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Source Apportionment of Particulate Matter in Urban and Rural Residential Areas of Ireland (SAPPHIRE)

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Rialtas na hÉireann
Government of Ireland

ENVIRONMENTAL PROTECTION AGENCY

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- Office of Environmental Enforcement
- Office of Evidence and Assessment
- Office of Radiation Protection and Environmental Monitoring
- Office of Communications and Corporate Services

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EPA RESEARCH PROGRAMME 2014–2020

Source Apportionment of Particulate Matter in Urban and Rural Residential Areas of Ireland (SAPPHIRE)

(2013-EH-MS-15)

EPA Research Report

Prepared for the Environmental Protection Agency

by

University College Cork

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The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Executive Summary

Ireland is seeking to reduce levels of particulate matter with a diameter of less than 2.5 microns ($PM_{2.5}$) in order to protect human health and the environment. This goal can be achieved only by developing and implementing policies that target reductions in the emissions of known sources of pollution. Residential solid fuel burning has been shown to be a significant source of $PM_{2.5}$ in the main cities of Ireland; however, no comparable information is available on the sources of particulate pollution in the many small towns across the country. The principal aim of the Source Apportionment of Particulate Matter in Urban and Rural Residential Areas of Ireland (SAPPHIRE) project was therefore to determine the sources of $PM_{2.5}$ in residential areas of small towns in Ireland.

Field measurement campaigns were conducted during wintertime in three towns where residential solid fuel burning was expected to significantly affect air quality – Killarney, Enniscorthy and Birr. The selection of these towns was based on the following criteria: (1) no natural gas supply, (2) located outside Ireland's smoky coal ban areas (which applies to towns with > 15,000 inhabitants) and (3) residents who are likely to use solid fuels (wood, peat and coal) for space heating.

At each location, levels of $PM_{2.5}$ during evening hours were often an order of magnitude higher than those during the day, and huge spikes in pollution were regularly observed when wind speeds were low. Particulate pollution was highest in Enniscorthy, where $PM_{2.5}$ levels averaged 29.2 $\mu g/m^3$ over a 38-day period and the World Health Organization (WHO) 24-hour mean guideline value of 25 $\mu g/m^3$ was exceeded on 42% of the days. Killarney experienced a mean $PM_{2.5}$ value of 15.3 $\mu g/m^3$ and four exceedances of the WHO 24-hour guideline value in 40 days. Birr was the least polluted site, with a mean $PM_{2.5}$ value of 7.9 $\mu g/m^3$ and no exceedances of the WHO 24-hour mean guideline value in 43 days. However, stormy weather conditions during most of the Birr campaign probably contributed to lower $PM_{2.5}$ mass concentrations.

Real-time monitoring of the chemical composition of $PM_{2.5}$ showed that residential solid fuel burning was the dominant source category at all three locations, accounting for 72%, 82% and 60% of $PM_{2.5}$ measured in Killarney, Enniscorthy and Birr, respectively. Traffic and sea spray were minor sources of $PM_{2.5}$, while new evidence was found to suggest that gaseous amines and ammonia released from the agricultural sector can effectively combine with combustion aerosols to accelerate particle growth and increase $PM_{2.5}$ mass.

State-of-the-art receptor modelling approaches were used to confirm that solid fuel burning was the major source of $PM_{2.5}$ at each site. The receptor models also identified traffic, sea spray and mixed agricultural/combustion sources as contributors to $PM_{2.5}$.

A key element of this project was the use of sophisticated single particle mass spectrometry techniques to differentiate combustion particles produced from the main solid fuels – coal, peat and wood. The results show that peat burning was the main contributor, accounting for 31%, 27% and 26% of the $PM_{2.5}$ mass in Killarney, Enniscorthy and Birr, respectively. Wood was the second most dominant combustion source (17%, 21% and 23%, respectively), followed by coal (16%, 17% and 5%, respectively).

Based on Irish census data, all three solid fuels appear to be popular choices for domestic space heating in Killarney, while coal dominates in Enniscorthy and peat is most common in Birr. However, the results obtained in this study indicate that particles from combustion of all three fuel types were present in each town. As there was not one dominant solid fuel type that contributed to particulate pollution, measures such as a smoky coal ban in these areas may be only partly successful in reducing $PM_{2.5}$ concentrations. Future efforts to improve air quality in these towns, and other similar towns, will need to address how domestic residences are heated in general, rather than attempting to discourage the use of one specific solid fuel. If measures such as a nationwide ban on the use of smoky coal are implemented, it is recommended that a follow-up study is conducted in these three towns to assess their impact on air quality.

This research clearly showed the benefits of deploying state-of-the-art instrumentation for the real-time monitoring of chemical composition in order to deliver

highly time-resolved information on the sources of $PM_{2.5}$. It is therefore recommended that further investment is made in this area, with efforts focusing on expanding the source apportionment capabilities across the national air quality monitoring network. One cost-effective way of doing this could be through the deployment of aethalometers, which have been shown to be very effective in apportioning black carbon to solid fuel and traffic sources in near real time. Further research on black carbon is also recommended, as reductions in this pollutant would have co-benefits for both air quality and climate.

1 Introduction

Airborne particulate matter (PM) is a mixture of solid and liquid particles suspended in the atmosphere, often referred to as atmospheric aerosols. These particles are important because they have a major impact on climate (Fuzzi *et al.*, 2015) and human health (Rückerl *et al.*, 2011; Kelly and Fussell, 2012). Indeed, the direct link between exposure to PM and a range of respiratory and cardiovascular problems (Brook *et al.*, 2010; Kelly and Fussell, 2011) is now well established and the latest research points to an even wider range of health impacts (Kelly and Fussell, 2015), including negative effects on brain function (Suades-González *et al.*, 2015). Furthermore, several large-scale studies have also established that PM reduces life expectancy (Pope and Dockery, 2006; Pope *et al.*, 2009), with recent estimates indicating that long-term exposure to PM causes around 400,000 premature deaths annually in Europe (EEA, 2017). This is in spite of the fact that the European Union has air quality legislation in place, with limit values set for both PM with a diameter of less than 10 microns (PM_{10}) and PM with a diameter of less than 2.5 microns ($PM_{2.5}$) (EU, 2008).

The air quality in Ireland is generally better than in many other European countries (EEA, 2017) and the ambient levels of PM_{10} and $PM_{2.5}$ are usually within the legislated limits (EPA, 2017). However, the more stringent guideline values for PM_{10} and $PM_{2.5}$ set down by the World Health Organization (WHO, 2005) are exceeded at a number of sites in Ireland's national monitoring network. Reductions in the levels of these pollutants are highly desirable because there is no threshold below which PM_{10} and $PM_{2.5}$ do not affect human health (WHO, 2005). Therefore, understanding the composition and sources of PM in Ireland is important for evaluating its health effects and further establishing policies to reduce PM emissions. This was the main aim of the Source Apportionment of Particulate Matter in Urban and Rural Residential Areas of Ireland (SAPPHIRE) study.

1.1 Sources and Chemical Composition of Particulate Matter

Particles are released directly into the atmosphere as primary emissions or formed in the atmosphere as secondary aerosols by gas-to-particle conversion, nucleation or condensation of species onto existing particles (Pöschl, 2005; Calvo *et al.*, 2013). The chemical composition of PM can vary hugely, depending on the nature of the sources and the extent of atmospheric processing experienced by the particles. Table 1.1 provides a brief list of the main chemical components and sources of ambient PM (AQEG, 2005).

Primary and secondary components have both natural and anthropogenic origins. Natural sources of atmospheric aerosols include plant emissions, mineral dust, sea spray, volcanic eruptions and lightning (Calvo *et al.*, 2013). Anthropogenic emissions sources include traffic, industrial activities, domestic/residential solid fuel burning (SFB), power generation and incineration (Calvo *et al.*, 2013). Carbonaceous aerosol is a major component released by anthropogenic activity. It consists of elemental carbon (EC) or black carbon (BC) and organic carbon (OC). The terms EC and BC are often used interchangeably to represent the soot-like material present in particles, with the difference between the two being largely due to the analytical method used to measure them. EC is determined using thermal methods, while BC is measured by optical methods (Lavanchy *et al.*, 1999). EC/BC is directly emitted into the atmosphere from the incomplete burning of fuels. However, OC can be both primary and secondary in origin, with strong variations in source, depending on the time of year and meteorological conditions (Zhang *et al.*, 2011; Guzman-Morales *et al.*, 2014).

Anthropogenic activities also emit large quantities of sulfur dioxide (coal combustion and shipping), nitrogen oxides (NO_X) (traffic) and ammonia (farming, traffic and industrial activities), which can lead to the

Table 1.1. Main components and sources of PM

Components	Major sources
Primary components	
Sodium chloride	Sea salt
EC or BC	Formed during high-temperature combustion of fossil fuel (coal, natural gas, diesel, petrol) and biomass fuel (wood, forest fires, etc.).
Trace metals	Includes Pb, Cd, Ni, Cr, Zn and Mn. Generated by metallurgical processes (e.g. steel-making), impurities or additives in industrial fuels, and mechanical abrasion (e.g. brake and tyre wear).
Mineral components	Includes Al, Si, Fe and Ca. Found mostly in coarse dusts from quarrying, construction and demolition, and in wind-driven dusts.
Secondary components	
Sulfate	Formed by oxidation of atmospheric sulfur dioxide to form sulfuric acid, which can react with ammonia to produce ammonium sulfate.
Nitrate	Formed by oxidation of nitrogen oxides (NO_x), which can react with ammonia to produce ammonium nitrate, and also through condensation of nitric acid (via the reaction of $OH + NO_2$) and sometimes present as sodium nitrate through the replacement of chloride in sea salt by NO_x.
Water	Components such as ammonium sulfates and ammonium nitrates take up water from the atmosphere.
Primary and secondary components	
OC	Primary OC comes from traffic or industrial combustion. Secondary OC comes from the *in situ* oxidation of volatile organic compounds. There may be several thousand individual components; OC is the most difficult ambient particle component to accurately identify and measure in real time.

Adapted from AQEG (2005).

formation of secondary particles. Sulfur dioxide can be oxidised to form sulfuric acid, while NO_x can undergo oxidation to form nitric acid. These acidic species can be neutralised by ammonia to form ammonium sulfate and ammonium nitrate particles, respectively. In the atmosphere, the production of ammonium sulfate is favoured; most of the sulfate must be neutralised prior to ammonium nitrate production (Bauer *et al*., 2007; Pathak *et al.*, 2009). While ammonia is the major base that is present in the atmosphere, amines have also been observed in particles as aminium salts of nitrate and sulfate (Pratt *et al.*, 2009). Amines can be emitted by industrial activities, traffic, farming and sewage plants (Angelino *et al.*, 2001). In addition to the production of secondary species through the homogeneous gaseous reactions mentioned above, heterogeneous (gas–particle) and aqueous phase (fog, cloud) reactions can also contribute to particle formation and growth.

1.2 Chemical Analysis of Particulate Matter

Traditionally, the chemical composition of atmospheric aerosols has been examined by offline chemical analysis of particles collected onto filters. A combination of different analytical techniques is typically used for the identification and quantification of the various elements, ions and organic compounds (Finlayson-Pitts and Pitts, 2000; Heard, 2006). There are, however, several limitations to offline measurements that have catalysed the development of real-time online monitoring techniques. First, the trace nature of many analytes means a sufficient amount of material must be collected onto the filters to pass the detection limits of the analytical techniques. This results in sampling times of several hours to days, therefore limiting the time resolution. High time resolution is particularly desirable when trying to identify pollution sources, such as traffic and SFB, that emit at different times of the day. Second, filter measurements are also subject to several sampling artefacts. Semi-volatile species may evaporate, and collected particles may react with other particles or gases on the filter during and even after sampling.

A number of online instruments have been developed for *in situ* measurements of the chemical composition of atmospheric particles. As for offline analysis, a combination of different techniques is required to measure the whole range of chemical species in PM. The carbonaceous content of PM can be determined using thermal–optical techniques (Karanasiou *et* *al*., 2015), e.g. using a semi-continuous carbon analyser to measure OC and EC, or light absorption methods, e.g. using an aethalometer (Drinovec *et al*., 2015) to measure BC. Both instrumental approaches have proved to be especially valuable in the source apportionment of PM. Ionic species present in PM can be measured hourly by coupling a particle-into-liquid sampler with ion chromatography (Heard, 2006), while elemental composition can also be determined at high time resolution using X-ray fluorescence (Furger *et al*., 2017).

The last two decades have seen the rapid development of online mass spectrometry for the chemical analysis of atmospheric particles in real time (Prather *et al*., 2008; Pratt and Prather, 2012). A number of these instruments have been developed, including the aerosol time-of-flight mass spectrometer (ATOFMS) and the aerosol mass spectrometer (AMS), which operate on different principles. The AMS utilises thermal desorption and electron impact ionisation coupled with mass spectrometry to quantify nitrate, sulfate, ammonium, chloride and organic species in the range 50–700 nm but is unable to measure the refractory portion (EC, sea salt, metals) of atmospheric aerosols (Heard, 2006). The ATOFMS uses triggered laser desorption/ionisation and time-of-flight mass spectrometry to provide the composition (EC, OC, metals, sea salt, inorganic species, etc.) of individual particles in the range 100–3000 nm. As these instruments measure the average chemical composition or mixing state of individual particles in real time, they are now widely used for the identification and apportionment of the various sources of atmospheric particles (Pratt and Prather, 2012).

1.3 Source Apportionment of Particulate Matter

Source apportionment is the practice of deriving information about pollution sources and the amount they contribute to ambient air pollution levels. This information is essential for designing air quality policies and, as a result, source apportionment is required explicitly or implicitly for the implementation of the air quality directives (2008/50/EC and 2004/107/EC). Identification of pollution sources is also required to assess the effectiveness of abatement measures and for the quantification of pollution arising from specific sources, including transboundary transport.

Receptor models are used to accomplish source apportionment by analysing chemical and physical parameters measured at one or more specific sites. They start with the measured mass of an atmospheric pollutant at a given site (the receptor) and attempt to apportion it to various emission sources by solving a mass balance equation. The fundamental assumption behind this approach is that mass is conserved between the emission source and the study site. These models have the advantage of providing information derived from real-world measurements. Receptor models are extensively used for source contribution quantification at local and regional scales all over the world (Hopke, 2016). In the past decade, the number of scientific publications and applications in this field has multiplied, and software tools and mathematical foundations have been constantly improving, with a view to obtaining better source resolution and greater accuracy of source contribution (Belis *et al*., 2013).

In environmental studies, factor analysis techniques are widely used to perform source apportionment from data taken at receptor sites. Positive matrix factorisation (PMF) is one such technique that attempts to identify the contributing factors, or sources, in a time series of atmospheric measurements. It is a weighted least-squares fitting of factors and species profiles for each source and the amount of mass contributed by each factor to each individual sample. The experimental uncertainty of each measurement point is also taken into account in PMF. An object function in the fitting algorithm is minimised under the constraint that all or some of the measurements in each sample and the mass contributions are non-negative values. There are a number of mathematically correct solutions, because it is a bilinear model with rotational ambiguity. The choice of the best solution, i.e. the number of factors that best represent the reality, must be physically meaningful and supported by relevant indicators, such as minimising the value of the object function, and modelling the fit of the species variance and sample mass.

Positive matrix factorisation is often applied to data obtained from offline analysis of particles collected onto filters (Belis *et al*., 2013). However, because the time resolution is restricted by the duration of filter sampling (typically 24 hours), it is difficult to determine how particle sources vary within a daily cycle. This limitation can be overcome by performing PMF on chemical composition data collected with an hourly time resolution, e.g. by using an AMS or an ATOFMS (Healy *et al*., 2010; McGuire *et al*., 2011). Further improvements in source characterisation can be made when AMS and ATOFMS data are supplemented with other online measurements, such as $PM_{2.5}$ mass, EC/OC and trace gases (Dall'Osto *et al*., 2014). The use of higher time resolution datasets can also facilitate the understanding of the atmospheric processes that lead to changes in particle composition.

