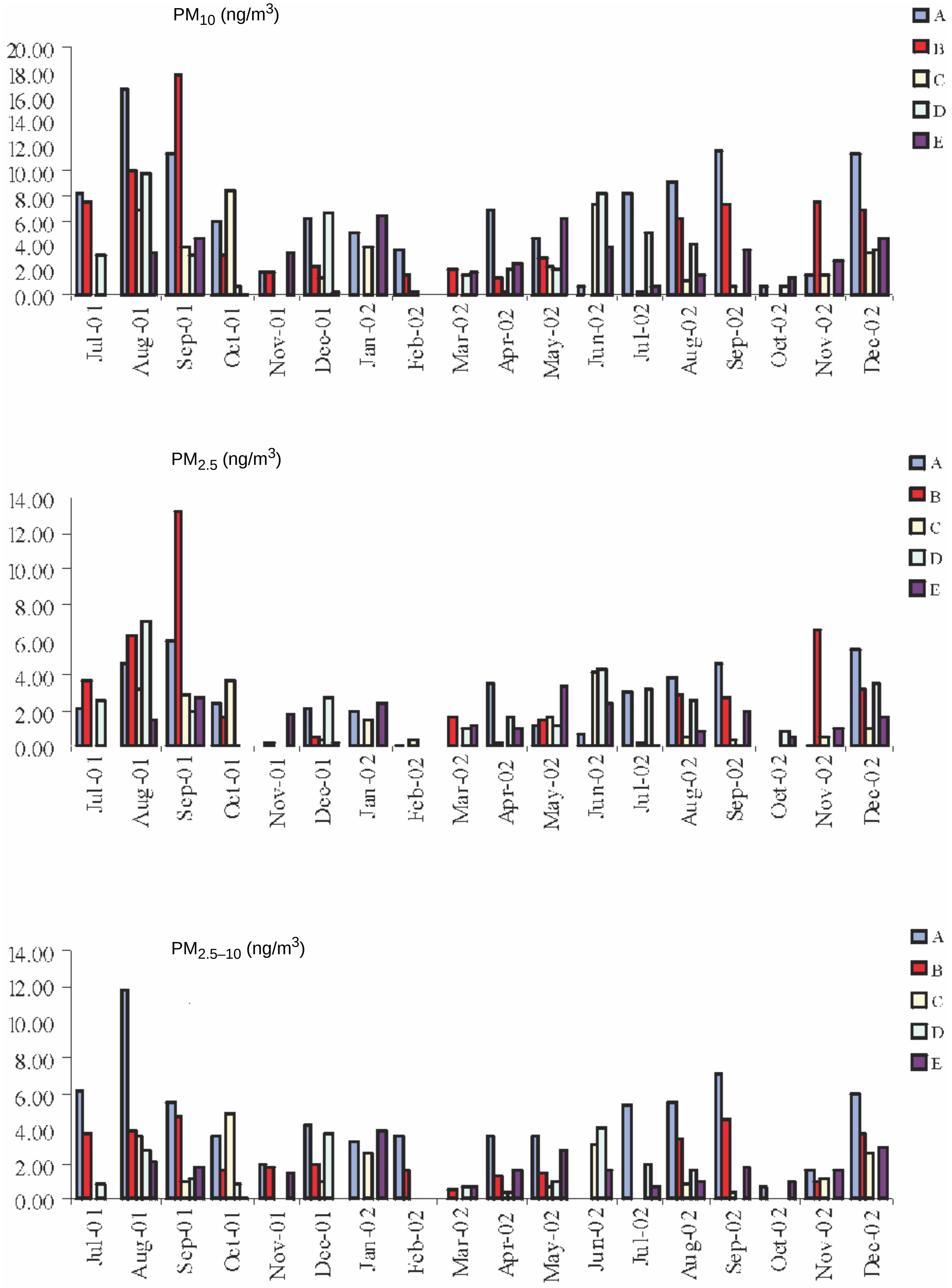


Figure 7.8. Monthly variation of chromium concentration in Ireland, July 2001–December 2002.

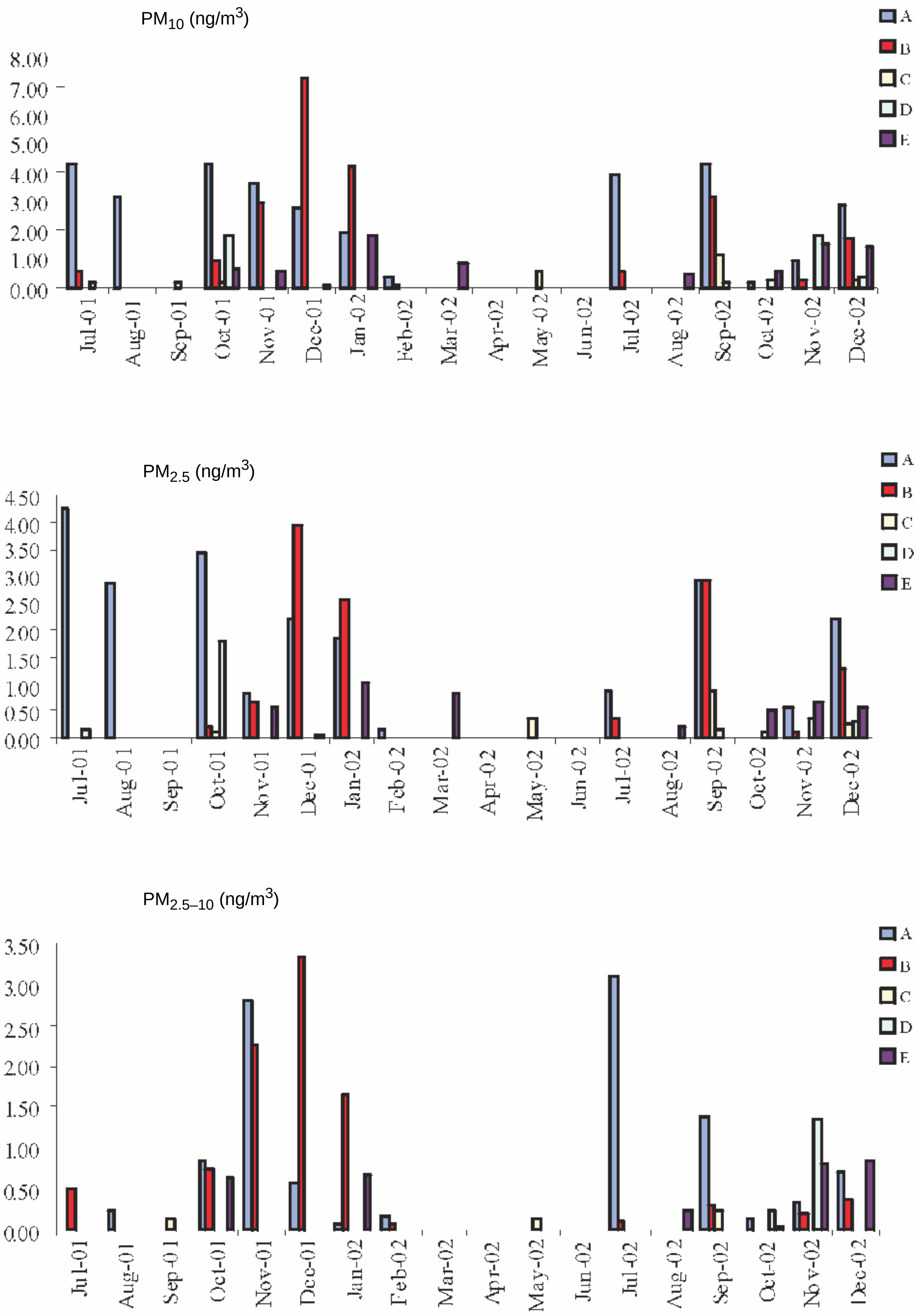


Figure 7.9. Monthly variation of vanadium concentration in Ireland, July 2001–December 2002.

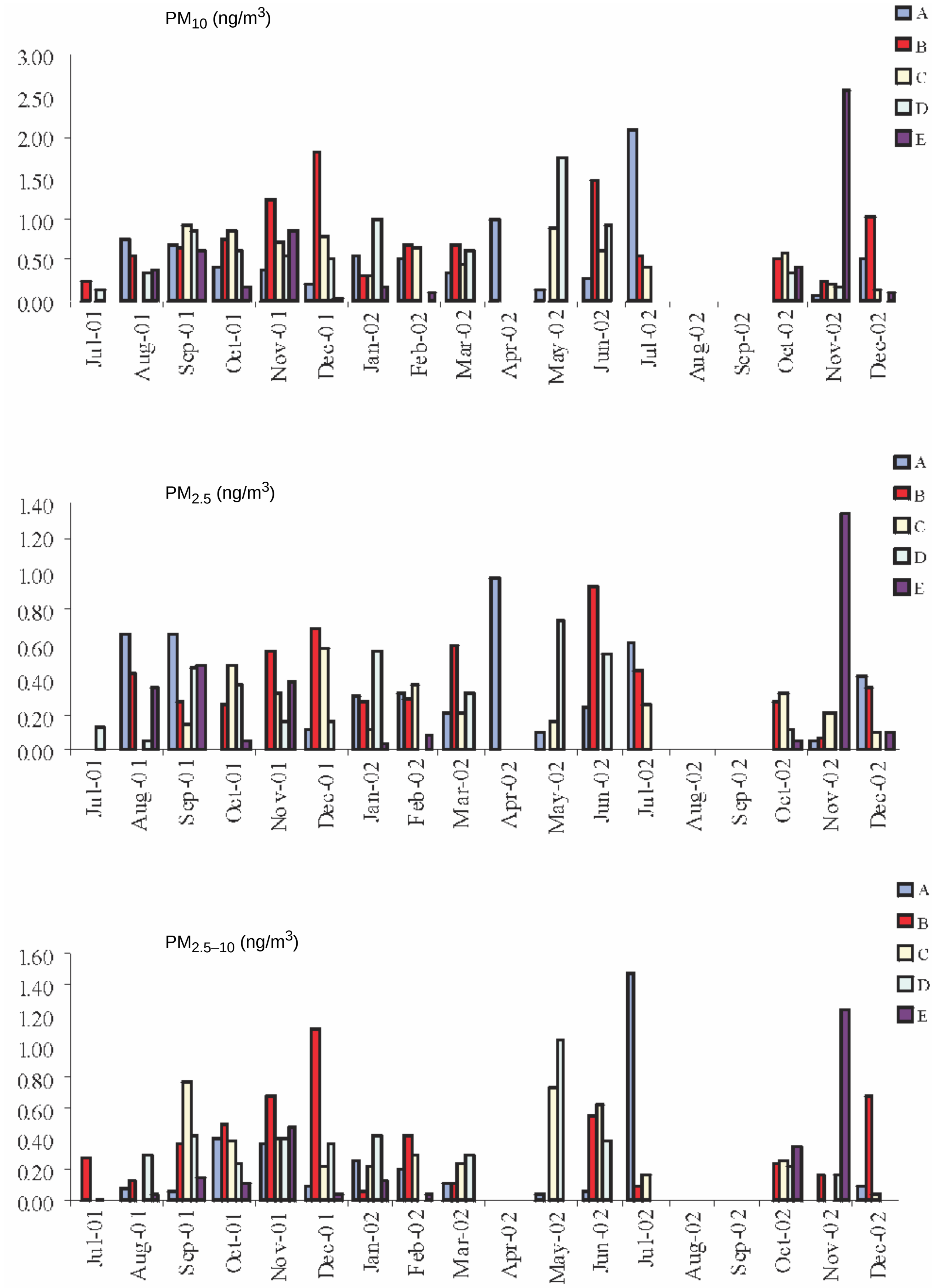


Figure 7.10. Monthly variation of cadmium concentration in Ireland, July 2001–December 2002.