1.4 Previous Particulate Matter Source Apportionment Studies in Ireland

The first detailed study of the chemical composition of PM in Ireland was published by Yin *et al*. (2005). Daily collections of fine and coarse PM were made in urban, rural and costal environments, and an offline chemical analysis was performed to measure EC, OC and water-soluble ions using ion chromatography. Mass closure procedures were subsequently used to provide estimates of the contribution to PM mass from the following sources: primary marine aerosols, secondary inorganic materials, primary anthropogenic combustion, secondary organic materials and re-suspended dusts. However, this relatively simple source apportionment approach did not allow for the provision of estimates for major sources such as road traffic and residential SFB.

Chemical composition measurements combined with receptor modelling (principal component analysis, PCA) has been used to identify and quantify the contributions of the various sources to ambient levels of PM_{10} at five locations within County Cork (Byrd *et al*., 2010). Elevated levels of PM_{10} were recorded when westerly winds dominated and brought with them sea salt and coarse mineral elements originating from re-suspension of road dust, which accounted for up to 28% of the current European Union (Directive 2008/50/EC) annual limit value (40 µg/m^3 of PM_{10}).

In a study of air quality in the city and harbour of Cork, real-time measurements of eight different marker pollutants were considered, along with meteorological data, in order to extrapolate the major sources of $PM_{2.5}$ using PCA and PMF (Hellebust *et al*., 2010). This approach led to the identification of four source categories (sea salt, shipping, crustal material and secondary inorganic aerosols) contributing to $PM_{2.5}$. However, these two studies by Byrd *et al*. (2010) and Hellebust *et al*. (2010) in Cork were somewhat limited, as they did not include the carbonaceous components of PM that are mainly produced from combustion processes and typically represent the largest component of PM mass.

A detailed assessment of the organic component of atmospheric aerosols in the Cork city/inner harbour region was performed by Kourtchev *et al*. (2011). Samples of $PM_{2.5}$ were collected and analysed for polar organic compounds, which are useful markers for aerosol source characterisation. The contributions of individual sources to OC were assessed using factors for isoprene secondary organic aerosols, fungal spores and smoke from the combustion of cellulose-containing fuels. The latter factor was experimentally derived for a set of solid fuels commonly used in Ireland for home heating, i.e. wood, peat, and bituminous and smokeless coals. The total contribution of residential SFB to the measured OC mass concentration was estimated to be 10.8%, 50%, 66.4% and 74.9% for the summer, autumn, late autumn and winter periods, respectively. This study clearly demonstrated that, despite the ban on the sale of bituminous coal in Cork city, residential SFB still represents a major source of $PM_{2.5}$ during autumn and winter months.

Although the organic marker method employed by Kourtchev *et al*. (2011) provided useful new information, it has two inherent disadvantages: (1) filter sampling of $PM_{2.5}$ needs to be performed for at least 6 hours to achieve sufficient sensitivity, resulting in relatively poor time resolution; and (2) it is unable to distinguish between different types of solid fuel, as the combustion particles contain the same marker compounds (levoglucosan, mannosan, galactosan). A more complete source apportionment study at the Cork site was performed by Healy *et al*. (2010), who used an ATOFMS as well as data from other online instruments and source receptor modelling to determine the source contributions to $PM_{2.5}$ during August 2008. Crucially, the ATOFMS was able to distinguish particles produced by burning the various solid fuels (coal, peat and wood) and, as expected, these particle classes showed a distinct daily variation, as shown in Figure 1.1. Other particle classes from different sources (traffic, ships, sea spray, etc.) were

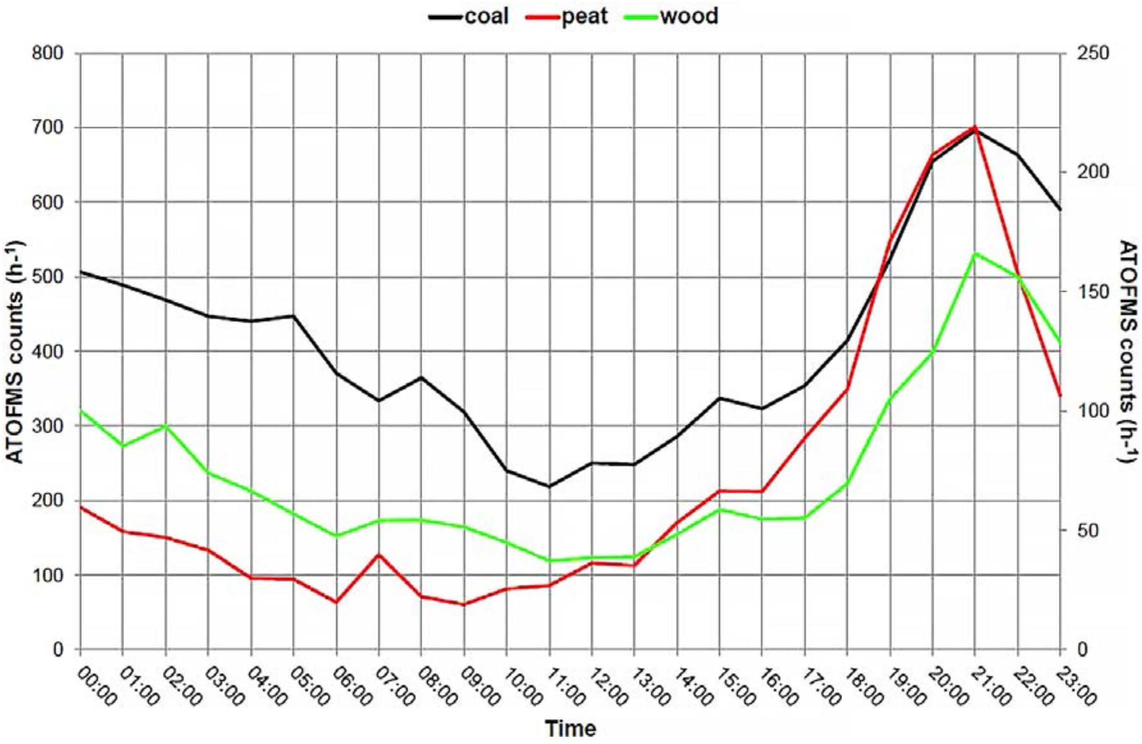


Figure 1.1. Average daily trend for coal, peat and wood particle classes detected by an ATOFMS in Cork Harbour, 7–28 August 2008. Source: Healy *et al.*, 2010. This work is distributed under the Creative Commons Attribution 3.0 License. See https://creativecommons.org/licenses/by/3.0/.

also identified, and the ATOFMS data were used in conjunction with semi-continuous measurements of EC, OC and sulfate to apportion $PM_{2.5}$ mass using PMF as follows: vehicular traffic – 23%; marine aerosol – 14%; long-range transport – 13%; general/industrial combustion – 11%; residential SFB – 5%; and shipping – 1.5%.

The final study at the Cork inner harbour site involved the co-deployment of an ATOFMS and an AMS for a 3-week period during February 2009. Organic aerosol (62%) was found to be the dominant species in non-refractory sub-micron aerosol measured by the AMS, and the subsequent PMF analysis produced a five-factor solution for sources of the organic aerosol that were attributed to domestic SFB (44%), traffic (20%), cooking (18%) and other sources (Dall'Osto *et al*., 2013). Similarly, the ATOFMS showed that domestic SFB accounted for around 60% of the total particles detected. The extensive dataset obtained in this measurement campaign was subsequently used in a source apportionment (PMF) study (Dall'Osto *et al*., 2014), which identified five sources of the measured $PM_{2.5}$: regional SFB (25%), local SFB (22%), road vehicles (18%), regional secondary aerosols (11%) and local secondary/aged aerosols (24%).

These recent studies highlight the importance of a combined measurement and source apportionment modelling approach to successfully identify and quantify the contributions of various sources to ambient PM. Furthermore, the use of short (up to 1 month) intensive field campaigns that utilise sophisticated instruments operating at high temporal resolution represents a more favourable strategy for source apportionment than longer term monitoring activities employing instruments with limited temporal resolution. Indeed, the use of online instruments such as the ATOFMS and the AMS not only enables the identification of specific sources that cannot be identified by offline analysis but also provides sufficient temporal resolution for monitoring fluctuations in source emissions on an hourly basis.

1.5 The SAPPHIRE project

As outlined above, three different air quality studies have shown that residential/domestic SFB is the major source of ambient $PM_{2.5}$ in Cork city during the winter months (Kourtchev *et al*., 2011; Dall'Osto *et al*., 2013, 2014). Two further studies have recently highlighted the dominant role that this pollution source plays in governing air quality in Galway and Dublin (Lin *et al*., 2017, 2018). This is despite the fact that there is a ban on the marketing, sale and distribution of bituminous fuel (or a "smoky coal ban") in all three cities. Indeed, all of these studies show that the residential burning of peat and wood is a significant contributor to PM in urban environments. Although elevated levels of wintertime PM have also been observed in some small towns in Ireland (EPA, 2017), there have been no source apportionment studies performed in these locations. The principal aim of the SAPPHIRE project was therefore to determine the sources of particulate pollution in residential areas of small towns in Ireland. The key project objectives were to:

- provide a comprehensive literature review of previous studies of the composition and sources of PM in Ireland;
- determine the chemical composition of fine PM ($PM_{2.5}$) present in locations representative of urban and rural residential areas in Ireland;
- conduct a source apportionment study of $PM_{2.5}$ at the selected monitoring locations and quantify the contributions of major sources, including road traffic and residential SFB;
- quantify the contribution that each solid fuel type (coal, peat and wood/biomass) makes to the measured $PM_{2.5}$;
- draw conclusions about the sources of $PM_{2.5}$ in rural and urban residential areas of Ireland and provide policymakers with relevant scientific information to support the development of effective strategies for reducing particulate pollution.

2 Methodology

2.1 Field Measurement Campaigns

Field measurement campaigns were conducted in three towns where residential SFB was expected to significantly affect air quality – Killarney (Co. Kerry), Enniscorthy (Co. Wexford) and Birr (Co. Offaly). The selection of these towns was based on the following criteria: (1) no natural gas supply, (2) outside Ireland's smoky coal ban areas (which applies to towns with > 15,000 inhabitants) and (3) residents who are likely to use solid fuels (wood, peat and coal) for space heating, based on national census data (Abbott *et al.*, 2016). In addition, Killarney had been included in a previous air quality study funded by the Environmental Protection Agency (EPA) (2010-AQ-MS-1), while PM_{10} levels in Enniscorthy are among the highest recorded in Ireland (EPA, 2016). Birr was selected as a representative town in the Midlands area, following a series of measurements at several locations in Offaly using a hand-held particle sensor.

Measurement sites in the three towns were identified and set up with the assistance of personnel in the local authorities and the EPA air quality team. Figure 2.1 shows maps of the environments surrounding the sites, while additional details concerning the locations and sampling periods are summarised in Table 2.1. The urban areas of Killarney, Enniscorthy and Birr have approximately 10,000, 3200 and 4000 inhabitants, respectively. The majority of the residential areas are to the south-east and north-west of the Killarney and Enniscorthy sites, while the Birr site is reasonably central in relation to residential areas. None of the three towns is home to any heavy industry, although several quarries are located to the east of Killarney. Land surrounding the urbans areas is

Figure 2.1. Maps of sampling site locations in Killarney, Enniscorthy and Birr. Residential areas are denoted by blue shading, quarries are denoted by yellow, and land where peat is harvested is denoted by orange.

Table 2.1. Locations and sampling periods for the field measurement campaigns

Location	Co-ordinates	Measurement period
Killarney Community Hospital	52°03′56.5″N, 9°31′00.4″W	12/11/2014 to 20/12/2014
Enniscorthy Public Library	52°30′01.8″N 6°34′13.0″W	8/01/2015 to 18/02/2015
Council Yard, St John's Place, Birr	53°05′47.1″N 7°54′29.9″W	16/11/2015 to 15/01/2016

primarily used for agriculture, specifically beef livestock and dairying (CSO, 2013). The prevailing winds at all locations are south-westerly.

2.2 Instrumentation and Analysis

A wide range of instrumentation for measuring the chemical and physical properties of atmospheric particles and other air quality parameters was deployed during the field campaigns, as shown in Table 2.2. The instruments were housed in a customised container and van, which were both fitted with appropriate sampling inlets. All instruments were operated on a continuous basis, with the measured parameters typically analysed to yield hourly values. Occasional periods of downtime were required for calibration and repair of some instruments, in particular the ATOFMS and the tapered element oscillating microbalance (TEOM). Intermittent problems were experienced with the wind speed and direction measured by the portable weather station. As a result, wind speed and direction data were obtained from Met Éireann synoptic weather stations, located approximately 59 km (Valentia Observatory), 26 km (Johnstown Castle) and 12 km (Gurteen College) from the Killarney, Enniscorthy and Birr sampling sites, respectively. Further details concerning the operation and analysis of data generated by the key instruments are provided below.

2.2.1 *Particle size, number and mass concentration*

$PM_{2.5}$ mass concentrations were measured on a continuous basis using a TEOM instrument. Data were analysed to yield average hourly and daily values. Particle size distributions and number concentrations were measured using a scanning mobility particle sizer (SMPS) and an optical particle sizer (OPS). The aerosol volume concentration data provided by these two instruments were converted to mass concentration using recommended particle density values for mixed urban aerosols ($d = 1.5\,g/cm^3$) and sea salt ($d = 2.2\,g/cm^3$). This "reconstructed" mass concentration was used to correct the values measured by the TEOM instrument in Enniscorthy, during the periods (identified after the campaigns) when instrumental issues were encountered.

2.2.2 *Carbonaceous content of particles*

The carbonaceous content of ambient particles was measured using two instruments – a thermal-optical carbon analyser and a seven-wavelength aethalometer. The former instrument collects $PM_{2.5}$ on a quartz fibre filter, which is then subjected to a two-stage heating process, to allow OC and EC mass concentrations to be determined. In this work, a slightly modified version of the National Institute for Occupational Safety and Health (NIOSH) 5040 protocol was used (NIOSH, 2003), which consisted of 108 minutes of sampling, followed by 12 minutes of heating, and analysis to deliver average values for EC and OC on a 2-hour basis. The aethalometer collects particles on a filter tape and measures the attenuation of light at seven different wavelengths, ranging from the ultraviolet (370 nm) to the infrared (950 nm). The BC mass concentration is calculated from the change in optical attenuation at 880 nm in the selected time interval using the mass absorption cross-section of $7.77\,m^2/g$ (Drinovec *et al.*, 2015). The aethalometer results were also analysed to apportion BC to two sources – traffic (traffic-related black carbon, BC_{Tr}) and SFB (solid fuel burning-related black carbon, BC_{SF}) – using the alpha values ($\alpha_{Tr} = 0.9$ and $\alpha_{SF} = 1.68$) most recently recommended in the literature (Zotter *et al.*, 2017).

2.2.3 *Online chemical characterisation of single particles*

The chemical composition of single airborne particles was determined in real time using an ATOFMS. A detailed description of the ATOFMS can be found elsewhere (Gard *et al.*, 1997). Briefly, it consists of (1) an aerodynamic focusing lens (TSI AFL100) (Su *et*

Table 2.2. Instrumentation deployed during the field campaigns

Instrument	Parameter(s) measured	Temporal resolution
Scanning mobility particle sizer (SMPS; TSI model 3081)	Particle number concentration (10–480 nm)	3 minutes
Optical particle sizer (OPS; TSI model 3330)	Particle number concentration (300–10,000 nm)	3 minutes
TEOM (Thermo Electron model 1400a)	$PM_{2.5}$ mass concentration	30 minutes
Thermal–optical carbon analyser (Sunset Laboratory Inc. model, third generation)	EC and OC mass concentrations	2 hours
Seven-wavelength aethalometer (Model AE33, Magee Scientific)	BC concentration	1 minute
NO_x analyser (Teledyne T200)	NO and NO_x mixing ratio	1 minute
O_3 analyser (Teledyne T400)	O_3 mixing ratio	1 minute
Weather station (Casella "Nomad")	Wind speed, wind direction, relative humidity, air temperature, rainfall, pressure, solar radiation	5 minutes
High-volume sampler (Digitel model DHA-80)	Collection of PM ($PM_{2.5}$)	6 hours
ATOFMS (TSI model 3800)	Single particle size and chemical composition (100–3000 nm)	1 minute

NO, nitric oxide; O_3, ozone.

al., 2004) that transmits particles in the aerodynamic diameter (D_a) range 100–3000 nm, (2) a particle sizing region and (3) a bipolar reflectron time-of-flight mass spectrometer. Single particles are desorbed/ionised using a pulsed neodymium-doped yttrium aluminium garnet (Nd:YAG) laser ($\lambda = 266$ nm, approximately 1 mJ/pulse). Positive and negative ion mass spectra of individual aerosol particles are obtained that enable the identification of the chemical constituents.