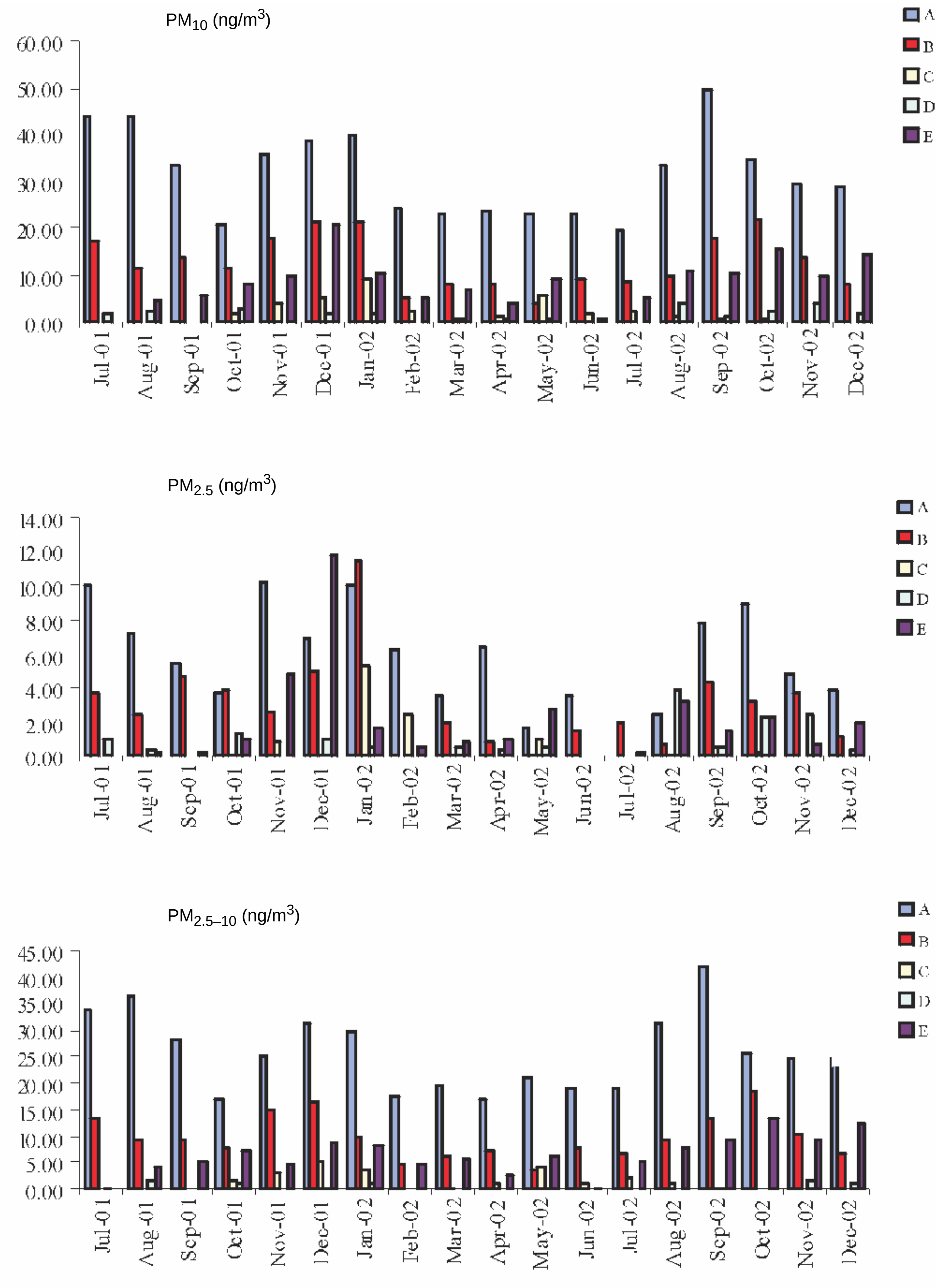


Figure 7.11. Monthly variation of copper concentration in Ireland, July 2001–December 2002.

Table 7.1. Seasonal mean concentration (ng/m^3) of measured trace metals at five sites in Ireland, July 2001–December 2002.

			Ca	Mn	Fe	Ni	Zn	Mg	Pb	Cr	V	Cd	Cu
Site A	Fine	Autumn	205.96	1.73	137.60	1.31	44.71	50.64	11.82	2.15	1.29	0.12	6.81
		Winter	356.53	2.91	120.34	1.41	30.00	68.68	19.06	3.44	1.78	0.33	5.78
		Spring	175.66	1.00	113.30	1.39	14.34	51.83	8.02	1.52	0.00	0.43	3.85
		Summer	288.44	1.43	107.66	3.25	26.22	33.33	9.58	2.90	1.92	0.31	5.31
	Coarse	Autumn	770.67	8.26	584.41	2.34	27.63	112.60	18.44	3.38	0.91	0.14	27.18
		Winter	915.24	9.62	576.29	4.17	24.23	171.85	12.03	4.78	0.47	0.14	25.48
		Spring	523.50	5.63	402.09	1.57	11.73	113.57	3.56	2.35	0.00	0.05	19.21
		Summer	999.51	11.35	624.96	4.62	27.55	107.26	10.51	6.26	0.57	0.27	29.22
Site B	Fine	Autumn	159.22	1.20	80.13	1.62	18.08	30.65	12.33	4.08	0.65	0.24	3.70
		Winter	111.16	2.82	70.46	1.58	16.45	39.37	10.69	1.74	1.73	0.39	3.33
		Spring	181.23	1.44	60.93	2.07	11.00	52.41	8.09	1.07	0.00	0.20	0.93
		Summer	296.07	0.54	51.21	2.16	11.66	42.39	5.85	2.98	0.07	0.34	2.20
	Coarse	Autumn	627.01	5.09	302.12	1.40	11.63	111.22	14.79	2.22	0.57	0.32	12.31
		Winter	555.88	5.78	237.38	1.61	10.82	138.29	16.58	2.44	1.03	0.60	8.72
		Spring	489.00	3.83	204.00	1.14	7.38	112.20	2.80	1.11	0.00	0.04	5.73
		Summer	602.69	4.36	208.43	1.46	10.55	89.29	3.92	2.47	0.14	0.21	9.57
Site C	Fine	Autumn	171.62	0.82	31.73	1.68	7.88	81.87	5.11	1.24	0.17	0.25	0.27
		Winter	254.02	1.14	29.88	2.14	7.87	86.79	6.13	0.80	0.13	0.22	1.29
		Spring	365.58	2.13	44.10	1.57	9.31	124.01	4.16	0.56	0.12	0.13	0.38
		Summer	230.43	0.00	20.45	0.75	4.25	45.31	5.40	2.46	0.00	0.04	0.02
	Coarse	Autumn	229.90	0.94	38.78	1.00	7.17	169.28	12.85	1.20	0.06	0.30	0.83
		Winter	278.33	1.11	49.96	0.69	5.59	301.84	5.49	1.87	0.00	0.14	1.41
		Spring	263.03	1.30	60.90	0.76	3.93	210.66	0.88	0.31	0.04	0.32	1.81
		Summer	225.34	0.18	36.41	0.92	5.46	130.44	10.56	2.35	0.00	0.13	0.71
Site D	Fine	Autumn	290.57	1.12	23.95	1.51	7.96	31.86	6.84	0.49	0.40	0.18	1.07
		Winter	214.76	3.01	26.21	1.78	12.44	39.14	8.62	2.48	0.16	0.18	0.56
		Spring	190.70	0.73	42.79	1.60	23.27	55.82	8.10	1.25	0.00	0.35	0.45
		Summer	160.07	0.13	27.00	1.14	6.06	25.17	3.78	4.03	0.05	0.13	0.97
	Coarse	Autumn	210.85	0.42	23.56	1.06	7.01	55.83	5.16	0.33	0.26	0.24	0.53
		Winter	218.94	1.43	48.28	1.31	9.32	69.81	10.93	0.95	0.00	0.20	0.88
		Spring	288.46	0.63	35.20	0.73	2.54	96.84	2.09	0.64	0.00	0.44	0.11
		Summer	186.39	0.15	20.96	0.48	2.57	47.22	1.88	2.14	0.00	0.14	0.53
Site E	Fine	Autumn	156.32	1.07	70.54	1.04	9.25	34.64	6.37	1.32	0.29	0.38	1.74
		Winter	284.42	1.54	83.60	1.56	15.52	71.12	10.54	1.29	0.47	0.07	3.24
		Spring	162.77	0.86	48.42	1.57	12.38	57.86	7.49	1.83	0.28	0.00	1.51
		Summer	153.33	0.17	43.93	0.67	10.07	23.93	4.70	1.22	0.04	0.17	0.67
	Coarse	Autumn	463.17	5.54	226.60	1.41	9.30	130.91	8.66	1.30	0.24	0.38	8.09
		Winter	518.39	6.85	264.94	2.86	10.77	170.12	9.82	2.09	0.52	0.03	9.90
		Spring	329.35	3.76	179.97	1.32	7.28	119.19	3.46	1.69	0.00	0.00	4.93
		Summer	399.73	2.67	165.80	0.85	9.90	82.71	4.35	1.59	0.04	0.02	4.30

7.4 Summary

7.4.1 Coarse fraction

Coarse particles arise either as primary particles or as a result of different reactions of gaseous compounds with pre-existing larger aerosols such as sea salt. The coarse fraction includes a variety of components of either natural (biological sources, ocean spray, crustal metals like Ca and Fe) or anthropogenic origin (coal ash, oil combustion, resuspension of industrial dust and soil, construction materials such as cement or limestone) (Lindgren, 1996; Legret and Pegotto, 1999; Garg *et al*., 2000).

For all metals, except magnesium, the highest concentrations were detected in Site A. This was expected, mainly due to the large number of vehicles passing the site. Within the urban sites, Site A had the highest concentration of the crustal elements Ca and Fe. Average Ca levels in Site B were almost equal to those at Site A. The concentrations at these Dublin sites were almost double those observed in Site E (Cork). This difference could be due to higher amounts of resuspended road dust in the Dublin sites, probably due to the higher volumes of traffic.

The Ca concentrations at Sites C, D and E were quite similar, with higher values for the urban site (E). Fe concentrations are highest at Site A, with Sites B and E possessing higher levels than the rural and coastal sites. Since Fe is associated with vehicle emissions, then these results are not surprising.

For the toxic trace metals (Mn, Pb, Cd, Zn, Ni, Cr, V and Cu), Site A showed higher concentrations than either of the other urban sites. Again this is not surprising since the metals are all anthropogenically produced either from the incomplete combustion of fossil fuels or from industry. The large volumes of traffic within Dublin city centre are the principal reason for the higher values at Site A.

In general, Site D (Co. Galway) shows the lowest level of all metals. This was to be expected as this site was removed from any direct vehicle emissions and had no industry within the vicinity. Site C (Co. Wicklow) was also a background site, removed from traffic and industry. However, this site was particularly close to the sea and showed the highest concentration of magnesium in the coarse fraction in comparison to all other sites. Normally there are high levels of magnesium in sea spray so these observations are consistent with other results (Harrison and Jones, 1995; Harrison *et al.*, 2003a).