The large numbers (around 0.5–2 million) of single particle mass spectra generated by the ATOFMS during the measurement campaigns were clustered using the K-means algorithm ($K = 80$), as described in detail elsewhere (Healy *et al*., 2009, 2010; Gross *et al*., 2010). Clusters exhibiting very similar average mass spectra (including those with the same major ions but varying relative signal intensities), comparable temporal trends and size distributions were merged. The final clusters were then identified as particle classes.

Number concentrations for the ATOFMS particle classes were scaled using quantitative data from the particle-counting instruments (SMPS and OPS) at a temporal resolution of 1 hour. This involved the conversion of the electrical mobility diameter and the optical diameter measured with the SMPS and OPS into the corresponding vacuum aerodynamic diameter measured by the ATOFMS, using well-established procedures (Healy *et al*., 2012a, and references therein). In addition, the ATOFMS data were converted to give mass concentrations for each particle class by using the procedures reported in the literature (Healy *et al*., 2012a, 2013, and references therein). This step requires knowledge of the particle density, which is primarily dependent on its chemical composition. A range of densities was therefore used to calculate mass concentrations for each particle class, which can be found in Table 3.4. For particle classes containing metals, the densities were estimated from the bulk densities of the main chemical components identified in the mass spectra (Bein *et al*., 2006; Reinard *et al*., 2007). A value of 1.8 g/cm^3 was used for wood-burning particles based on the detailed work of Pagels *et al.* (2013). For all other carbonaceous particles mixed with inorganic components, a density value of 1.5 g/cm^3 was used as this is viewed as being a representative average for urban locations dominated by solid fuel combustion and vehicular emissions (Healy *et al*., 2010, 2012a). Reconstructed ATOFMS mass concentrations were then compared with those obtained by the TEOM, particle sizers (SMPS + OPS) and thermal–optical carbon analyser (EC and OC mass concentrations).

2.2.4 *Filter collection of PM2.5 for offline analysis*

Samples of $PM_{2.5}$ were collected onto quartz fibre filters (Pallflex 150-mm-diameter filters, pre-baked for 24 hours at 580°C) using a high-volume sampler at a flow rate of 500 L/minute, as described previously

(Kourtchev *et al*., 2011). A collection interval of 6 hours was selected to allow variations in the loading of the chemical constituents over a 24-hour period to be investigated. Given the extensive range of online instrumentation used in the measurement campaigns, it was decided that offline chemical analysis would not add sufficient value to this source apportionment study, especially when considering the labour-intensive nature of the work. The filters were therefore stored in a freezer for use in follow-up projects.

2.3 Combustion Experiments

Combustion experiments were performed to obtain mass spectral "fingerprints" of particles produced from burning different solid fuels to aid the identification of the sources of combustion particles detected during the measurement campaigns. Preliminary experiments were conducted in March 2015 on a range of solid fuels burnt in a chimney located outdoors. A more comprehensive set of measurements was performed using a solid fuel stove in a cottage in County Tipperary from 16 to 21 January 2016, as shown in Figure 2.2. Commercially available solid fuels – bituminous coal, "smokeless" coal, locally cut and seasoned peat sod, compacted peat briquettes, seasoned wood and "wet" wood (measured relative humidity > 20%) – were burnt in turn during the 5-day period. Experiments involving each fuel type lasted 6–12 hours, with new fuel being added to maintain combustion, as in real-world operating conditions. During each of the experimental runs, the stove was operated in two different modes: (1) with the glass door closed and using filtered outdoor air (Pallflex 150-mm filter) supplied to the combustion chamber by a 100-mm pipe; and (2) with the glass door open and the stove fed by oxygen from indoor air through the open glass door. The sampling line was made of an ordinary half-inch copper pipe, which extended approximately 10 cm inside the chimney flue (see Figure 2.2). An automobile fuel filter was fitted 2 m downstream of the inlet, for the effective trapping of moisture and large PM. This was followed by a gate valve to restrict the flow of smoke and allow dilution with clean air. The gate valve was adjusted to allow a dilution rate in the range of 80–160:1. The total length of the copper pipe between the chimney and the van housing the instruments was around 10 m, which provided sufficient time for the aerosol to cool down to ambient temperature before measurement.

The following instruments were used in the combustion experiments: an ATOFMS, a SMPS, an OPS, an aethalometer and an aerosol chemical speciation monitor operated by colleagues from the National University of Ireland Galway. Samples of $PM_{2.5}$ were also collected onto filters using the high-volume sampler. For all instruments, background aerosol was measured for approximately 30 minutes prior to burning each type of fuel. For the purposes of this work, the key instrument was the ATOFMS, which was operated in the same manner as that during the field measurements. Mass spectra generated during the experiments were clustered using the *K*-means algorithm ($K = 50$), as described above. Each fuel type presented a number of dominant particle classes,

Figure 2.2. Photographs of the solid fuel stove (left) and sampling set-up (right) for the combustion experiments performed in a cottage in County Tipperary.

the mass spectra of which were subsequently used to confirm the identification of solid fuel combustion classes in the ambient datasets.

2.4 Source Apportionment

Source apportionment was performed using version 5.0 of the PMF multivariate factor analysis tool provided by the US EPA (Norris *et al.*, 2014). Two model approaches were employed. In the first model, averaged hourly data from all of the online instruments were used, while the second model also incorporated the ATOFMS particle classes as particle counts per hour. The uncertainty matrix associated with the data was calculated on the basis of method detection limits (MDLs) and the precision (relative error) of the method, in accordance with Norris *et al.* (2014). The values for the various measured parameters are listed in Table 2.3. For concentrations less than or equal to the MDL provided, the uncertainty was calculated using the relationship:

$$\text{Uncertainty} = \frac{5}{6} \times MDL \tag{2.1}$$

If the concentration was greater than the MDL provided, an alternative relationship was employed:

$$\text{Uncertainty} = \sqrt{(\text{precision} \times \text{concentration})^2 + (0.5 \times MDL)^2} \tag{2.2}$$

For missing values, the uncertainty was set to the extreme value of 999 to reduce the influence of missing values on model output. In line with recommendations (Norris *et al.*, 2014), the uncertainty of PM was increased to a high value (400% in this case) to ensure that it was given no weight in the fitting of the model, i.e. the chemical profile dictates the identification of sources, rather than the mass loading. Extra modelling uncertainty of 10% was also included. This process resulted in uncertainty estimates that were similar to those used in previous PMF source apportionment studies involving ATOFMS datasets (Grover *et al.*, 2008; Giorio *et al.*, 2012; Dall'Osto *et al.*, 2014). The $PM_{2.5}$ source contribution estimates (SCEs) were produced by the inclusion of the $PM_{2.5}$ mass concentration in the model as an additional variable (directly from the TEOM data or from reconstructed SMPS + OPS data) but with sufficiently high uncertainty to prevent this variable from influencing the factor profiles (Giorio *et al.*, 2012; Norris *et al.*, 2014).

In performing PMF, the number of factors to be identified is defined by the user. However, a higher order solution does not necessarily contain the same factors as a lower order solution. Experimentation with the number of factors was performed (three to six) until the most reasonable results were obtained.

Table 2.3. Parameters used in PMF analysis, assigned limits of detection and relative errors

Parameters	MDL	Relative error (%)
Particle number concentration in three size bins (<66 nm, 66–300 nm, 300–480 nm)	10 particles per cm^3	5
EC, OC	0.3 µg/m^3	10
$PM_{2.5}$ mass concentration	0.01 µg/m^3	400
BC, BC_{SF} and BC_{Tr}	0.1 µg/m^3	10
Gases (NO, NO_2, O_3, SO_2[a], CO[a])	0.4 ppm	10
ATOFMS particle classes	1 particle count per hour	10

[a]Only for Enniscorthy.

CO, carbon monoxide; NO, nitric oxide; NO_2, nitrogen dioxide; O_3, ozone; SO_2, sulfur dioxide.

3 Results

3.1 Particle Size, Number and Mass Concentration

Mass concentrations of $PM_{2.5}$ for the duration of each campaign are shown in Table 3.1 and Figure 3.1. The most noticeable feature of the data is the huge variation in $PM_{2.5}$ observed at each site, with spikes in hourly average values occurring regularly during the evening and at night-time. Particulate pollution was the highest in Enniscorthy, where $PM_{2.5}$ levels averaged 29.2 µg/m^3 across the whole campaign and a peak value of 236.6 µg/m^3 was recorded. Furthermore, the WHO 24-hour mean guideline value of 25 µg/m^3 was exceeded on 42% of the days (16 out of 38). The same pattern was observed at the other sites, although the pollution levels were lower. Killarney experienced a mean $PM_{2.5}$ value of 15.3 µg/m^3, a peak of 134.6 µg/m^3 and four exceedances of the WHO 24-hour mean guideline value in 40 days. Thus, Killarney was slightly more polluted than Cork Harbour during a similar air quality study in February 2009 (Dall'Osto *et al*., 2013), where the mean $PM_{2.5}$ value was 13 µg/m^3. Birr was the least polluted site, with a mean $PM_{2.5}$ value of 7.9 µg/m^3 and no exceedances of the WHO 24-hour mean guideline value in 43 days. A closer inspection of Figure 3.1 shows that wind speed is the factor with the highest impact on local pollution levels. High wind speeds cause greater dispersion of locally emitted pollution, resulting in lower $PM_{2.5}$ levels. As shown in Figure 3.1, all of the large spikes in night-time pollution coincide with a drop in wind speed.

A very strong daily (24-hour) variation in $PM_{2.5}$ mass was clearly observed at all sites (see Figure 3.2), with elevated levels of pollution extending from 17:00 to 23:00, consistent with emissions from residential SFB. Again, it is worthwhile noting the huge variation in hourly average $PM_{2.5}$ levels at night, which can change by an order of magnitude, depending on the wind speed. A small rise in $PM_{2.5}$ was also apparent from 8:00 to 10:00 at each site, presumably because of emissions from motor vehicles. As expected, very similar trends were also observed for particle number concentrations (see Figure 3.3). Each site experienced a gradual rise in particle numbers during the daytime (from 7:00 to 15:00), followed by a rapid increase, which peaked from 18:00 to 20:00. Interestingly, the SMPS data for Birr indicate a larger number of smaller particles than in Killarney. This is also confirmed by the size-resolved plots in Figure 3.4. The size distributions for both Killarney and Enniscorthy are virtually identical and centred on the range 70–100 nm, typical for fresh combustion particles. While the Birr data also show that this size range is present, an intense smaller mode – up to 30 nm in size – was also observed, possibly indicating the importance of nucleation or new particle formation at the site.

Table 3.1. Mean values for particle number and mass concentration across the whole campaign at the three sampling locations

	Killarney (11/11/14–20/12/14)		Enniscorthy (8/1/15–14/2/15)		Birr (3/12/15–14/1/16)	
Parameter	Mean (± SD)	Range	Mean (± SD)	Range	Mean (± SD)	Range
$PM_{2.5}$ (µg/m^3)[a]	15.3 (± 16.7)	1.2–134.6	29.2 (± 31.9)	0–236.6	7.9 (± 7.2)	0.1–62.6
Number (#/cm^3)[b]	4394 (± 6762)	40–40,896	8096 (± 10,349)	105–75,855	5922 (± 7184)	70–48,965
Number (#/cm^3)[c,d]	195 (± 407)	1–2552	404 (± 522)	0–4646	63 (± 101)	0–1112

[a] **$PM_{2.5}$ measured by the TEOM instrument. Data for Enniscorthy are corrected (see text).**

[b] **Particle numbers determined by the SMPS (10–480 nm).**

[c] **Particle numbers determined by the OPS (0.3–2.5 µm).**

[d] **The OPS malfunctioned in Birr on 21/12/15; measurements ceased at that point.**

SD, standard deviation.

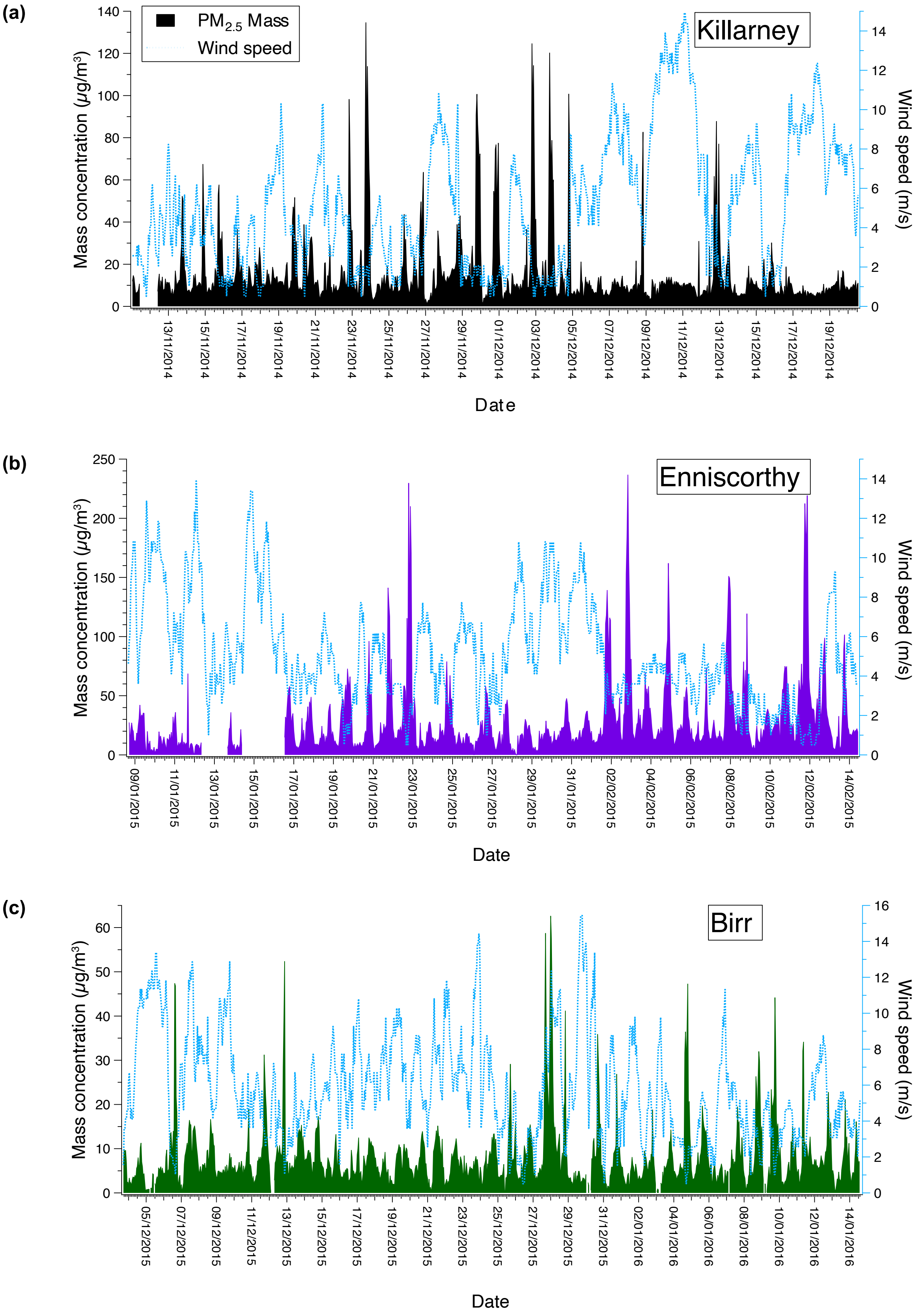


Figure 3.1. Mass concentrations of $PM_{2.5}$ during the field measurement campaigns in (a) Killarney, (b) Enniscorthy and (c) Birr. Data for Killarney and Birr were provided directly by the TEOM. Data for Enniscorthy were obtained by applying corrections derived from the particle sizing instruments to the TEOM measurements.