7.4.2 Fine fraction

As with the coarse fraction, the higher concentrations of trace metals in the fine fraction were usually observed at Site A. Within the urban sites (A, B and E), Site A had consistently higher concentrations than B and E, except for Ni (highest at Site B). Sites B and E showed similar concentrations for all metals in this fraction. This was expected since B and E are both urban background sites.

The coastal (C) and rural (D) sites generally showed lower concentrations of the metals than the urban sites. As many of the metals found in the fine fraction originate from industrial sources and incomplete combustion of fossil fuels, the concentrations observed in both of these sites are expected.

8 Polycyclic Aromatic Hydrocarbons (PAHs)

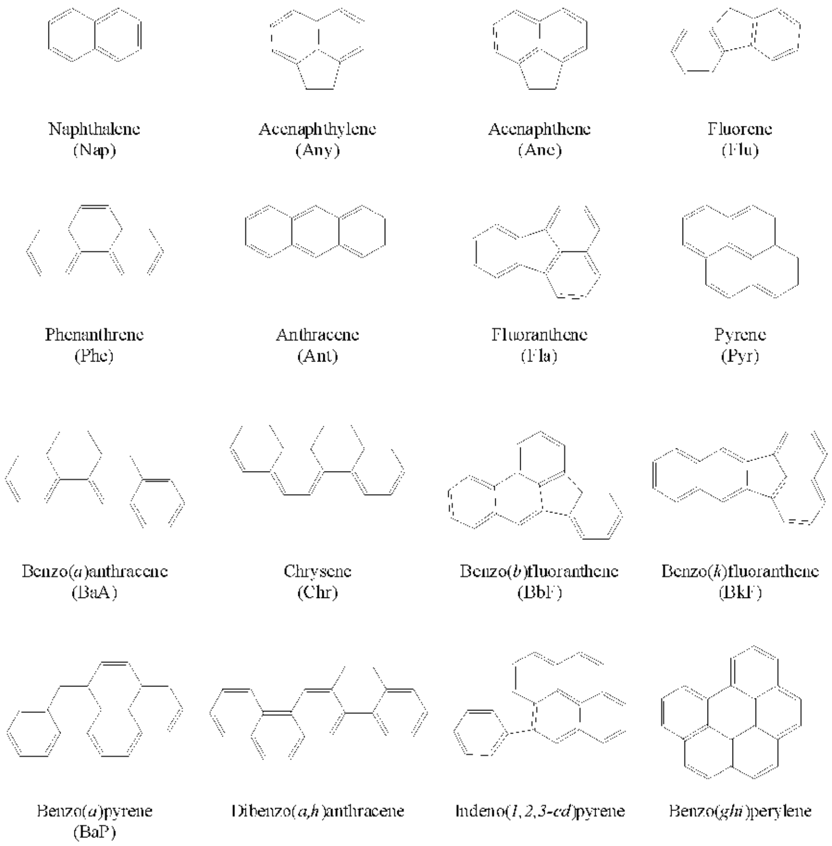
8.1 Sources of PAHs

Polycyclic aromatic hydrocarbons are products of incomplete combustion formed during the burning of fossil fuels. They are present in the atmosphere as gases (e.g. naphthalene), solids adsorbed/absorbed to the surfaces of fine particles (e.g. benzo(*a*)pyrene), and semi-volatile compounds that are partitioned between the gas and particle phase (e.g. phenanthrene, fluoranthene). The widespread presence of PAHs in the atmosphere is due to their emissions from a wide range of combustion sources including diesel and petrol engines, coal fires, power stations, biomass burning and incinerators. There are hundreds of different PAHs, including many derivatised compounds such as nitro-PAHs. Many of these compounds are known or suspected carcinogens and there is currently great concern over the effects of PAHs on human health. To this end, the US EPA has selected 16 PAHs as 'priority pollutants', based on their abundance in the atmosphere and known impact on human health. These compounds are shown in Fig. 8.1.

8.2 Monthly Variation in Concentration of PAHs

In this work the concentrations of the 16 PAHs were measured in the fine and coarse fractions collected at the five sites. The mean monthly concentrations of the PAHs detected in PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$ over the period from September 2001–October 2002 are presented in Figs 8.2–8.14.

Thirteen of the 16 US EPA priority PAH pollutants were detected in particulate matter collected at the sites. The concentrations of dibenzo(*a,h*)anthracene, indeno(*1,2,3-cd*)pyrene and benzo(*ghi*)perylene were below the detection limits of the method employed in this work. As expected, the concentration of the PAHs was highest at the urban sites due to the large number of combustion



Naphthalene (Nap)
Acenaphthylene (Any)
Acenaphthene (Ane)
Fluorene (Flu)
Phenanthrene (Phe)
Anthracene (Ant)
Fluoranthene (Fla)
Pyrene (Pyr)
Benzo(*a*)anthracene (BaA)
Chrysene (Chr)
Benzo(*b*)fluoranthene (BbF)
Benzo(*k*)fluoranthene (BkF)
Benzo(*a*)pyrene (BaP)
Dibenzo(*a,h*)anthracene
Indeno(*1,2,3-cd*)pyrene
Benzo(*ghi*)perylene

Figure 8.1. The 16 US EPA 'priority PAH pollutants'.

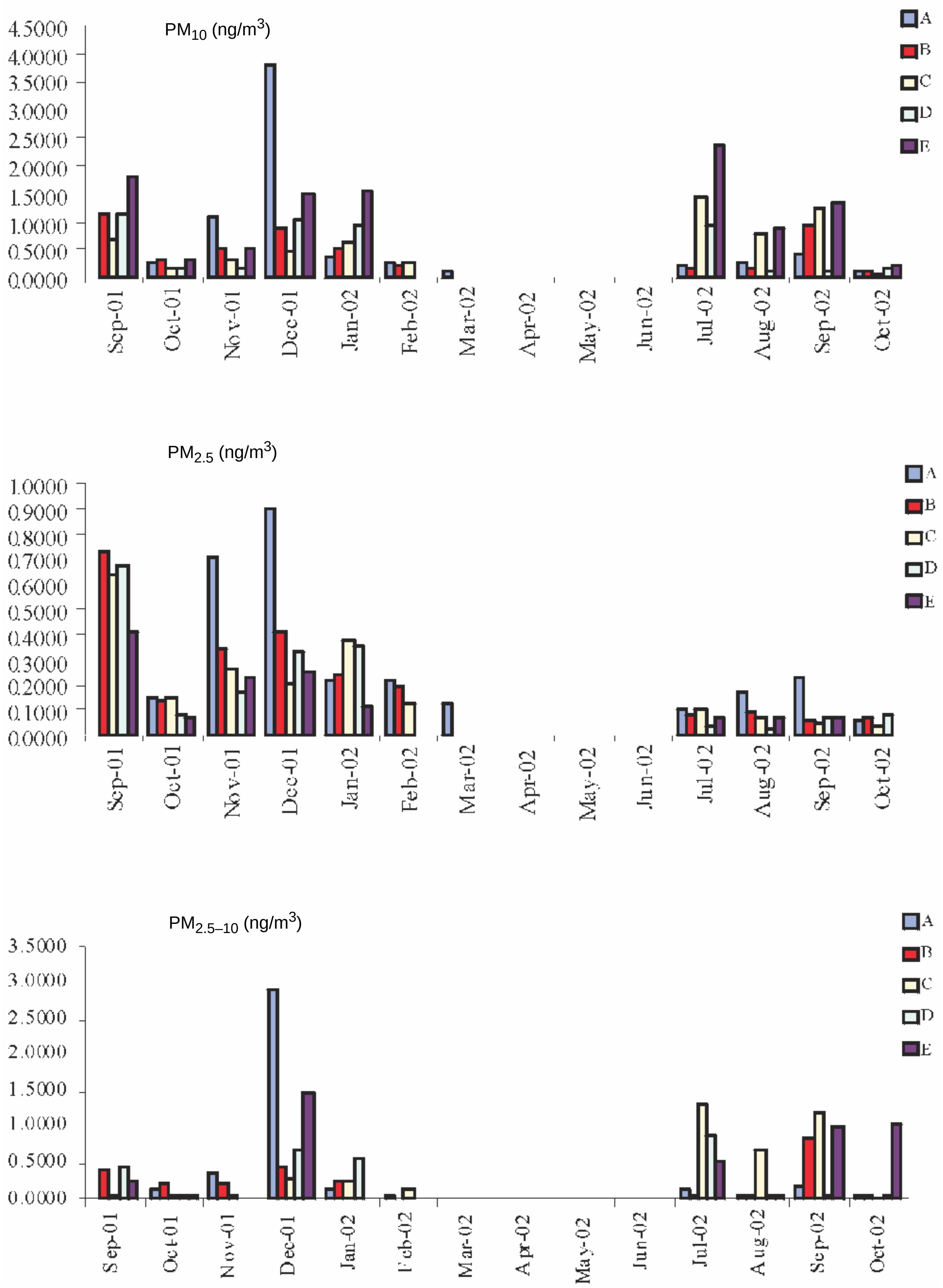


Figure 8.2. Monthly variation of naphthalene concentration in Ireland, September 2001–October 2002.

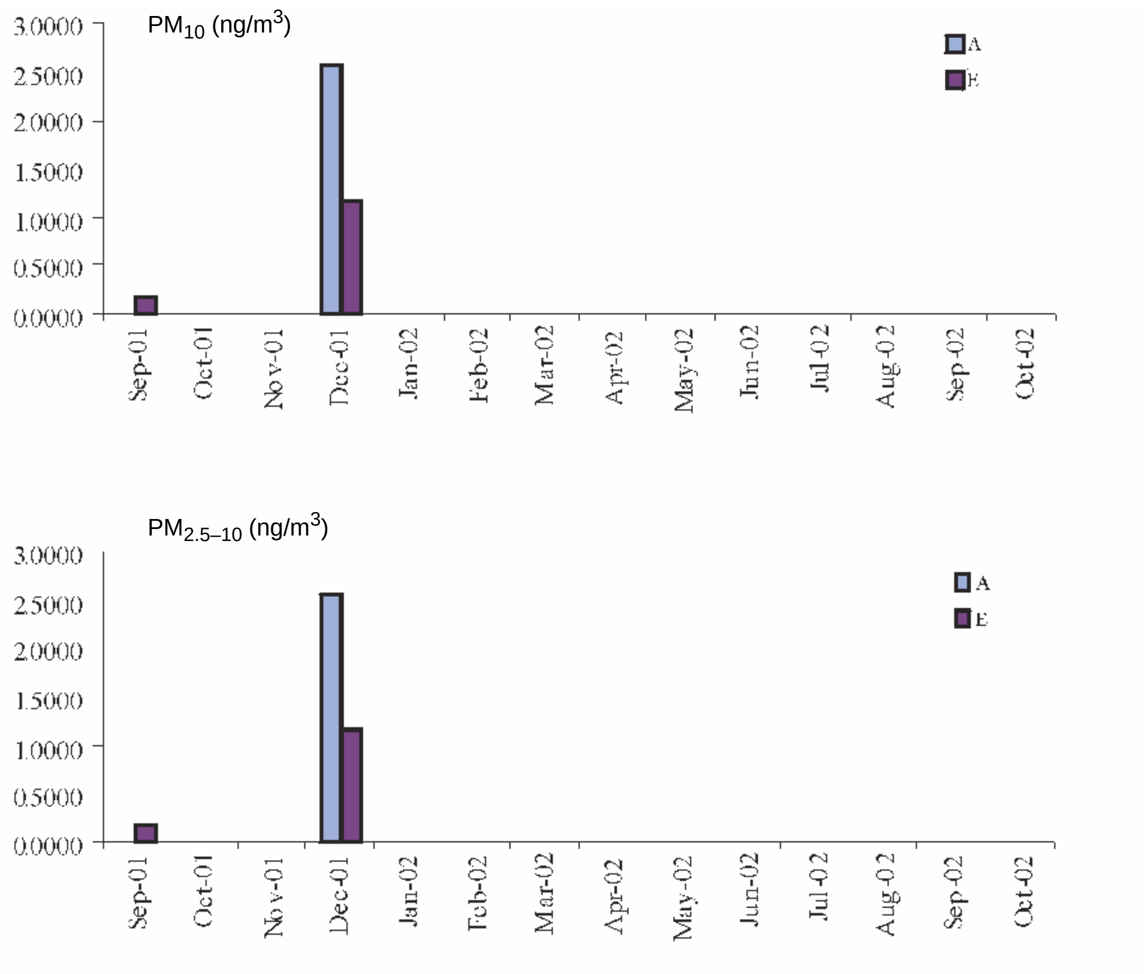


Figure 8.3. Monthly variation of acenaphthylene concentration in Ireland, September 2001–October 2002. (Note: not detected in the $PM_{2.5}$ fraction.)

sources, especially automobile traffic. The levels of PAHs were largest at the Dublin roadside (Site A), whilst similar concentrations were observed at the urban background sites in Dublin (B) and Cork (E). Very low concentrations of the PAHs were observed at the coastal and rural sites due to the lack of significant sources.

The concentrations of the particle-phase PAHs measured at the five sites are similar to those observed at other locations around the world (Smith and Harrison, 1998). The concentration of benzo(*a*)pyrene is of particular interest because a threshold value of 1 ng/m^3 will be introduced in 2005 as part of a new EU directive. At Site A, the monthly average value exceeded this threshold on five occasions. At Sites B and E, the monthly average value exceeded this threshold on three and four occasions, respectively. Further monitoring of benzo(*a*)pyrene concentrations is clearly required.

8.3 Trends in PAH Concentration

The first eight PAHs, naphthalene to pyrene, exist predominantly in the gas phase, although the extent of partitioning between gas and solid-phase strongly depends on temperature and the amount of available surface material. Consequently, the concentrations measured for these compounds, and in particular the first four PAHs, are low. Although naphthalene was observed at all sites, acenaphthylene, acenaphthene and fluorene were only detected at the urban sites in the autumn and winter months at very low concentrations. The fact that these first four PAHs were found predominantly in the coarse fraction indicates that they probably condensed onto existing coarse particles in the atmosphere. In contrast, the five least volatile measured PAHs, benzo(*a*)anthracene to benzo(*a*)pyrene, were detected mainly in the fine fraction, indicating that they were probably adsorbed onto particles in the accumulation

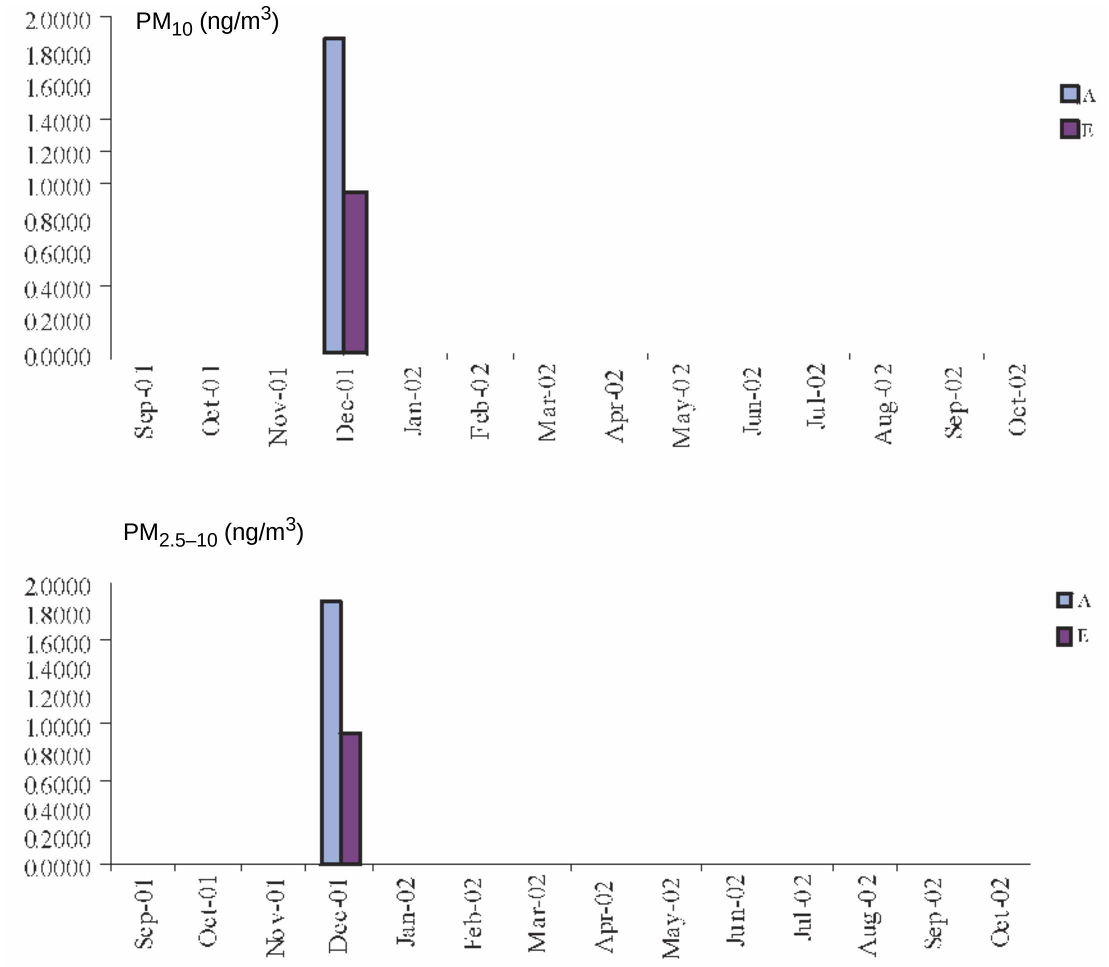


Figure 8.4. Monthly variation of acenaphthene concentration in Ireland, September 2001–October 2002. (Note: not detected in the $PM_{2.5}$ fraction.)

mode. The remaining four PAHs, phenanthrene, anthracene, fluoranthene and pyrene, were detected at all sites with similar concentrations in the fine and coarse fractions. This is readily understood because these compounds readily partition between the gas and particle phases in the atmosphere.

The concentrations of the measured PAHs in the fine and coarse fractions are also presented as seasonal mean values in Table 8.1: autumn (September–November), winter (December–February), spring (March–May) and summer (June–August). There is a reasonably strong seasonal variation in the concentration of PAHs. In the majority of cases, the mean concentrations in the autumn and winter months were significantly higher than those in the summer months. This is more clearly seen in the data for the urban sites. The difference between PAH concentrations in winter and summer has been attributed to the following (Smith and Harrison, 1998): (i) increase in emissions from domestic heating, (ii) winter traffic (from congestion and cold starts), (iii) meteorological conditions which favour less pollutant dispersion in winter, and (iv) possible loss of PAHs due to photochemical decay in summer.

8.4 Summary

The concentration of the PAHs was highest at the urban sites due to the large number of combustion sources, especially automobile traffic. The levels of PAHs were largest at the Dublin roadside (Site A), whilst similar concentrations were observed at the urban background sites in Dublin (B) and Cork (E). Very low concentrations of the PAHs were observed at the coastal and rural sites due to the lack of significant sources. The concentrations of the particle-phase PAHs measured at the five sites are similar to those observed at other locations around the

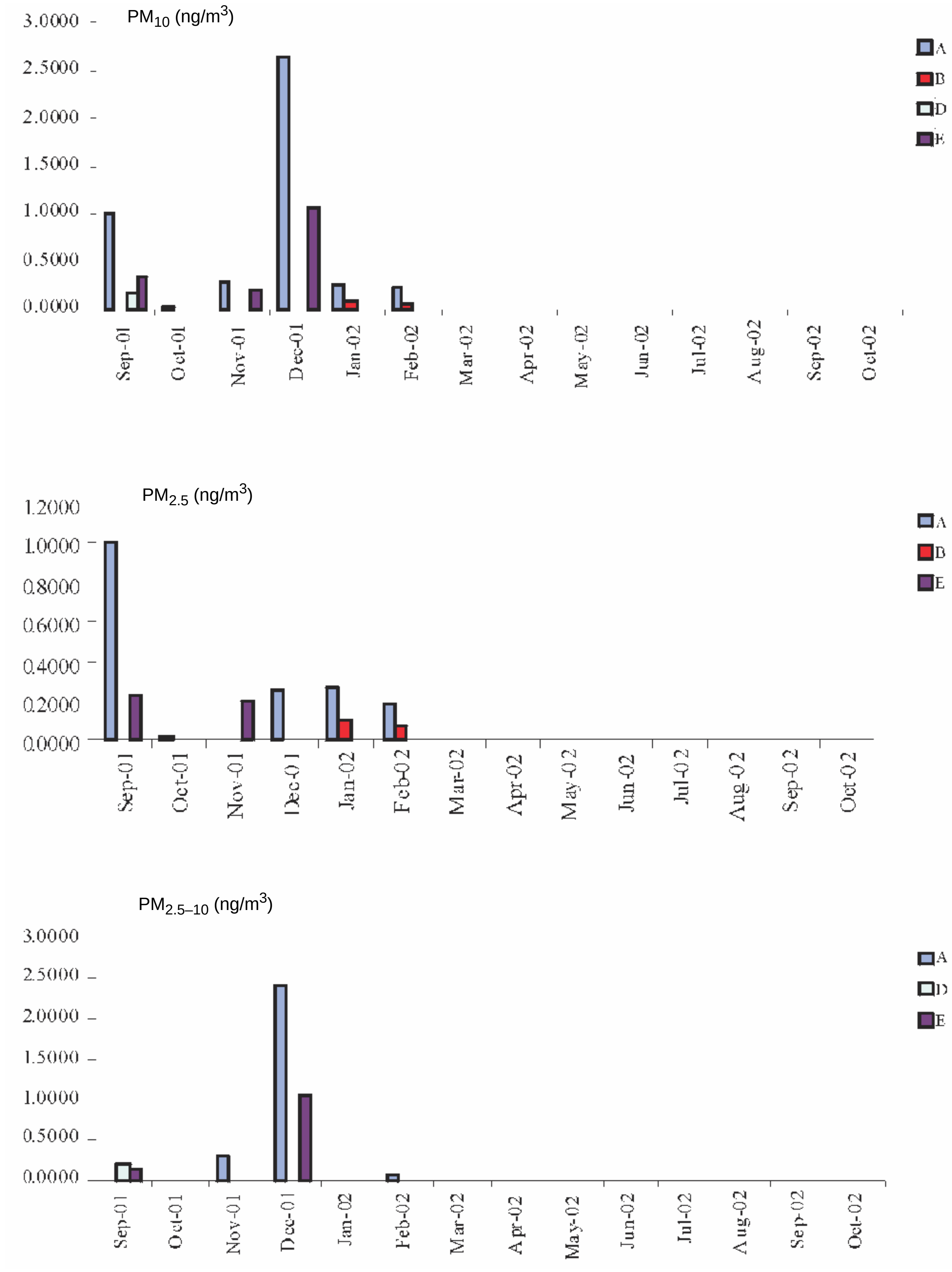


Figure 8.5. Monthly variation of fluorene concentration in Ireland, September 2001–October 2002.