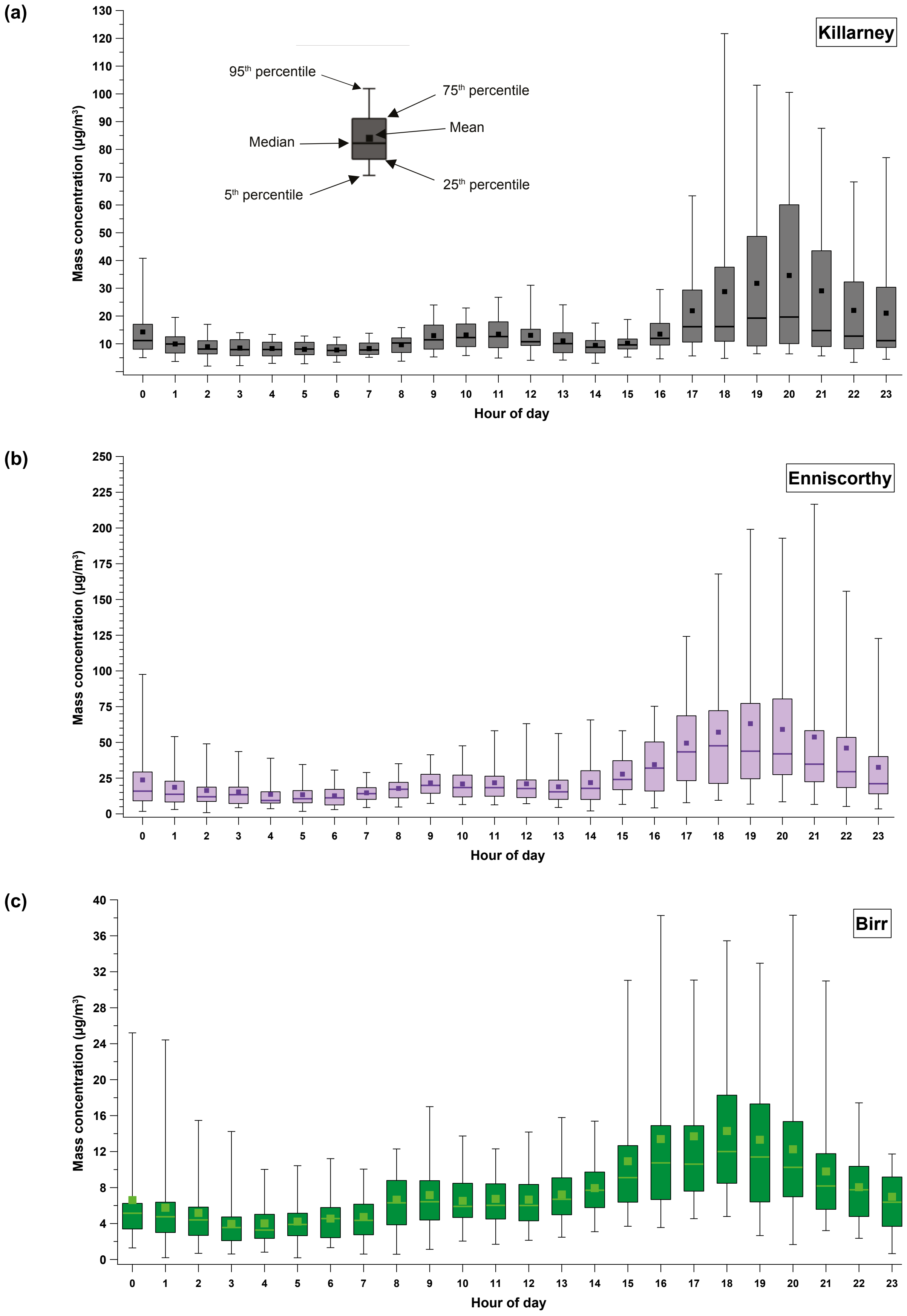


Figure 3.2. Daily variation in mass concentrations of $PM_{2.5}$ during the field measurement campaigns in (a) Killarney, (b) Enniscorthy and (c) Birr. Data for Killarney were measured by the TEOM, while data for Enniscorthy and Birr were derived from particle counting and sizing instruments.

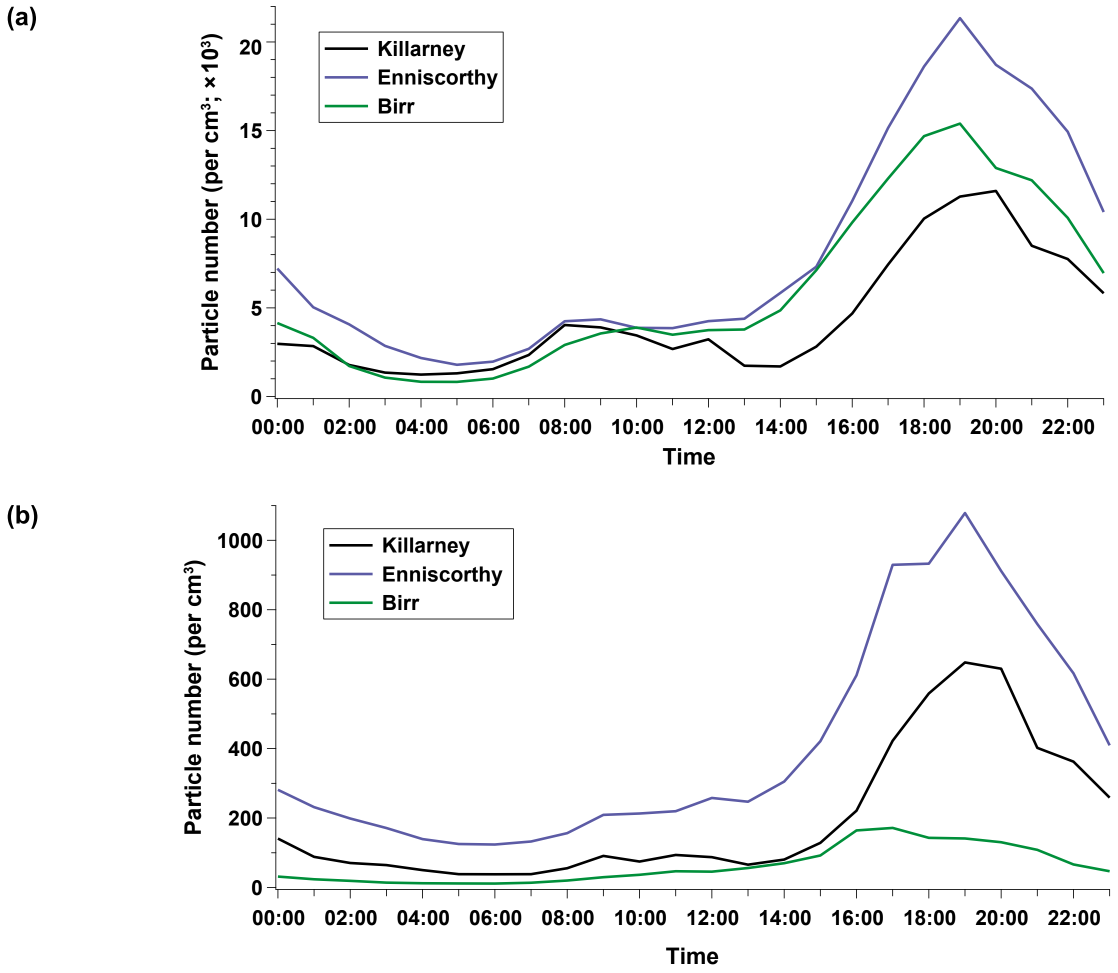


Figure 3.3. Daily variation in particle number concentrations measured by (a) the SMPS (10–480 nm) and (b) the OPS (300–2500 nm) during the field measurement campaigns in Killarney, Enniscorthy and Birr.

3.2 Carbonaceous Content of Particles

Values of EC and OC determined by the thermal–optical analyser are shown in Figure 3.5 and summarised in Table 3.2. The temporal profiles follow the $PM_{2.5}$ mass concentrations of Figure 3.1 very closely, indicating that carbonaceous aerosol is a dominant component of the particulate pollution at all sites. This is confirmed by regression analysis, which shows that the total carbon (OC + EC) accounts for 35–55% of the measured $PM_{2.5}$ mass concentration across the three sites. This is similar to the value of 55% total carbon observed in Cork Harbour during February 2009 (Dall'Osto *et al*., 2014). The main carbonaceous component at all sites is clearly OC, indicating a strong contribution from biomass burning. Indeed, the OC/EC ratio is a good indicator of the relative influence of biomass and fossil fuel burning sources on the PM loading. A very detailed study by Ni *et al*. (2018) suggests indicative values for OC/EC of 5 for biomass burning and 2.38 for coal burning. The OC/EC values obtained in this work are listed in Table 3.2 and indicate that Birr is probably dominated by biomass burning, while Killarney and Enniscorthy are probably dominated by both biomass and coal burning (Ni *et al*., 2018). Incidentally, the OC/EC value of 2.7 obtained in Cork Harbour (Dall'Osto *et al*., 2013) is also indicative of the fact that both coal and biomass burning are contributing to ambient $PM_{2.5}$.

Values of BC determined by the aethalometer also followed the EC, OC, particle number and $PM_{2.5}$ mass concentrations very closely throughout each of the measurement campaigns. The daily (24-hour) variation in BC was also very similar at all three sites (see Figure 3.6). A small rise occurred from 7:00 to 10:00, which was followed by a much stronger increase in BC, peaking from 18:00 to 20:00 and persisting until midnight. The BC mass concentration

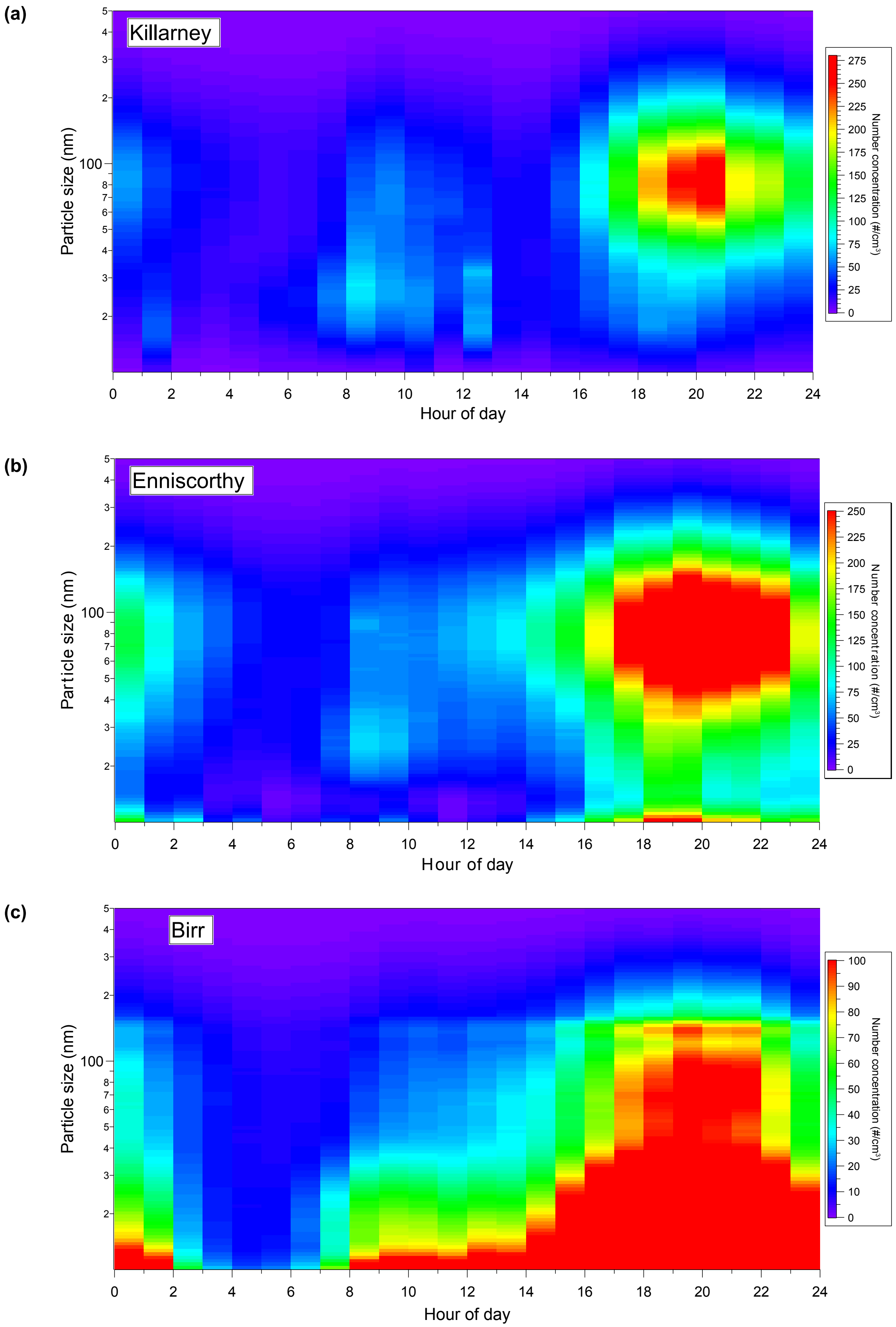


Figure 3.4. Daily variation in average size-resolved particle number concentrations measured by the SMPS during the field measurement campaigns in (a) Killarney, (b) Enniscorthy and (c) Birr.

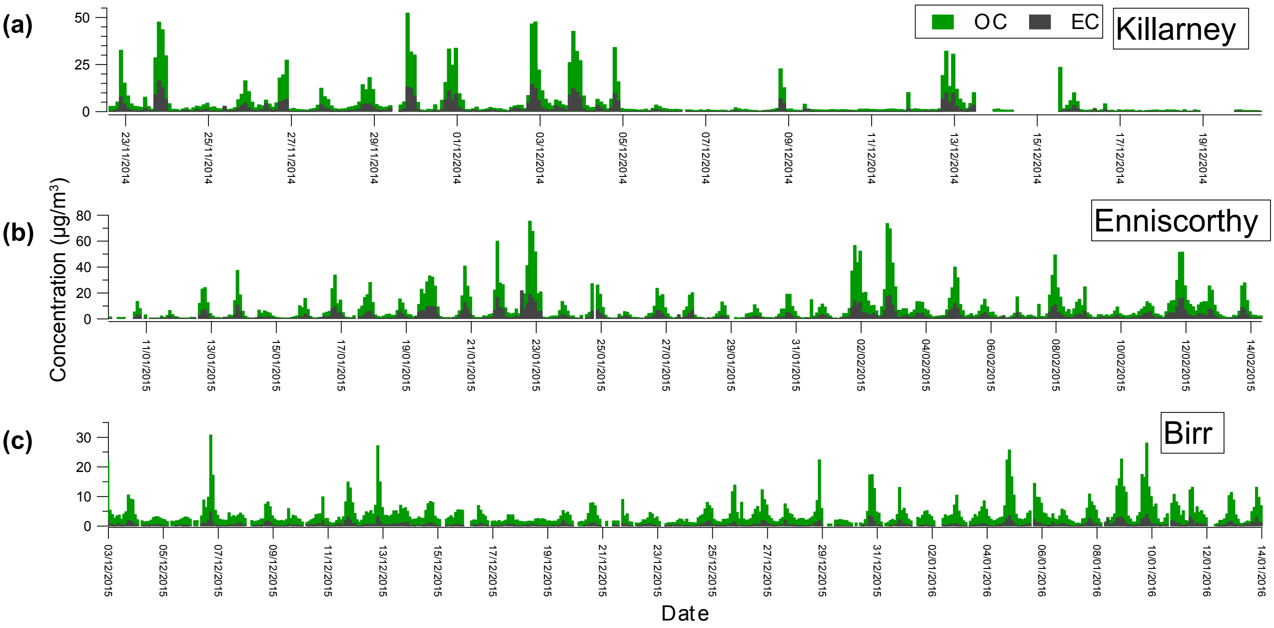


Figure 3.5. Mass concentrations of OC and EC measured by the thermal–optical analyser during the field measurement campaigns in (a) Killarney, (b) Enniscorthy and (c) Birr.