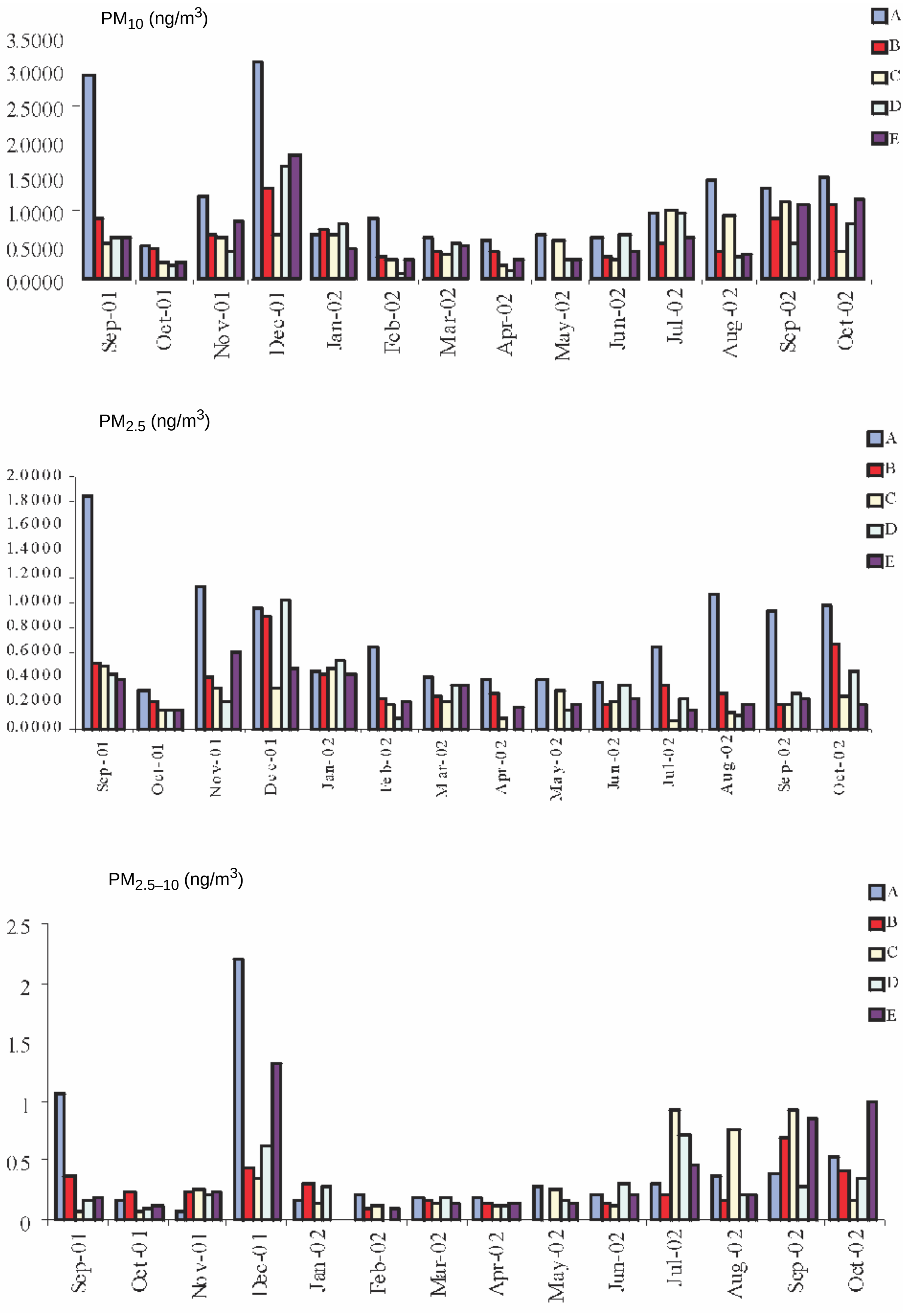


Figure 8.6. Monthly variation of phenanthrene concentration in Ireland, September 2001–October 2002.

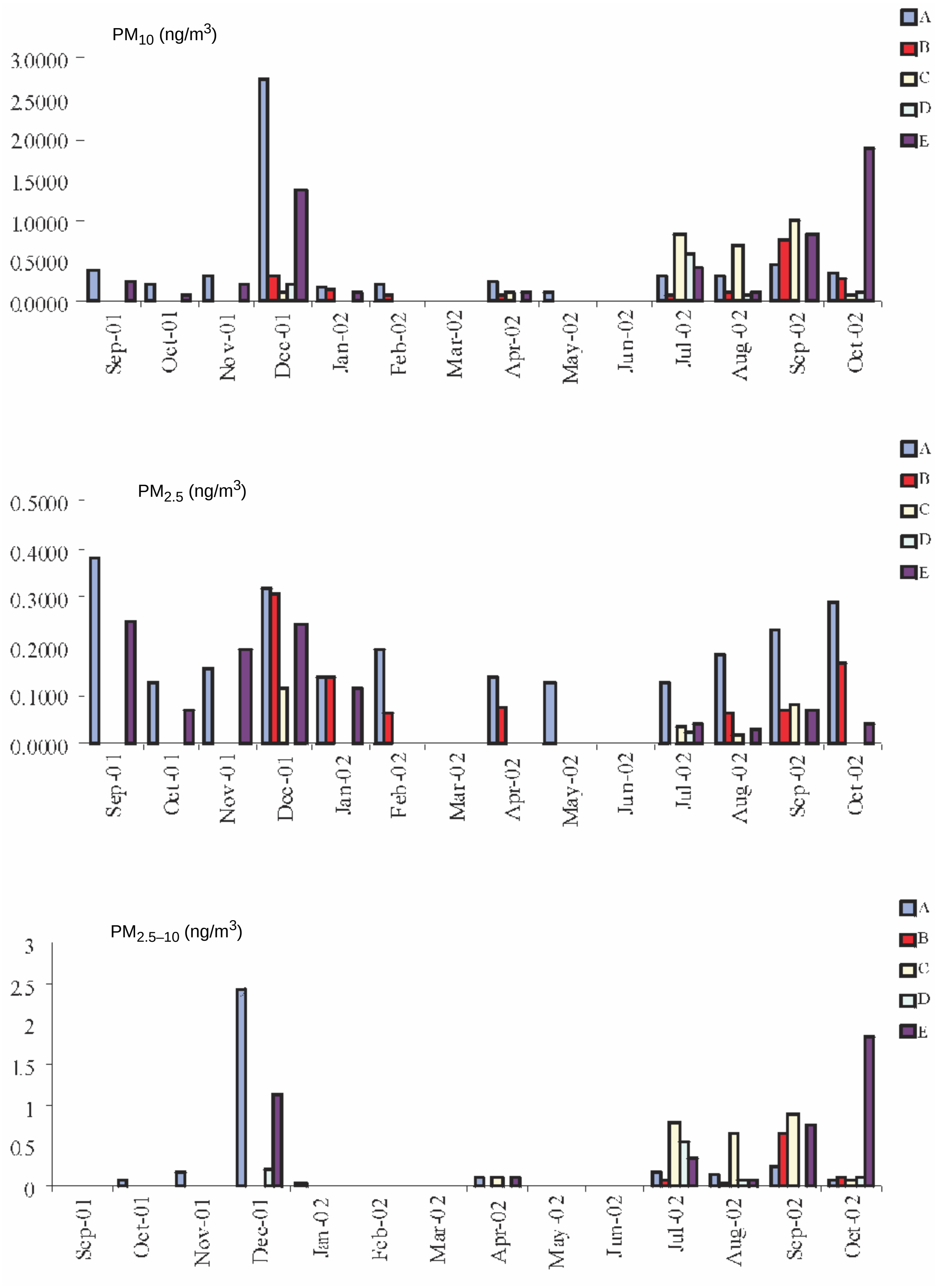


Figure 8.7. Monthly variation of anthracene concentration in Ireland, September 2001–October 2002.

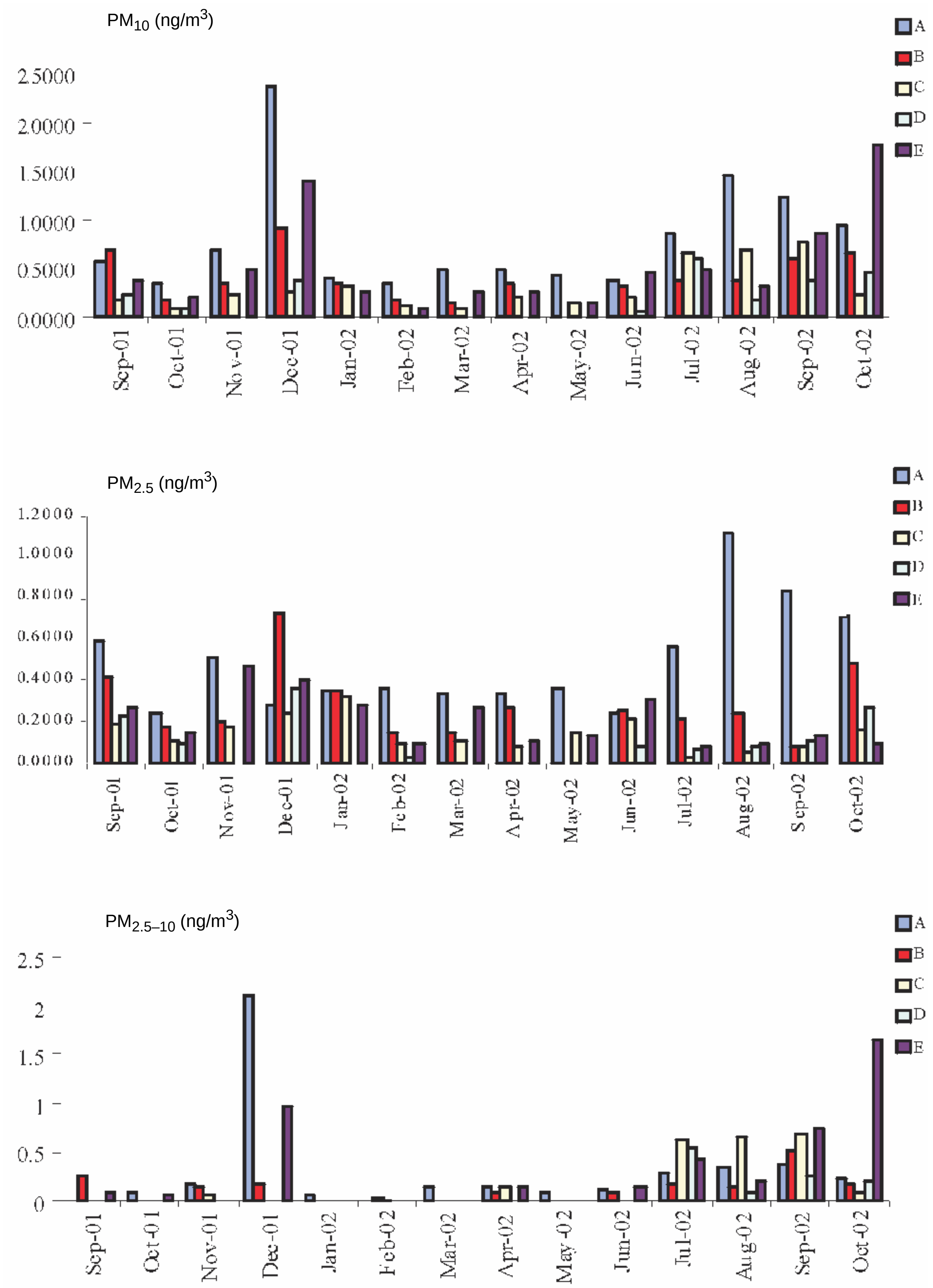


Figure 8.8. Monthly variation of fluoranthene concentration in Ireland, September 2001–October 2002.

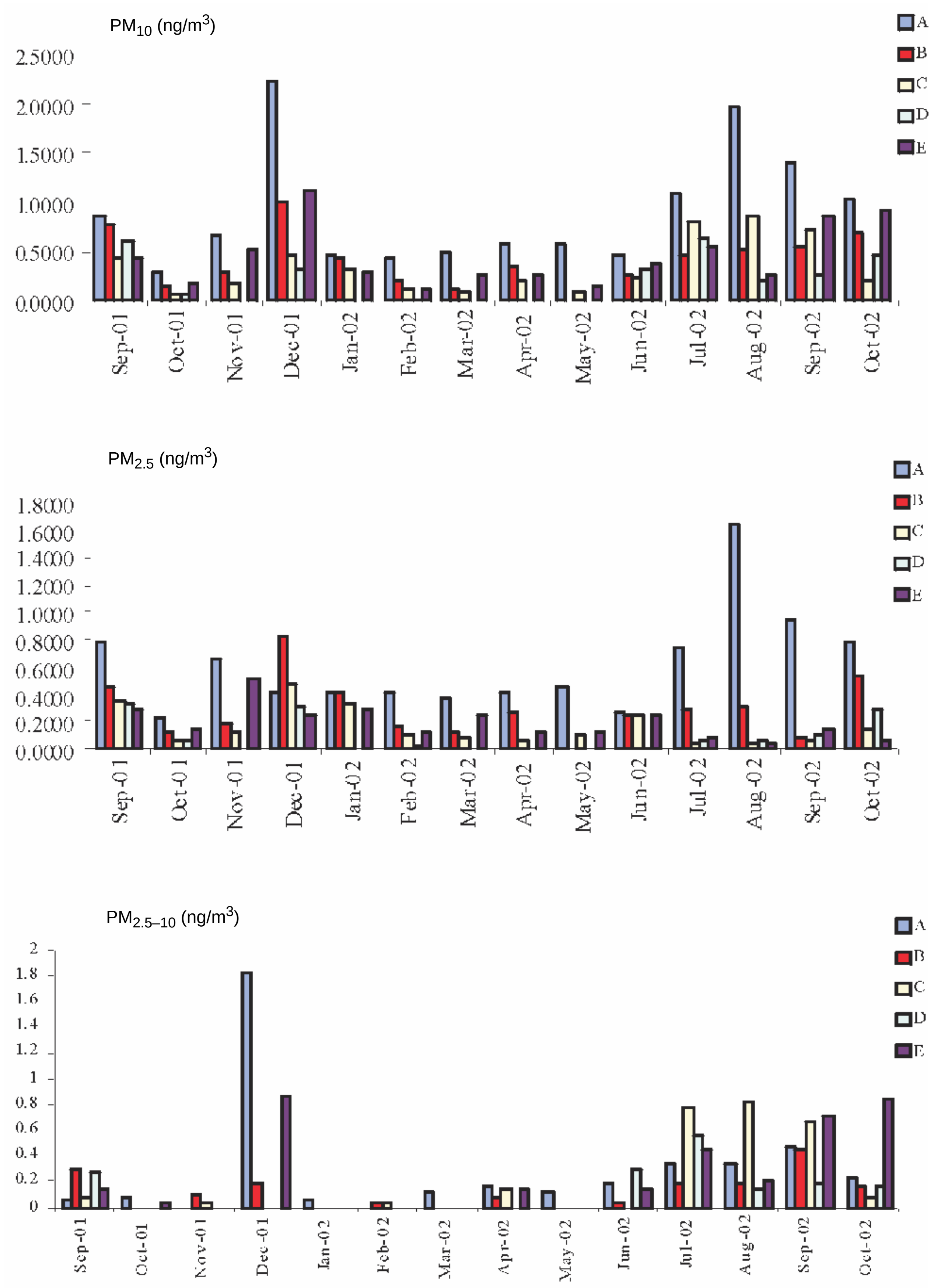


Figure 8.9. Monthly variation of pyrene concentration in Ireland, September 2001–October 2002.

Figure 8.10. Monthly variation of benzo(*a*)anthracene concentration in Ireland, September 2001–October 2002.

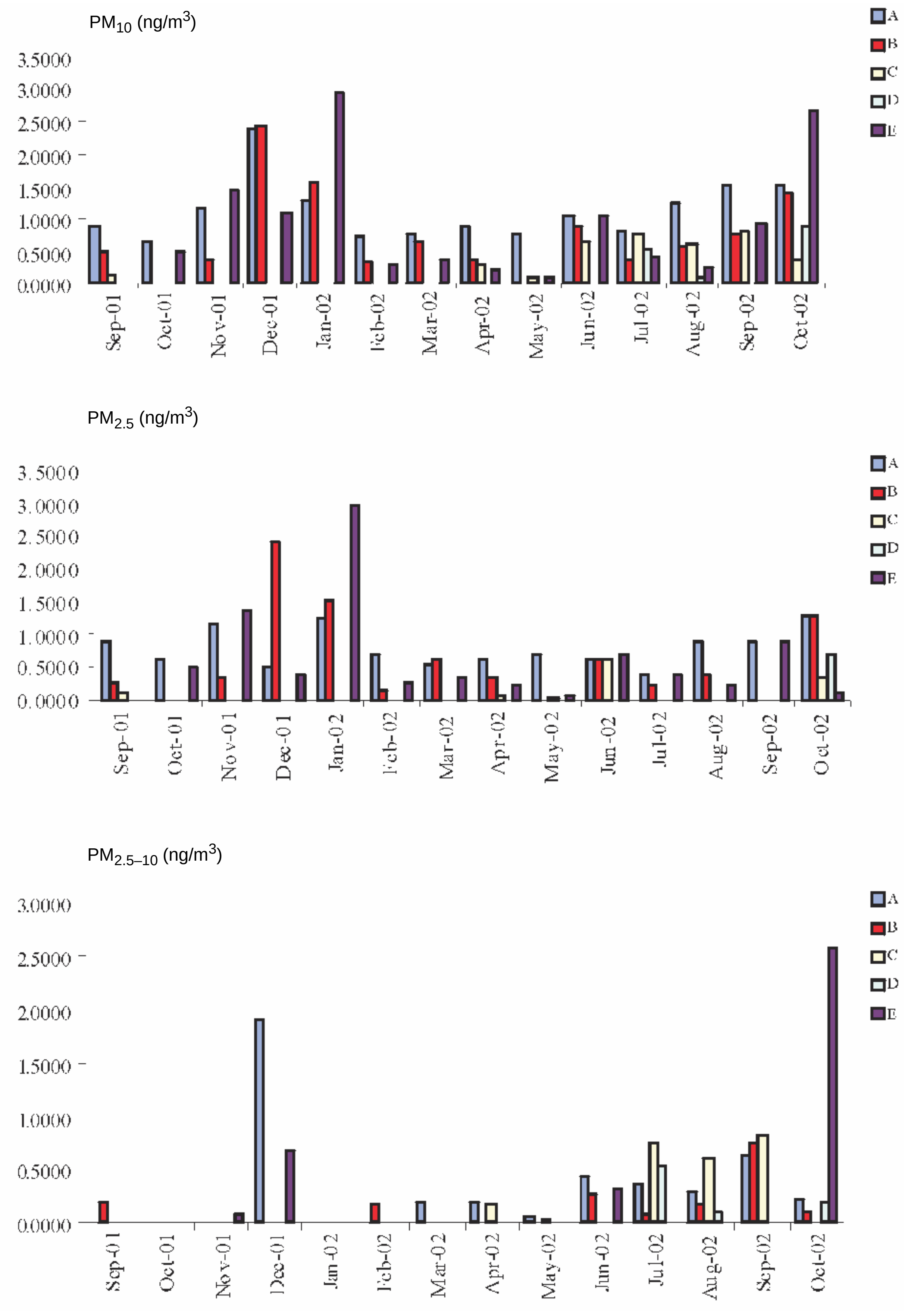
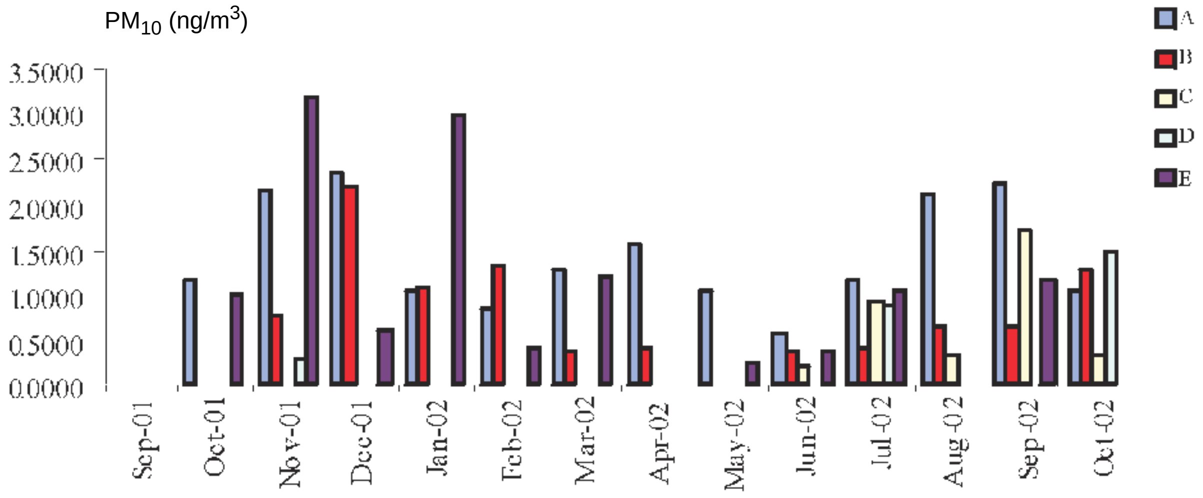
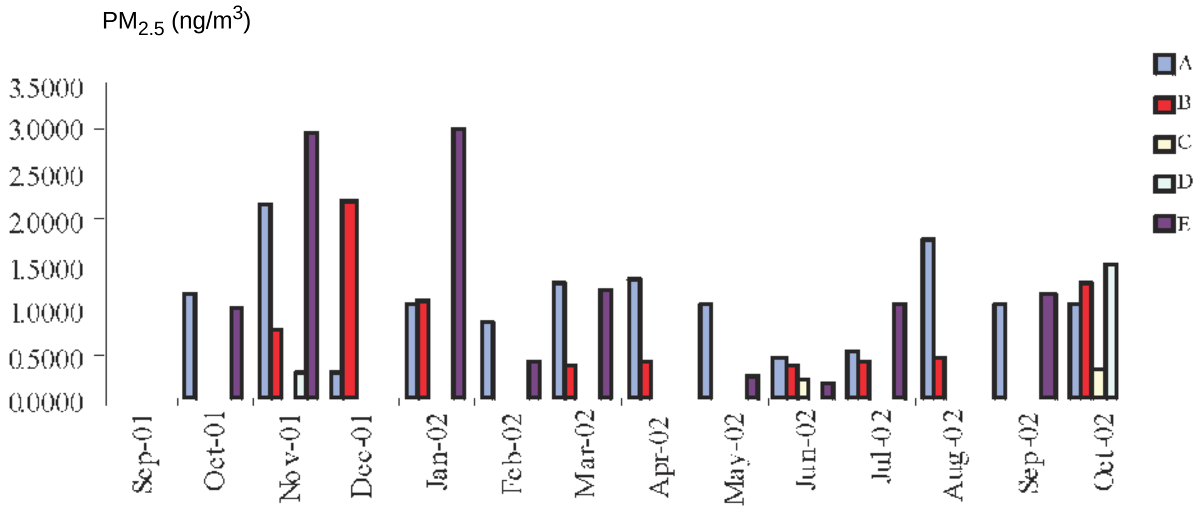


Figure 8.11. Monthly variation of chrysene concentration in Ireland, September 2001–October 2002.