Table 3.2. Two-hourly average concentrations of OC and EC at SAPPHIRE sites and comparison with $PM_{2.5}$ mass

	Killarney (22/11/14–20/12/14)		Enniscorthy (9/1/15–14/2/15)		Birr (3/12/15–14/1/16)	
Parameter	Mean (±SD)	Range	Mean (±SD)	Range	Mean (±SD)	Range
OC (µg/m³)	5.9 (±9.5)	0.6–52.6	9.6 (± 12.2)	0.5–75.8	4.1 (±3.5)	0.81–27.4
EC (µg/m³)	1.8 (±2.9)	0.0–16.6	2.9 (±3.5)	0.0–22.1	0.7 (±0.61)	0.0–3.7
OC/EC ratio	3.8	0.9–60.3	4.0	0.5–71.1	6.3	1.7–39.6
$PM_{2.5}$ (µg/m³)	15.6 (±16.7)	1.7–104.2	29.5 (±30.7)	0.7–205.2	7.9 (±7.2)	0.1–60.1
$(OC+EC)/PM_{2.5}$	0.35	0.07–1.0	0.37	0.06–1.0	0.59	0.05–1.0
$OC/PM_{2.5}$	0.28	0.07–0.89	0.29	0.05–0.88	0.51	0.05–1.0
$EC/PM_{2.5}$	0.08	0–0.26	0.08	0–0.48	0.08	0–0.35

SD, standard deviation.

was split into two components, attributed to SFB (BC_{SF}) and vehicular traffic (BC_{Tr}) using the two-source aethalometer model with updated alpha values for traffic and biomass burning (Zotter *et al.*, 2017). Although this approach is strictly not applicable to locations where other solid fuels (coal and peat in this case) are used for home heating, the results of the model are still informative. As shown in Figure 3.7 and Table 3.3, SFB dominates at each site, accounting for 61–80% of the total measured BC mass (BC_{Total}). As expected, there is very good agreement between the amount of BC and EC present in the measured $PM_{2.5}$ at all sites. On average, EC accounted for 8% of $PM_{2.5}$ mass at all sites (see Table 3.2), while BC ranged from 9.9% to 12.1%.

3.3 Online Chemical Characterisation of Particles

An analysis of the ATOFMS datasets enabled the identification of 15–25 distinct particle classes in each of the measurement campaigns. The contribution to total ATOFMS particle number and mass concentration of all particle classes can be found in Table 3.4. The particle class labelling scheme employed here is regularly used in the literature (Healy *et al.*, 2010, 2013; Pratt and Prather, 2012) and indicates either the probable source (e.g. sea salt) or the dominant species in the positive mass spectra (e.g. K, EC, Fe), with the ions listed in the same order as their relative mass spectral

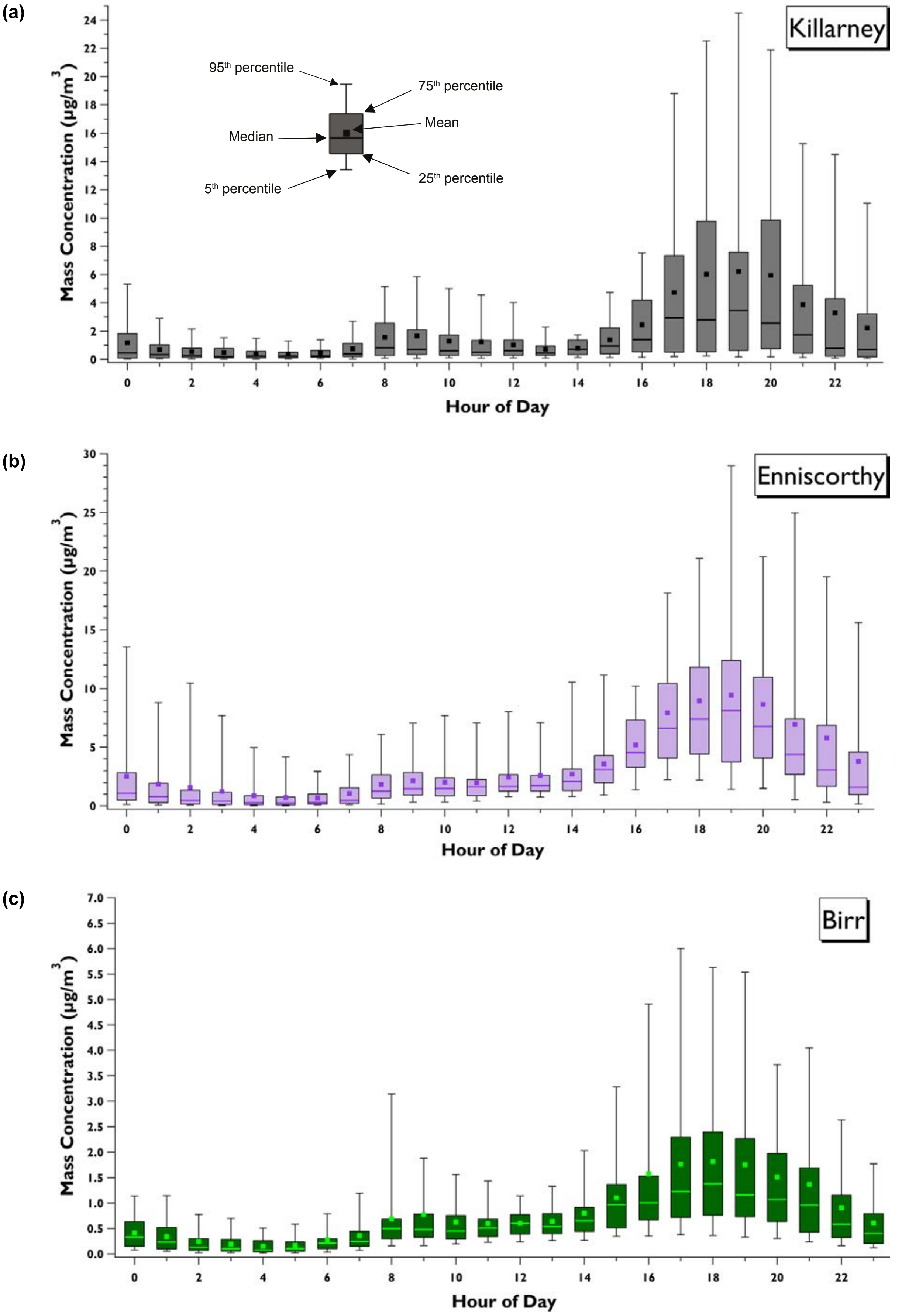
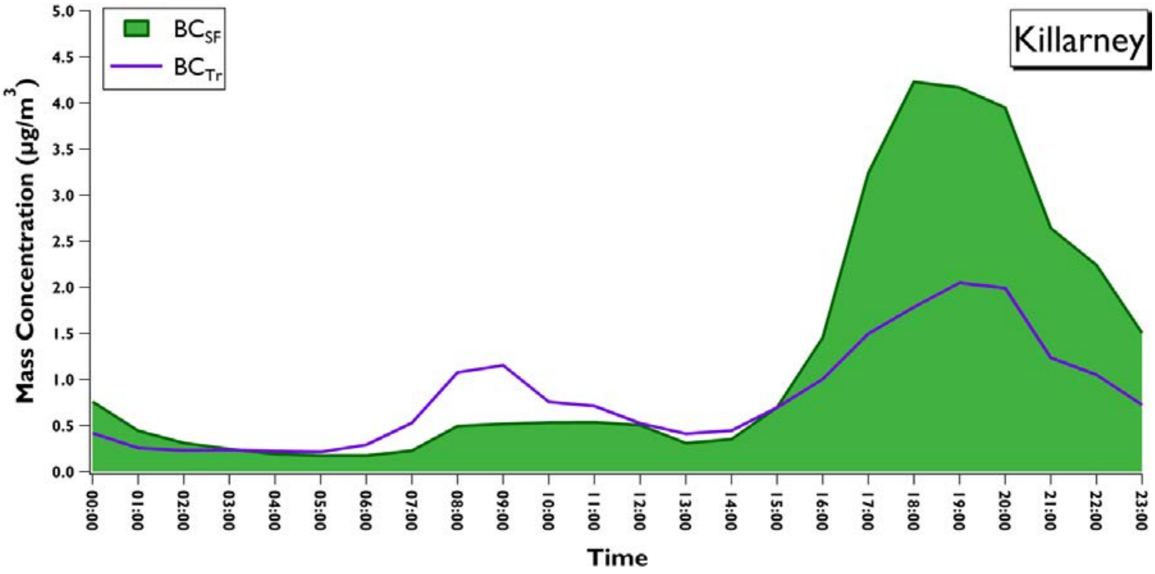
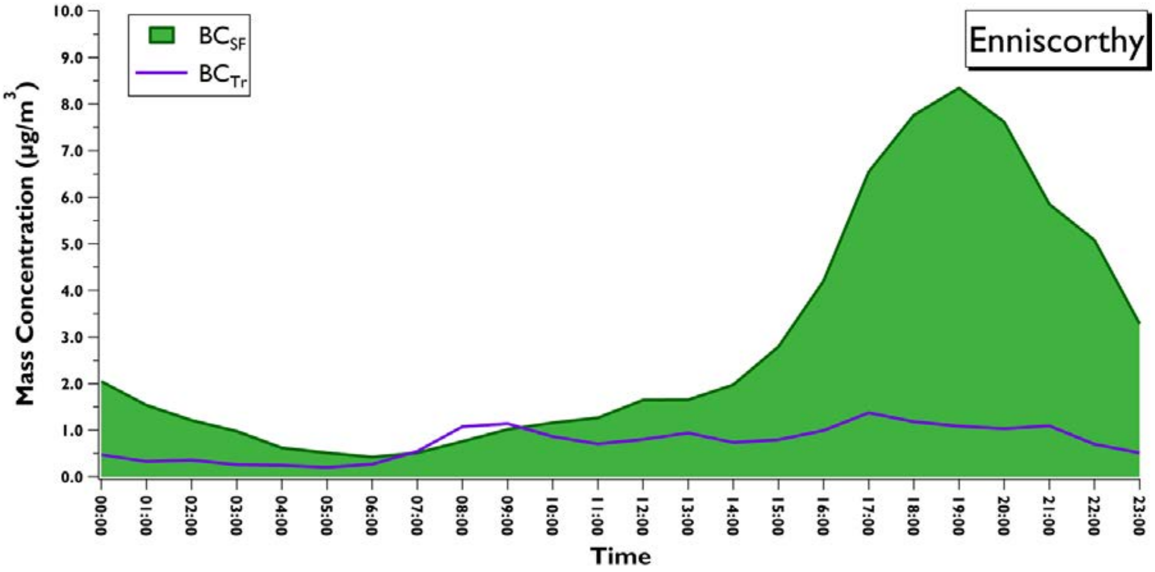


Figure 3.6. Daily variation in BC concentrations during the field measurement campaigns in (a) Killarney, (b) Enniscorthy and (c) Birr.

(a)



(b)



(c)

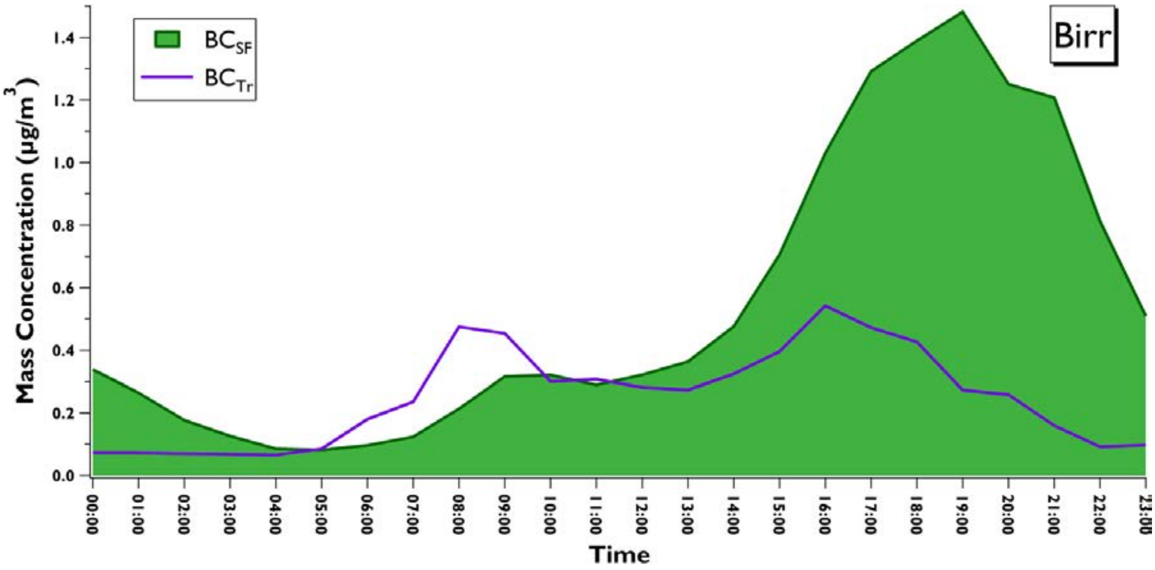


Figure 3.7. Daily variation in BC components attributed to solid fuel burning (BC_{SF}) and vehicular traffic (BC_{Tr}) during the field measurement campaigns in (a) Killarney, (b) Enniscorthy and (c) Birr.

Table 3.3. Hourly average BC concentrations at the SAPPHIRE monitoring locations and comparison with $PM_{2.5}$ mass concentration

	Killarney (12/11/14–20/12/14)		Enniscorthy (8/1/15–14/2/15)		Birr (3/12/15–14/1/16)	
Parameter	Mean (±SD)	Range	Mean (±SD)	Range	Mean (±SD)	Range
BC (µg/m^3)	2.06 (±3.8)	0.01–25.2	3.6 (±4.8)	0.01–35.2	0.8 (±0.9)	0.01–6.35
$PM_{2.5}$ (µg/m^3)	15.4 (±16.8)	1.2–134.6	29.2 (±31.9)	0–236.6	7.9 (±7.2)	0.1–62.6
$BC/PM_{2.5}$	9.9	0.3–79.9	13.2	0.07–90.0	12.1	0.13–95.5
BC_{SF}/BC_{Total}	0.61		0.80		0.68	

intensities. For example, a particle class with high-intensity mass spectral features for Na and EC is labelled Na-EC. In some cases, this is followed by a secondary species detected in the negative mass spectra (e.g. K-NO_X), which usually provides an insight into the atmospheric ageing that the particles have undergone locally or during transport (Reinard *et al.*, 2007). The particle classes were subsequently grouped into nine general categories for clarity: peat, wood, coal, peat/coal, amine, other solid fuel combustion, traffic, sea salt and metal particle classes. These assignments are based on a comparison with mass spectral “fingerprints” obtained during the combustion experiments and also reported in the literature. The contributions of each of these categories to the total $PM_{2.5}$ mass concentration is shown in Figure 3.8.

For each campaign, peat was the dominant source of domestic solid fuel combustion particles: 31%, 27% and 26% of $PM_{2.5}$ mass in Killarney, Enniscorthy and Birr, respectively. Wood was the second most dominant combustion source (17%, 21% and 23%, respectively), followed by coal (16%, 17% and 5%, respectively). In the Enniscorthy dataset, two particle classes could not be confidently assigned to either peat or coal combustion based on their mass spectral markers and, therefore, were placed in their own category of peat/coal. A more detailed discussion of this issue follows. Amine- and ammonium-containing particles accounted for 5%, 6% and 5% of $PM_{2.5}$ mass in Killarney, Enniscorthy and Birr, respectively, and were strongly associated with domestic solid fuel combustion and agricultural emissions, based on their composition and temporal profiles. Traffic accounted for very little of the $PM_{2.5}$ mass (1% or less) in all three locations. Sea salt particles contributed 4%, 4% and 5%, respectively, during specific periods, while other metals (mostly metal-containing particles) contributed 1% or less.