PM_{10} (ng/m^3)


$PM_{2.5}$ (ng/m^3)

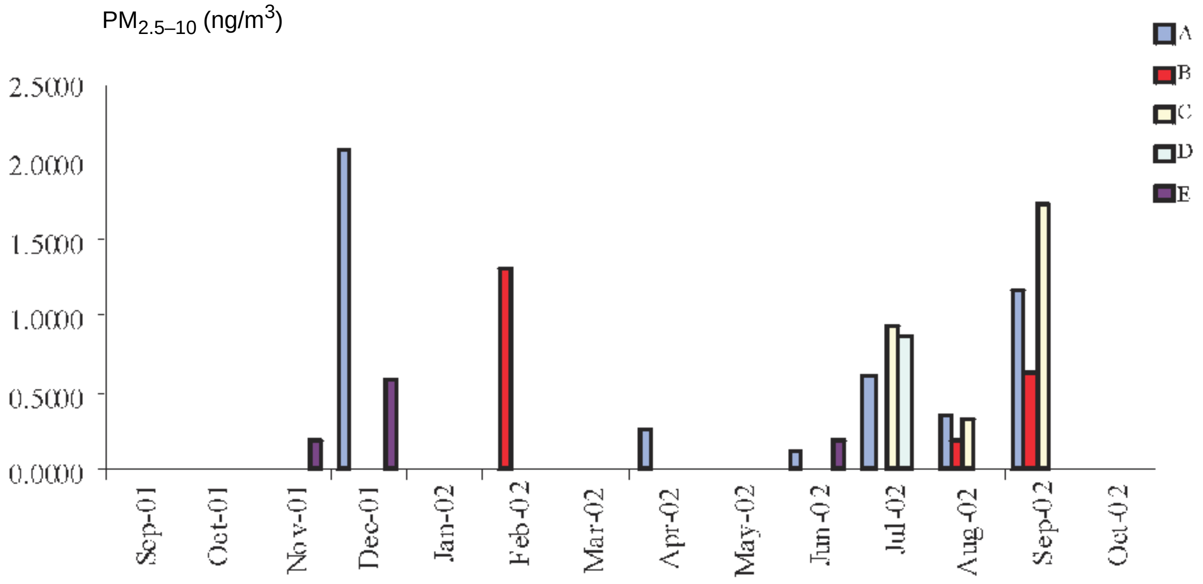

$PM_{2.5–10}$ (ng/m^3)

Figure 8.12. Monthly variation of benzo(*b*)fluoranthene concentration in Ireland, September 2001–October 2002.

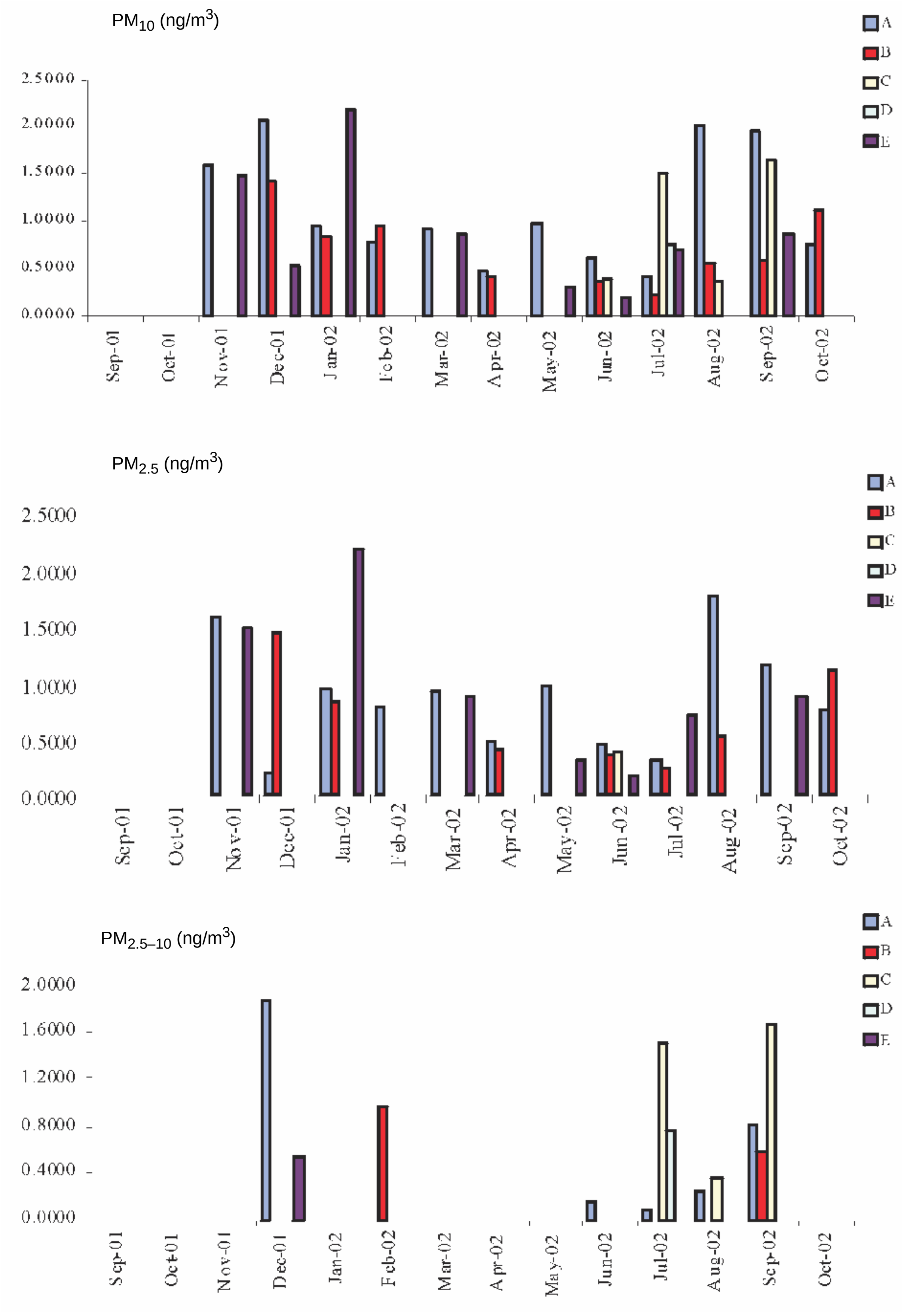


Figure 8.13. Monthly variation of benzo(*k*)fluoranthene concentration in Ireland, September 2001–October 2002.

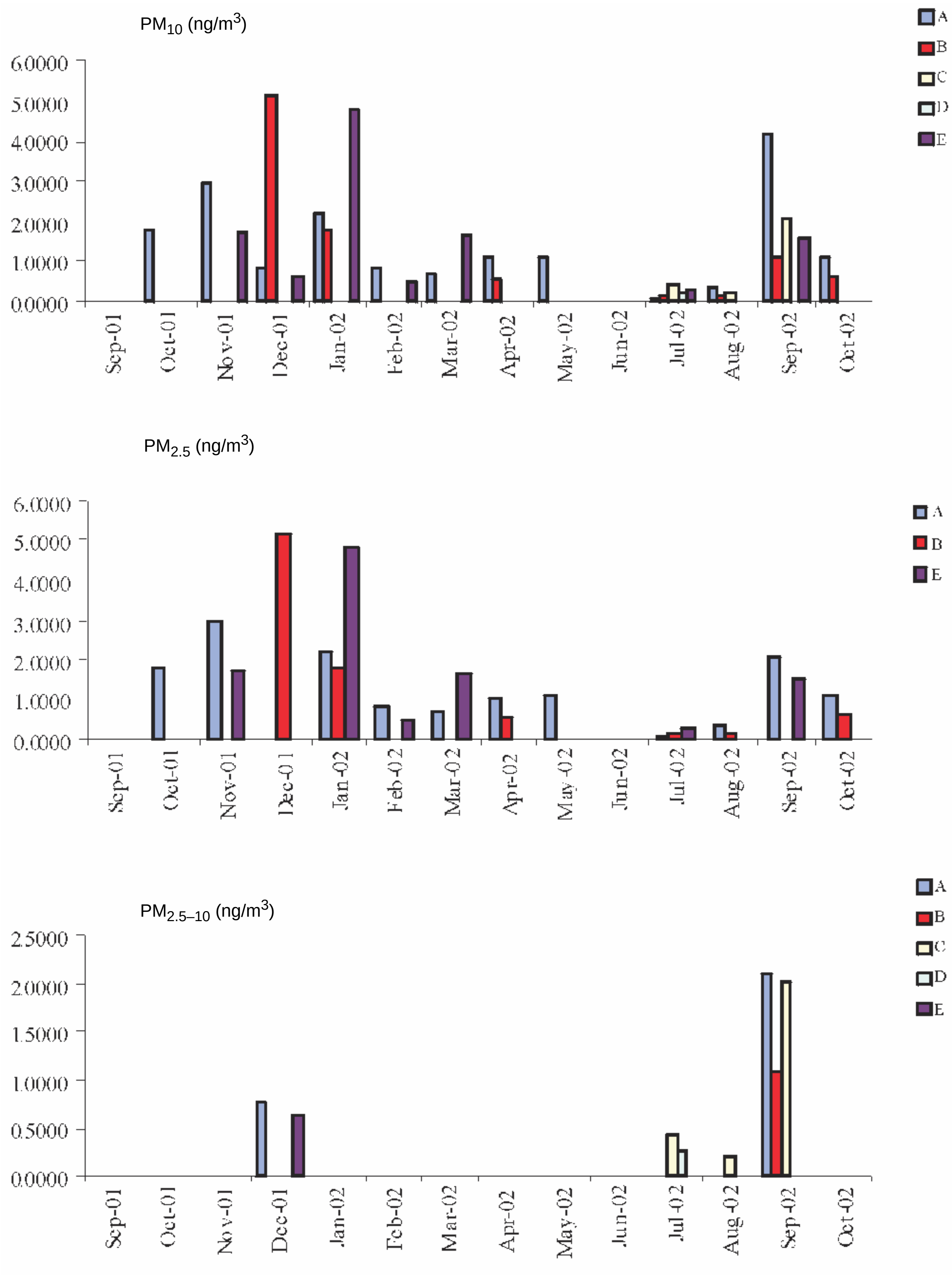


Figure 8.14. Monthly variation of benzo(*a*)pyrene concentration in Ireland, September 2001–October 2002.

Table 8.1 Seasonal mean concentration (ng/m^3) of measured PAHs at five sites in Ireland, September 2001–October 2002.

			Nap	Any	Ane	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP
Site A	Fine	Autumn	0.21			0.17	1.02	0.24	0.61	0.71	1.06	0.99	1.07	0.74	1.58
		Winter	0.44			0.23	0.68	0.22	0.33	0.42	0.60	0.82	0.71	0.64	0.99
		Spring	0.04				0.39	0.09	0.34	0.41	0.55	0.63	1.21	0.79	0.95
		Summer	0.09				0.69	0.10	0.64	0.88	0.44	0.65	0.90	0.85	0.14
	Coarse	Autumn	0.14			0.05	0.45	0.11	0.20	0.20	0.27	0.22	0.29	0.20	0.53
		Winter	1.04	0.86	0.62	0.81	0.86	0.82	0.72	0.63	0.59	0.63	0.69	0.62	0.26
		Spring					0.21	0.04	0.13	0.13	0.13	0.16	0.08		
		Summer	0.06				0.29	0.10	0.25	0.29	0.31	0.37	0.36	0.17	
Site B	Fine	Autumn	0.23				0.40	0.06	0.27	0.28	0.51	0.43	0.44	0.28	0.16
		Winter	0.28			0.06	0.52	0.17	0.41	0.47	1.04	1.38	1.10	0.76	2.31
		Spring					0.18	0.02	0.13	0.13	0.19	0.33	0.26	0.14	0.19
		Summer	0.06				0.26	0.02	0.23	0.28	0.30	0.42	0.42	0.37	0.09
	Coarse	Autumn	0.36				0.42	0.19	0.24	0.22	0.25	0.24	0.16	0.15	0.27
		Winter	0.25				0.27		0.07	0.07	0.04	0.06	0.44	0.32	
		Spring					0.10		0.03	0.03					
		Summer	0.04				0.17	0.03	0.13	0.14	0.13	0.18	0.06		
Site C	Fine	Autumn	0.19				0.27	0.02	0.13	0.15	0.14	0.12	0.08		
		Winter	0.24				0.32	0.04	0.22	0.30					
		Spring					0.20		0.11	0.08	0.08	0.05			
		Summer	0.06				0.13	0.02	0.10	0.10	0.17	0.21	0.07	0.13	
	Coarse	Autumn	0.33				0.34	0.24	0.20	0.20	0.28	0.20	0.43	0.42	0.51
		Winter	0.22				0.20	0.03	0.01	0.01					
		Spring					0.17		0.05	0.05	0.05	0.07			
		Summer	0.68				0.61	0.49	0.42	0.53	0.39	0.45	0.42	0.61	0.21
Site D	Fine	Autumn	0.19				0.31		0.15	0.16	0.20	0.17	0.43		
		Winter	0.23				0.54		0.13	0.11					
		Spring					0.16								
		Summer	0.02				0.23	0.01	0.07	0.05					
	Coarse	Autumn	0.11			0.03	0.23	0.02	0.11	0.13	0.05	0.05			
		Winter	0.42				0.30	0.06							
		Spring					0.16								
		Summer	0.32				0.41	0.21	0.21	0.34	0.21	0.21	0.29	0.25	0.08
Site E	Fine	Autumn	0.13			0.07	0.29	0.11	0.20	0.21	0.60	0.56	0.95	0.46	0.68
		Winter	0.12				0.37	0.12	0.26	0.22	1.07	1.21	1.14	0.72	1.75
		Spring					0.22		0.17	0.16	0.30	0.23	0.49	0.40	0.55
		Summer	0.05				0.19	0.02	0.16	0.13	0.40	0.44	0.40	0.30	0.09
	Coarse	Autumn	0.57	0.03		0.02	0.55	0.65	0.63	0.42	1.06	0.66	0.03		
		Winter	0.50	0.39	0.32	0.35	0.47	0.37	0.32	0.29	0.22	0.23	0.20	0.18	0.21
		Spring					0.14	0.04	0.05	0.05					
		Summer	0.19				0.28	0.14	0.26	0.27	0.07	0.11	0.07		

world (Smith and Harrison, 1998). The concentration of benzo(*a*)pyrene is of particular interest because a threshold value of 1 ng/m^3 is now introduced as part of a new EU directive. This EU Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relates to arsenic, cadmium, mercury, nickel and PAHs in ambient air and it sets a target for PAHs (using B(a)P as a marker for the carcinogenic risk of PAHs in ambient air) of 1.0 ng/m^3 for PM_{10} to be achieved by 31 December 2012. The average monthly $PM_{2.5}$ concentration exceeded the threshold value on a number of occasions at all urban sites. Further monitoring of benzo(*a*)pyrene and other PAH concentrations is clearly required for both the PM_{10} and $PM_{2.5}$ fractions.

9 General Conclusions and Recommendations for Future Work

9.1 General Conclusions

i. PM_{10} levels in Ireland lie within the range of other European countries and are similar to those in the neighbouring UK, but with a more marked maritime influence seen in higher sea salt concentrations in the coarse particle mode.

ii. Concentrations of PM_{10} and $PM_{2.5}$ at urban locations in Ireland were around four times the rural background, and at the roadside were around six times the rural background and often exceeded the current EU limits. This indicates the importance of road traffic as a source. There was a large urban increment in carbonaceous aerosols and resuspended dusts due to the rapid pace of development in the transport, energy and building/road construction sectors.

iii. Similar urban PM concentrations and variations were found in both Dublin and Cork, indicative of national uniformity of urban aerosol concentrations and behaviour, with concurrent episodes of elevated PM_{10} mostly being associated with increased levels of finer particles consisting of both local and long-range transported components. The highest PM levels were often associated with polluted UK/European air masses, when both local and long-range transported sources can be significant.

iv. In non-urban areas, high PM_{10} levels were influenced mainly by sea salt and secondary particles possessing a significant long-range transport component. On the other hand, mainly local sources dominate higher levels of PM during advection of clean westerly air masses.

v. Mass closure analysis explained 79–93% of the fine particle mass and 72–81% of the coarse particle mass, depending on location. In urban areas, the predominant components of fine particles are organics, EC and secondary inorganics, and the main components of coarse particles are resuspended materials and sea salt.

vi. In non-urban areas, $PM_{2.5}$ mostly consists of secondary inorganic and organic materials whilst sea salt contributes the most to coarse fractions. Uncertainties are likely to have arisen from underestimation of resuspended materials (at urban sites) and organics (at non-urban sites), as well as the presence of water within hygroscopic aerosols.

vii. The levels of PAHs were largest at the Dublin city roadside site, whilst similar concentrations were observed at the urban background sites in Dublin and Cork due to the large number of combustion sources. Very low concentrations of the PAHs were observed at the coastal and rural sites due to the lack of significant sources. The concentrations of the particle-phase PAHs measured at the five sites are similar to those observed at other locations around the world.

viii. Mass closure procedures using reconstructed chemical components were used to identify major source categories contributing to the aerosol mass, namely primary marine aerosol (NaCl), secondary inorganic materials (NH_4NO_3 + $(NH_4)_2SO_4$), primary anthropogenic combustion materials (EC), primary and secondary organic materials, and resuspended dusts. Source component contributions differed for fine and coarse particles and at different locations.

ix. In urban areas, the major components contributing to fine particle mass (together accounting for 79–84% of $PM_{2.5}$ mass) were, in order, organic compounds, EC, ammonium sulphate/ammonium nitrate, whilst in the coarse fraction resuspended material and sea salt were predominant (56–66%).

x. Chemical component (using secondary aerosol components of sulphate, nitrate and ammonium) analysis according to air mass origin from data in Chapter 5 indicates that long-range transport from an eastwardly direction – mainly from the continent and the UK – to Dublin (Site B) accounts for up to about 30% of the $PM_{2.5}$ mass (as a fraction of the total mass) over and above that measured under westerly or maritime air mass conditions, and up to about 25% of the PM_{10} mass.

xi. Results show that local sources contribute 50% or more to fine PM mass ($PM_{2.5}$) and to coarse PM (PM_{10}) for the city centre sites.

xii. At the rural and coastal sites, $PM_{2.5}$ mainly consisted of ammonium sulphate/ammonium nitrate and organic materials (65%), whilst sea salt was the largest contributor to coarse particles (39% rural, 56% coastal). Unexplained materials, accounting for about 7–28% of the mass, were attributed mainly to resuspended materials at urban sites and organic materials at the other sites, as well as unmeasured water content.

xiii. The levels of PAHs were largest at the Dublin roadside (Site A), whilst similar concentrations were observed at the urban background sites in Dublin (B) and Cork (E) due to the large number of combustion sources. Very low concentrations of the PAHs were observed at the coastal and rural sites due to the lack of significant sources. The concentrations of the particle-phase PAHs measured at the five sites are similar to those observed at other locations around the world.

xiv. The highest concentrations for all metals, except magnesium, for both the coarse and fine fractions, were obtained at the kerbside Dublin city centre site. In general, the rural site in Co. Galway shows the lowest level for all metals. The coastal site showed the highest concentration of magnesium in the coarse fraction in comparison to the other four sites. The coastal and rural sites generally showed lower fine fraction concentrations of the metals than at the urban sites.

xv. Intensive measurements carried out during 4 weeks in February–March 2002 showed, on average, that chemical species concentrations measured for the size-resolved impactor samples are very similar to those measured for the daily samples. Reasonable agreement (generally within 25%) was obtained between cumulative gravimetric mass from week-long MOUDI impactor samples and individual daily samples over the same week. Largest disagreement (up to 50%) was found at the rural site, which is largely due to relatively low levels at the site.

xvi. These measurements represent the first comprehensive air quality PM_{10}, $PM_{2.5}$ and $PM_{2.5–10}$ assessment in Ireland, coupled with quite detailed chemical composition data.

9.2 Recommendations for Future Work

i. It is strongly recommended that the future air quality programme should also include size-differentiated mass and size-differentiated chemical composition data. This could be facilitated by means of an extended EMEP activity at some selected sites.

ii. Very few $PM_{2.5}$ samplers are employed and there is need for the establishment of collocated $PM_{2.5}$ and PM_{10} monitors since increasing emphasis (by EMEP for example) is being given to lower sized particulate sampling in view of associated health effects.

iii. The monitoring of background baseline data on a more continuous basis is considered to be important, particularly in view of the more stringent EU limit values coming into operation in January 2010.

iv. Mass closure needs to be achieved between PM_{10}, $PM_{2.5}$ mass and the sum of PM components. The high percentage of unresolved mass (of order 40%) is thought to be mainly due to unaccounted OC.

v. Air quality sampling programmes should include measurement of ultrafine particles as they have been shown to be more toxic per unit mass than coarse sized particles. Therefore, measurement of number concentration levels of ultrafine particles should accompany conventional PM mass and chemical sampling.

vi. Particular PAHs, such as benzo(*a*)pyrene, are of particular interest because, as from 31 December 2012, in accordance with a new EU directive (EU Directive 2004/107/EC), concentrations of benzo(*a*)pyrene, used as a marker for PAHs in ambient air, must not exceed a target value of 1 ng/m^3 for PM_{10}. Such species should be monitored on a routine basis in anticipation of new directives involving the fine or $PM_{2.5}$ fraction.

vii. Further work on determination of the main source contributors to mass concentrations of PM_{10} (and $PM_{2.5}$) is recommended.

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