As the ATOFMS measures only particles larger than 100 nm D_a, mass concentrations for particles smaller than 100 nm D_a were calculated from the SMPS data; these accounted for 1% or less of $PM_{2.5}$ mass, indicating that the ATOFMS source apportionment was not hindered greatly by this missing size range. After accounting for all of the ATOFMS particle classes and particles of < 100 nm D_a, some of the $PM_{2.5}$ mass (measured by the TEOM or calculated from the SMPS + OPS data) remained unidentified in terms of composition. This unidentified group of particles contributed a relatively large amount to $PM_{2.5}$ mass at each location: 22%, 13% and 33% in Killarney, Enniscorthy and Birr, respectively. Contributions from this group were found to be highest during periods with high wind speed and increased sea salt particles – essentially periods of regional transport. It is likely that the decreased efficiency with which the ATOFMS detects supermicron particles resulted in the underestimation of sea salt mass concentrations, despite the scaling procedure. This was particularly evident during the Killarney campaign. Figure 3.8 compares the contribution of ATOFMS particle classes to $PM_{2.5}$ mass during periods identified as being influenced almost exclusively by local residential SFB and by regionally transported material. During the former, there was no $PM_{2.5}$ mass unaccounted for; however, during the latter the unidentified group accounted for 74% of $PM_{2.5}$ mass. It is also possible that particles rich in species that the ATOFMS has difficulty ionising effectively, such as ammonium sulfate or highly oxygenated organic aerosol, were present.

Table 3.4. Contributions of different particle classes to the ATOFMS particle number and mass concentrations during the three SAPPHIRE campaigns

		Killarney (total particles: 567,963)			Enniscorthy (total particles: 1,898,614)			Birr (total particles: 1,957,150)			
Particle category	Particle class	Particle number	% total ionised	% ATOFMS mass	Particle number	% total ionised	% ATOFMS mass	Particle number	% total ionised	% ATOFMS mass	Density (g/cm³)[a]
Peat	EC-OC	92,591	16	19	41,1498	22	20	242,243	12	10	1.5
	K-EC-OC	82,260	14	15	25,5961	13	6.5	393,044	20	17	1.5
	K-Na-EC	45,514	8	10	72,565	4	4.5	52,564	3	2	1.5
	OC-PAH[b]				See "Peat/coal"	See "Peat/coal"	See "Peat/coal"	30,363	2	1	1.5
	PAH-OC[b]				See "Peat/coal"	See "Peat/coal"	See "Peat/coal"	64,991	3	3	1.5
	PAH							165,106	8	8	1.5
Wood	K	117,365	21	22	40,9517	22	23	254,218	13	17	1.8
	K-OC				5092	0.3	0.5	241,188	12	10	1.8
	K-PAH high				21,800	1	1.4	15,756	3	3	1.8
	K-PAH low							60,715	5	5	1.8
Coal	EC(C_1)-K	46,231	8	8	284,210	15	14	120,665	6	5	1.5
	EC(C_3)-K				20,944	1	2	40,308	2	2	1.5
	K-EC	61,702	11	12	28,969	1.5	3	998	0.05	0.05	1.5
Peat/coal	OC-PAH[b]				57,187	3	4	See "Peat"	See "Peat"	See "Peat"	1.5
	PAH-OC[b]				138,976	7	8	See "Peat"	See "Peat"	See "Peat"	1.5
Amines	Amines	36,924	6	7	113,673	6	7	93,135	5	6	1.5
Traffic	EC-traffic	3584	0.6	0.5	5193	0.3	0.3				1.5
	Ca	3688	0.6	0.4	7826	0.4	0.6	9544	0.5	0.6	1.5
Other solid fuel combustion	Unassigned	6722	1.8	3.0	1724	0.2	0.2	59,344	1.5	1.0	1.5
Sea salt	Sea salt	66,006	12	5	44,584	2	4.5	105,217	5	8	2.2
Metals	Al	1034	0.2	0.5				920	0.05		3.7
	Ba	1368	0.2	0.3	268	0.01					1.5
	Fe	2127	0.4	0.6				407	0.02		3.6
	Li	218	0.04	0.1	2928	0.2					2
	Mg							3775	0.2		2.2
	Pb							110	0.01		4.3
	V	532	0.09	0.2	115	0.01		2539	0.1	0.2	3.1
	Zn	97	0.02	0.1	63	0.003					3.8

[a] The density of the various particle classes was obtained from literature values (see section 2.2.3).

[b] Polycyclic aromatic hydrocarbon (PAH)-containing particles were found in both peat and coal combustion datasets – their composition was very similar and in Enniscorthy, where similar contributions were found from both fuel combustion sources, OC-PAH and PAH-OC particles could not be assigned to one source over the other. In Birr, where the fraction of coal combustion particles was much smaller, most of the OC-PAH and PAH-OC particles were assumed to have originated from peat combustion.

PAH, polycyclic aromatic hydrocarbon.

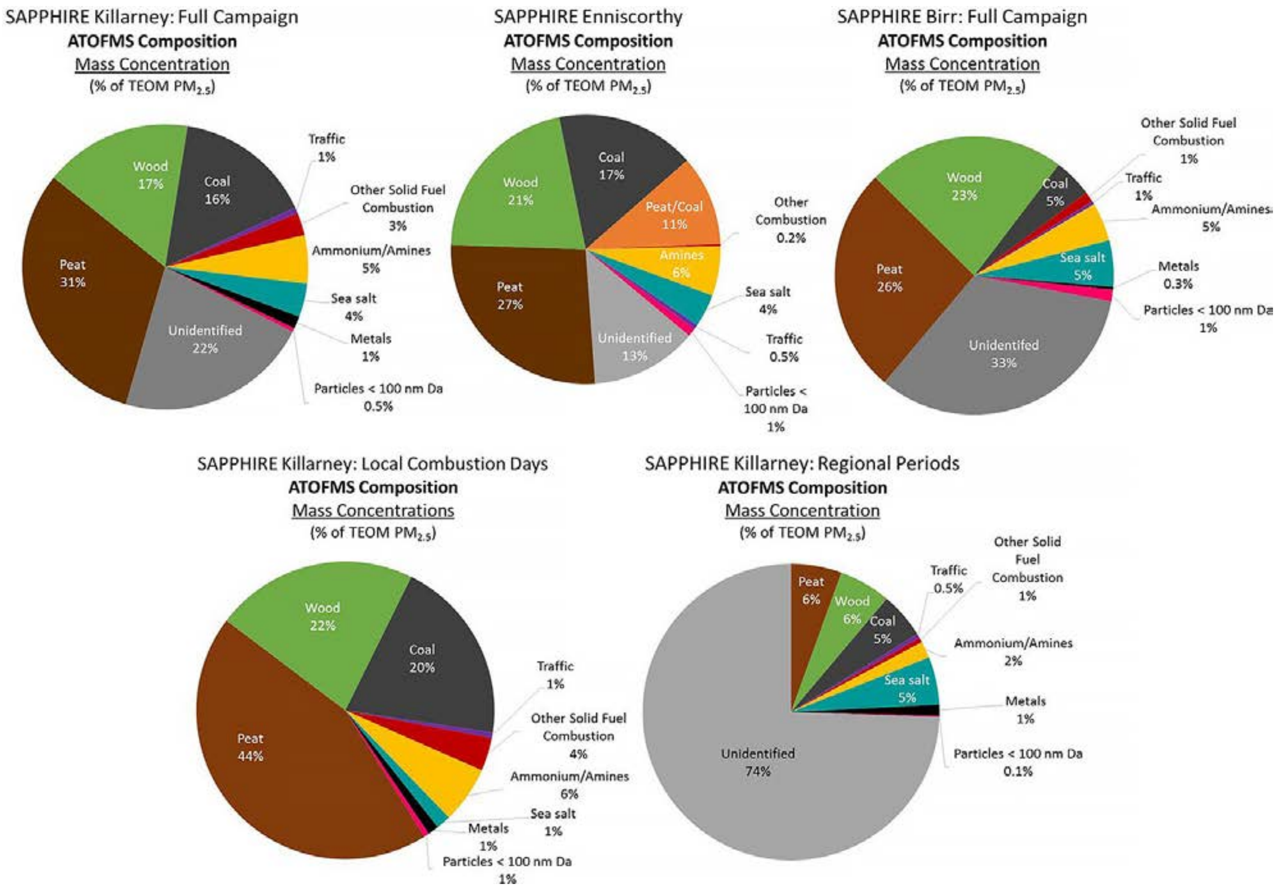


Figure 3.8. Contributions of ATOFMS particle categories to $PM_{2.5}$ mass concentration during the three SAPPHIRE campaigns.

3.3.1 *Peat-burning particles*

Figure 3.9 shows the average mass spectra of particle classes (EC-OC, K-EC-OC and K-Na-EC) that were identified as peat-burning emissions, based on a comparison with mass spectra obtained from the combustion experiments. The positive mass spectra of EC-OC and K-EC-OC are characterised by EC ($^{12}C^+$, $^{24}C_2^+$, $^{36}C_3^+$) and hydrocarbon ($^{27}C_2H_3^+$, $^{37}C_3H^+$, $^{43}C_2H_3O^+$, $^{50}C_4H_2^+$, $^{51}C_4H_3^+$, $^{63}C_5H_3^+$, $^{74}C_6H_2^+$) fragments and sodium ($^{23}Na^+$), while a strong signal for potassium ($^{39}K^+$) in K-EC-OC particle mass spectra relative to the $^{36}C_3^+$ and $^{37}C_3H^+$ ions distinguishes them from EC-OC particles. Strong signals for sulfate ($^{97}HSO_4^-$) and organic nitrogen ($^{26}CN^-$) dominate the average negative mass spectra of both of these classes. K-EC-OC particles also displayed strong signals for nitrate ($^{46}NO_2^-$, $^{62}NO_3^-$) and signals for chloride ($^{35}Cl^-$), while EC ions ($^{24}C_2^-$, $^{36}C_3^-$, $^{48}C_4^-$) were found in EC-OC particles. The particle class K-Na-EC was characterised by strong signals for $^{23}Na^+$ and $^{39}K^+$, EC ions in both positive and negative mass spectra and a strong sulfate signal. Particles similar to K-EC-OC and EC-OC were detected in Cork by Healy *et al*. (2010) and assigned to peat combustion, while the particle class EC-domestic, which is very similar in composition to K-Na-EC particles, was also thought to have originated from domestic combustion, but a fuel type was not identified.

Three polycyclic aromatic hydrocarbon (PAH)-containing classes were assigned to peat emissions for the Birr campaign – PAH, OC-PAH and PAH-OC. The PAH class was observed only during the Birr campaign, while the OC-PAH and PAH-OC classes were seen in both Enniscorthy and Birr. No PAH-containing particles were observed during the Killarney campaign; it is still unclear why this was the case. Particles of PAH were characterised by $^{39}K^+$, hydrocarbon peaks (as above) and prominent signals for PAH ions at mass-to-charge ratio (*m*/*z*) 78, 189, 202 and 215, with *m*/*z* 202 previously being assigned to pyrene and/or fluoranthene (Dall'Osto and Harrison, 2012). The particle composition of OC-PAH and PAH-OC is discussed below under the peat/coal section.

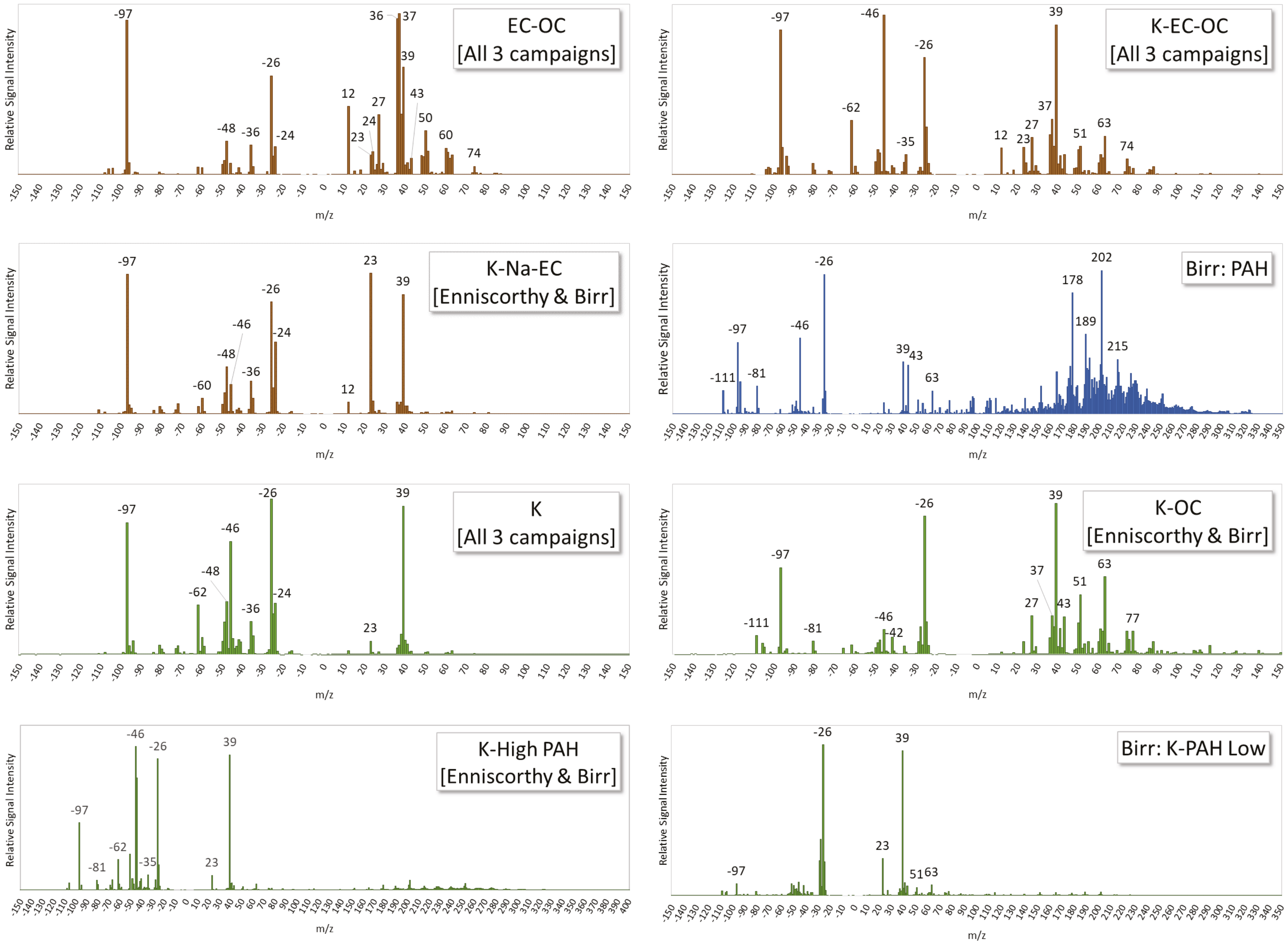


Figure 3.9. Average mass spectra of ATOFMS particle classes, during all three campaigns, assigned to the peat category (EC-OC, K-EC-OC, K-Na-EC and PAH classes) and the wood category (K, K-OC, K-high PAH and K-low PAH classes).

Particles containing PAH produced from burning peat and coal during the combustion experiments were actually indistinguishable from each other based on their mass spectra. The decision to assign these classes to the peat category for the Birr campaign was made based on the relatively low contribution from coal combustion. During Enniscorthy, the contribution from coal combustion was larger so the PAH-containing classes were placed in their own category, peat/coal.

3.3.2 Wood-burning particles

The average mass spectra of particle classes (K, K-OC, K-high PAH and K-low PAH) that were identified as wood-burning emissions, based on a comparison with mass spectra obtained from the combustion experiments, can also be found in Figure 3.9. The K class dominated the wood category and is typical of biomass-burning combustion emissions seen in numerous other studies (Pratt and Prather, 2012; Pagels *et al.*, 2013). Particles of K are characterised by a dominant peak for $^{39}K^{+}$ and a smaller peak for $^{23}Na^{+}$. In the negative mass spectra, organic nitrogen ($^{26}CN^{-}$) is dominant, followed by sulfate ($^{97}HSO_4^{-}$). Also present are EC ($^{24,36,48}C^{-}$) and nitrate ($^{46}NO_2^{-}$, $^{62}NO_3^{-}$). K-OC particles are similar in composition to K particles but with the addition of hydrocarbon fragments. Aqueous-phase or fog processing markers $^{81}HSO_3^{-}$ and hydroxymethanesulfonate (HMS; $^{111}HOCH_2SO_3^{-}$) (Whiteaker and Prather, 2003) are present in the negative mass spectra, indicating that some of the K-OC particles were aged to some degree. Particles containing PAH, in the form of the K-high PAH class seen in Enniscorthy and Birr and the K-low PAH class seen only in Birr, were assigned to the wood category, based on their similarity to PAH-containing particles from the wood combustion experiments. Both classes are characterised by a dominant $^{39}K^{+}$ peak, the typical marker for wood-burning particles detected by an ATOFMS, $^{23}Na^{+}$ and PAH signals; for K-high PAH these signals range from *m*/*z* 150 to 330 (dominant peaks at *m*/*z* 152, 165, 178, 189, 202, 215, 228, 239, 252 and 276), while for K-low PAH they range from *m*/*z* 100 to 240 (dominant peaks at *m*/*z* 115, 128, 139, 152, 178, 189 and 202). The PAH ion signal intensity for high molecular weight fragments such as *m*/*z* 225 has been shown to increase with decreasing desorption/ionisation laser energy (Healy *et al.*, 2012b); it is therefore possible that variation in laser energy produced the K-low PAH class seen in Birr and that the two classes are in reality the same type.

3.3.3 Coal-burning particles

Figure 3.10 shows the average mass spectra of the particle classes EC(C_1)-K, EC(C_3)-K and K-EC that were identified as coal-burning emissions, based on a comparison with mass spectra obtained from the combustion experiments. These coal classes are readily distinguished from peat and wood particles by their large signals for EC ions ($^{12}C^{+}$, $^{24}C_2^{+}$, $^{36}C_3^{+}$) and $^{39}K^{+}$. This is in contrast to peat particles, where hydrocarbon ions (e.g. $^{37}C_3H^{+}$ and $^{27}C_2H_3^{+}$) and $^{39}K^{+}$ dominate, and wood particles, where $^{39}K^{+}$ is virtually the sole dominant signal in their positive mass spectra. The intensity of $^{12}C^{+}$, $^{36}C^{+}$ and $^{39}K^{+}$ seen in the coal particle classes differs for each; the dominant ions are $^{12}C^{+}$ in EC(C_1)-K particles, $^{36}C^{+}$ in EC(C_3)-K particles and $^{39}K^{+}$ in K-EC particles. Most coal particles produced a signal only for sulfate ($^{97}HSO_4^{-}$) in their negative mass spectra, another feature that has been considered characteristic of particles from this solid fuel combustion source (Healy *et al.*, 2010). In contrast, peat and wood particles also displayed signals for organic nitrogen ($^{26}CN^{-}$), EC ($^{24,36,48}C^{-}$) and nitrate ($^{46}NO_2^{-}$, $^{62}NO_3^{-}$).

3.3.4 Peat/coal-burning particles

The average mass spectra of particle classes (OC-PAH and PAH-OC) that were identified as peat- or coal-burning emissions, based on a comparison with mass spectra obtained from the combustion experiments, can also be found in Figure 3.10. Particles of OC-PAH are characterised by large signals for $^{39}K^{+}$ and hydrocarbon fragments ($^{43}C_2H_3O^{+}$, $^{51}C_4H_3^{+}$, $^{63}C_5H_3^{+}$), with smaller peaks for PAH fragments (*m*/*z* 152, 165, 178, 189, 202, 215, 226, 239). For PAH-OC particles, this situation was reversed, with PAH signals (*m*/*z* 189, 202, 215, 225, 239, 252, 265, 276) dominating the positive mass spectra. Particles of PAH-OC also displayed larger signals for nitrate ($^{46}NO_2^{-}$, $^{62}NO_3^{-}$) and chloride ($^{35}Cl^{-}$), relative to the signals for organic nitrogen ($^{26}CN^{-}$) and sulfate ($^{81}HSO_3^{-}$, $^{97}HSO_4^{-}$).

Particles containing PAH produced from burning peat sod, peat briquettes, coal and “smokeless” coal in the combustion experiments did not produce any unique

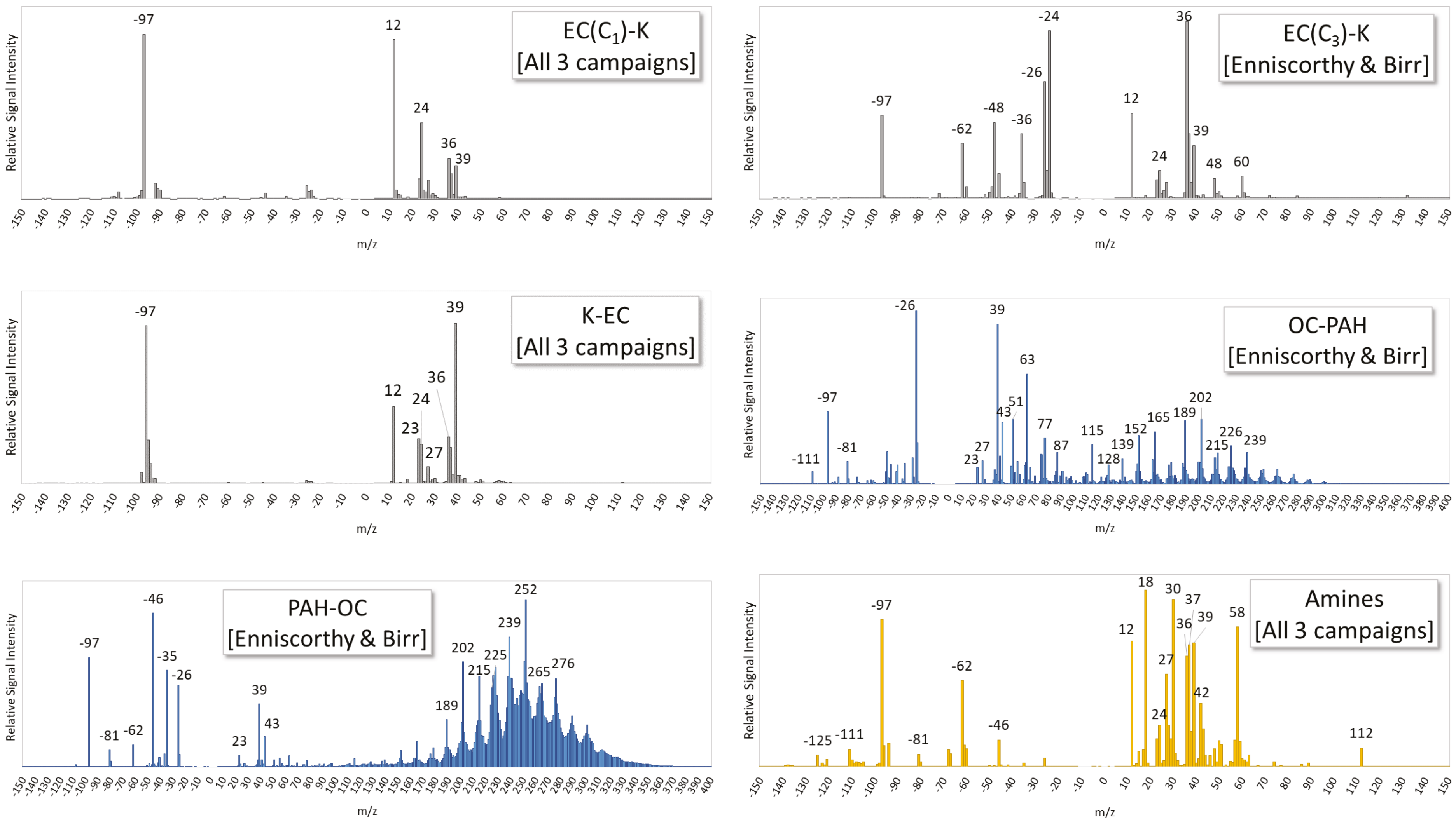


Figure 3.10. Average mass spectra of ATOFMS particle classes related to domestic solid fuel combustion, during all three campaigns, assigned to the coal category (EC(C$_1$)-K, EC(C$_3$)-K and K-EC classes), the peat/coal category (OC-PAH and PAH-OC classes) and the amine-containing category (amines class).

mass spectral markers that identified the fuel from which they originated. As discussed in section 3.2.1, most PAH-containing particles detected during the Birr campaign were assigned to peat because of the small proportion of particles from domestic coal combustion. However, for the reasons outlined above, PAH-containing particles observed during the Enniscorthy campaign could not be definitively assigned to either peat or coal. However, they were clearly of domestic solid fuel combustion origins, as indicated by their mass spectra and temporal profiles.

3.3.5 Amine/ammonium-containing particles

Particles containing diagnostic ions for amines and ammonium were observed during all three sampling campaigns. The dominant alkylamine ion signal is at *m*/*z* 59, which corresponds to the molecular ion for trimethylamine (TMA; $^{59}N(CH_3)_3^+$), the most abundant alkylamine emitted globally, through animal husbandry activities (Ge *et al.*, 2011). Another peak for TMA was observed at *m*/*z* 42 ($C_2H_4N^+$), while the signal at *m*/*z* 114 ($^{114}(C_3H_7)_2NCH_2^+$) could be due to dipropylamine or tripropylamine. As shown in Figure 3.10, large signals were observed for ammonium ($^{18}NH_4^+$) and a marker for ammonium nitrate ($^{30}NO^+$), although this latter feature has also been assigned to methylamine ($^{30}CH_2NH_2^+$) in laboratory studies (Liu *et al.*, 2012). The average negative mass spectrum was dominated by sulfate, with smaller peaks for nitrate ($^{46}NO_2^-$, $^{62}NO_3^-$, $^{125}H(NO_3)_2^-$) and HMS ($^{111}HOCH_2SO_3^-$), which is further indicative of the aged nature of these particles (Moffet *et al.*, 2008). The average mass spectrum of this particle type also contained mass spectral signals for EC ($^{12}C^+$, $^{24}C_2^+$, $^{36}C_3^+$), hydrocarbon fragments ($^{27}C_2H_3^+$, $^{37}C_3H^+$, $^{43}C_2H_3O^+$) and $^{39}K^+$, suggesting that this particle class originates from SFB. However, fresh domestic SFB particles generated in the combustion experiments did not appear to contain amines, and it is therefore most likely that these particles were produced from the interaction of agricultural emissions of gaseous amines and ammonia with pre-existing combustion particles.

Amine-containing particles appear most similar in composition to the peat classes EC-OC and K-EC-OC, which were the dominant particle classes in each town and therefore the most abundant particles for gaseous alkylamine species to condense onto or react with. The three coal classes could also have acted as core particles for alkylamine gas-to-particle partitioning. Although the mass spectra for coal particles contain much larger signals for EC than for OC, the ATOFMS ion intensity is known to vary with the chemical composition of the particle (Reilly *et al.*, 2000). A particle containing EC, OC and amines will probably produce different ion intensities for each of these species, compared with the original combustion particle. Alkylamines have relatively low ionisation potentials (Angelino *et al.*, 2001) and ATOFMS sensitivity to ammonium is also much lower than for alkali metals such as K^+ and Na^+, particularly when these are in the same particle (Gross *et al.*, 2000). The large signals for NH_4^+ and TMA in the amine-containing particles are therefore indicative of a significant change in composition of the original combustion particle; direct comparison of the amine-containing, peat and coal particle mass spectra to identify which fuel type the processed combustion particles originated from may not be accurate.

3.3.6 Mass concentrations of particle categories

Figure 3.11 shows hourly mass concentrations for the ATOFMS particle categories during each of the three campaigns. Mass concentrations for the categories have been stacked to show how the combined ATOFMS mass concentrations compare with the $PM_{2.5}$ mass. It is clear that peak mass concentrations occurred in the evenings and were due to domestic solid fuel combustion. In Killarney, $PM_{2.5}$ and total ATOFMS mass concentrations peaked around 160 µg/m³, while in Enniscorthy concentrations exceeded 200 µg/m³ on four evenings and exceeded 50 µg/m³ on most other evenings. Stormy weather conditions during most of the Birr campaign probably contributed to lower $PM_{2.5}$ mass concentrations, which peaked around 60 µg/m³.

Figure 3.12 shows the averaged 24-hour profile for mass concentrations of ATOFMS particle categories during the three SAPPHIRE campaigns. Peat, wood and coal particles dominated the $PM_{2.5}$ mass; mass concentrations increased sharply between 15:00 and 16:00, peaked around 19:00 and by midnight had decreased to levels similar to those prior to the onset of evening burning activities. Averaged daily peak mass concentrations of all ATOFMS particles combined were 45 µg/m³, 60 µg/m³ and 9 µg/m³ for

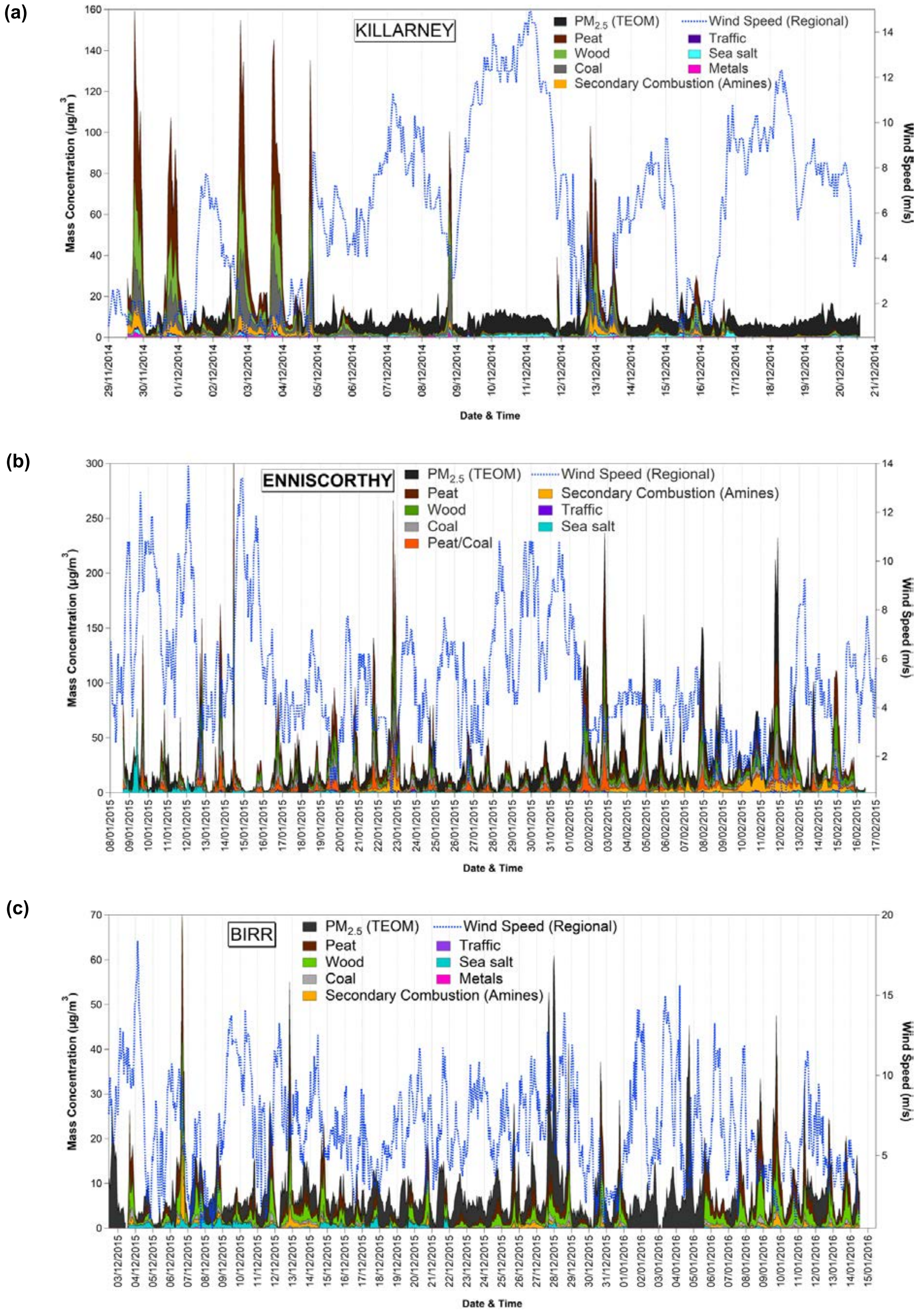


Figure 3.11. Time series of wind speed and hourly mass concentrations for the ATOFMS particle categories (stacked), compared with $PM_{2.5}$ mass concentrations, during the three SAPPHIRE campaigns: (a) Killarney, (b) Enniscorthy and (c) Birr.

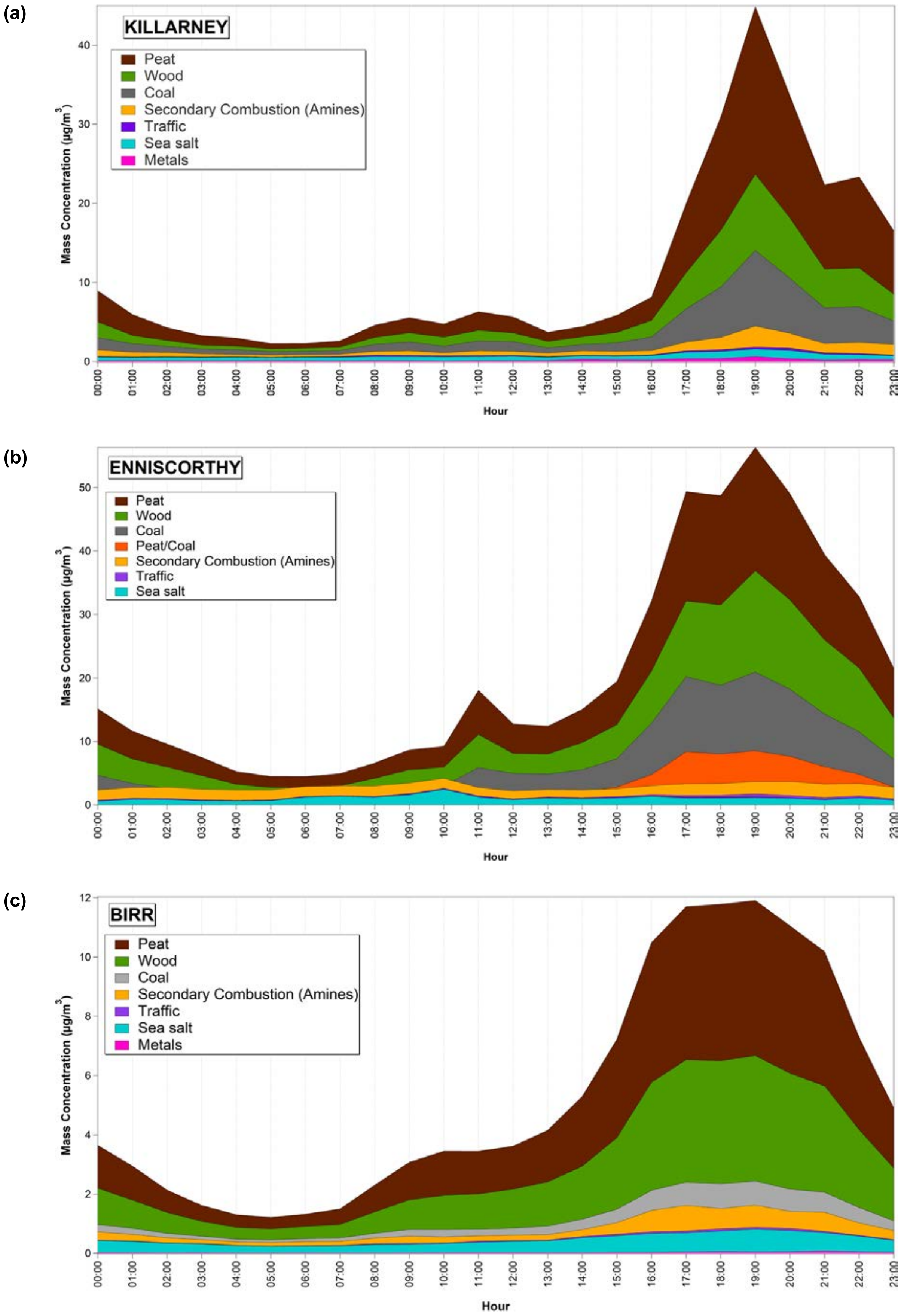


Figure 3.12. Averaged daily mass concentrations for ATOFMS particle categories during the three SAPPHIRE campaigns: (a) Killarney, (b) Enniscorthy and (c) Birr.

Killarney, Enniscorthy and Birr, respectively, and did not exceed 10 μg/m^3, 15 μg/m^3 and 3 μg/m^3, respectively, throughout the remainder of the averaged day. Average daily mass concentrations of all ATOFMS particles were 11 ± 12 μg/m^3 (range 2–45 μg/m^3) for Killarney, 24 ± 17 μg/m^3 (range 7–60 μg/m^3) for Enniscorthy and 5 ± 4 μg/m^3 (range 1–12 μg/m^3) for Birr.

Based on the composition and temporal profiles, it was possible to distinguish between local emissions (domestic solid fuel combustion) and regionally transported material (sea salt). In contrast to the regular nightly local emissions seen during the three campaigns, sea salt particles were observed only during specific periods. In Killarney, mass concentrations of these particles were clearly influenced by increases in wind speed (and, conversely, local emissions peaked significantly during nights with low wind speed – approximately 2 m/s); their regional origin is further supported by their wind direction dependence, shown in Figure 3.13. These "regional" periods also coincided with a large proportion of $PM_{2.5}$ mass that was unaccounted for by the ATOFMS particle categories. This could have been as a result of poor particle transmission efficiency in the supermicron size range. In Birr, sea salt particles were transported to the site by the three major Atlantic depressions (Desmond, 3–8 December; Eva, 22–25 December; Frank, 28–31 December) and effectively disappeared after these extended stormy conditions had passed (the next storm was Gertrude, around 29 January, after the campaign concluded).

Figure 3.13 shows the wind direction and wind speed dependences of the peat, amine and sea salt particle categories during the three SAPPHIRE campaigns. Wood and coal particles have identical dependences to peat, so they are not shown. For both the Killarney and Birr campaigns, peat particles exhibited a dependence on low wind speeds (< 5 m/s) and no strong dependence on any one wind direction, indicating an accumulation of particles from multiple domestic combustion sources. During the Enniscorthy campaign, the highest concentrations were seen during periods with winds of 8–10 m/s from the south-east. Amine-containing particles also exhibited a clear dependence on low wind speeds (< 5 m/s for Killarney and Enniscorthy; < 10 m/s for Birr) during all three campaigns and no strong directional dependence that would indicate a specific source. In contrast to locally produced domestic solid fuel combustion and amine-containing particles, the highest mass concentrations of sea salt particles were seen during the periods of highest wind speeds for all three campaigns. They also exhibited clear wind dependences: westerly for Killarney and Birr and south-westerly for Enniscorthy. This is consistent with the prevailing westerly or south-westerly winds from over the Atlantic that Ireland usually experiences.

Processed domestic solid fuel combustion particle composition (the presence of EC and $^{39}K^+$ markers) suggested that a strong association with freshly emitted combustion particles could be expected. Figure 3.14 shows a time series of mass concentrations of these processed, amine-containing particles compared with mass concentrations of peat particles, with meteorological variables (wind speed, temperature, relative humidity). Temporal behaviour of processed combustion particles varied for each campaign. In Killarney, peaks in mass concentrations for these particles coincided with every peak in peat mass concentrations. However, this was not the case during the other two campaigns; processed combustion particle mass concentrations did not display any regular nightly occurrence and were instead detected sporadically throughout the campaigns. Some peaks in mass concentrations did coincide with freshly emitted combustion particles: on 22 January 2015 in Enniscorthy and on 6 and 12 December 2015 in Birr. Variability was also apparent when comparing the average daily processed combustion particle mass concentrations for the three campaigns, as shown in Figure 3.12. Processed, amine-containing particles exhibited a clear diurnal variation in mass concentrations in Killarney, with a strong peak at 19:00 (approximately 2.7 μg/m^3), again coinciding with freshly emitted domestic combustion particles. Smaller evening peaks were seen in Enniscorthy and Birr, relative to concentrations during the rest of the day. Compared with fresh combustion particles, mass concentrations of amine-containing particles in Enniscorthy peaked 1–2 hours later, while in Birr their temporal profiles were very similar. This suggests that local conditions (possibly wind direction and speed, and proximity to agricultural activities), particularly in Enniscorthy, affected the processing of fresh combustion particles to form amine-containing particles.

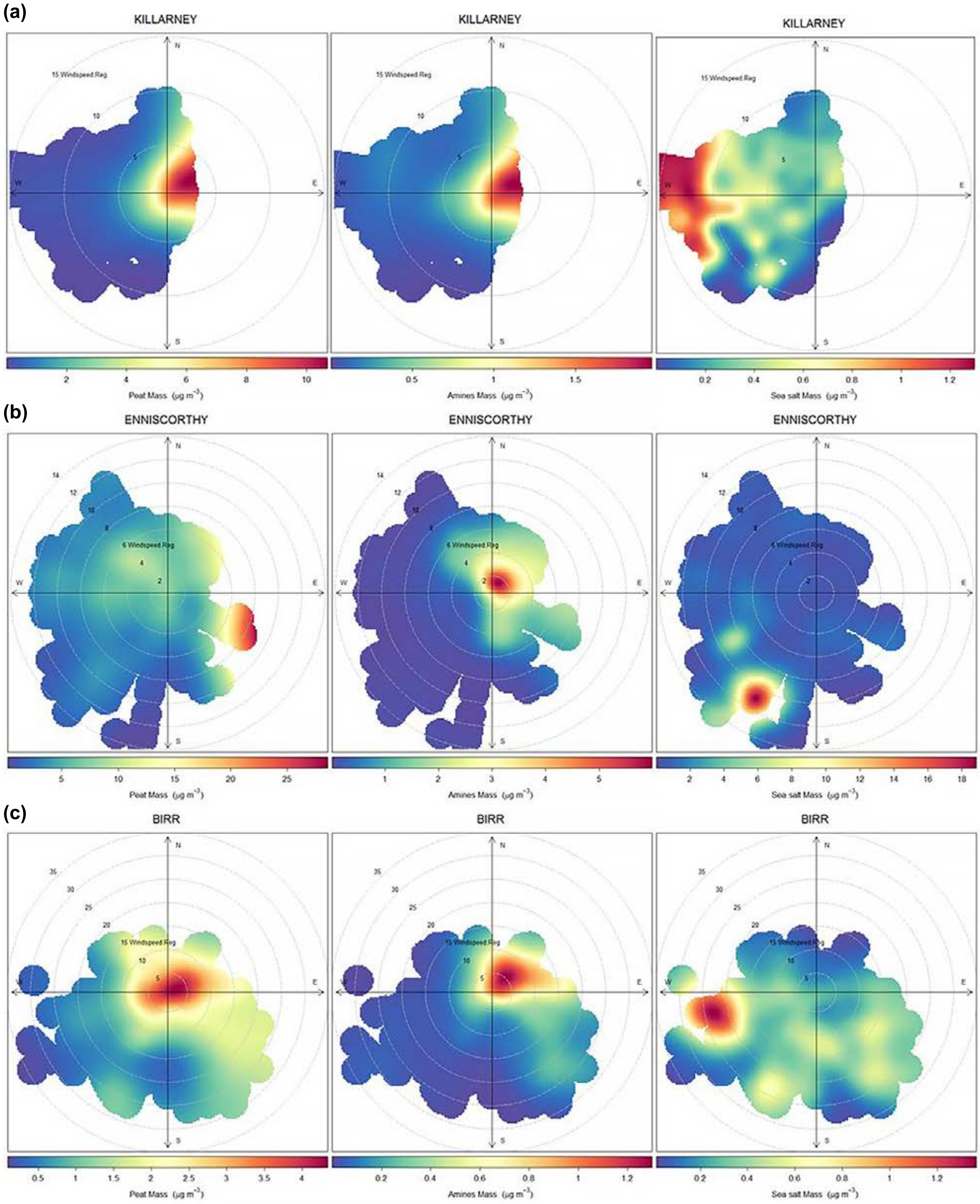


Figure 3.13. Wind speed and direction dependences of mean mass concentrations of ATOFMS peat, amine and sea salt particles during the three SAPPHIRE campaigns: (a) Killarney, (b) Enniscorthy and (c) Birr.

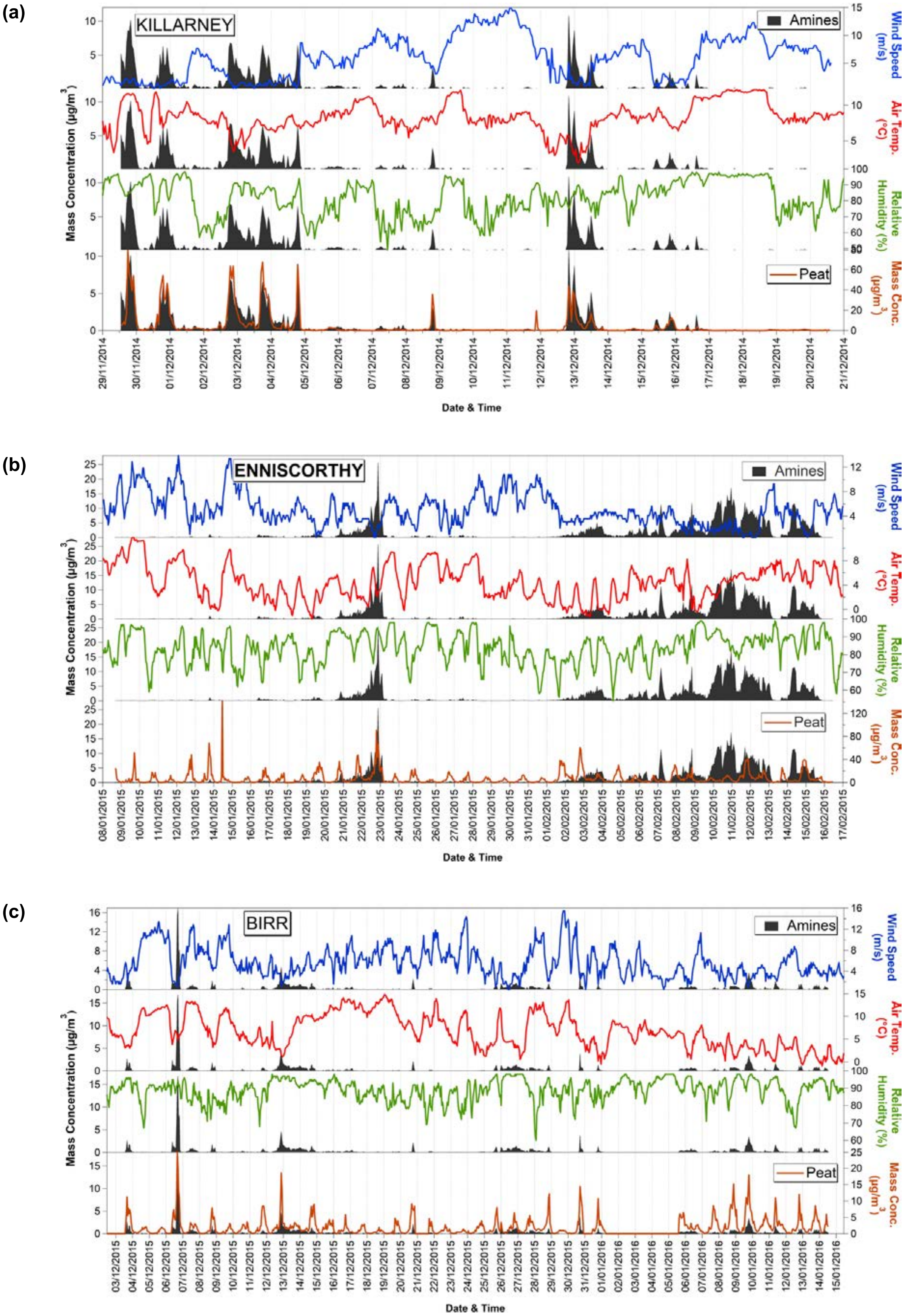


Figure 3.14. Time series of hourly mass concentrations of ATOFMS amine-containing particles and peat particles, wind speed, air temperature and relative humidity during the three SAPPHIRE campaigns: (a) Killarney, (b) Enniscorthy and (c) Birr.

This variability in the association with fresh combustion particles could have been influenced by meteorological conditions. During a winter ATOFMS study in Cork, Ireland, the highest numbers of coal, peat and wood particles with strong signals for ammonium and nitrate were seen during the periods of lowest wind speed (Healy *et al.*, 2010). The enrichment of particles in alkylamines during periods of high relative humidity or fog events (Angelino *et al.*, 2001; Rehbein *et al.*, 2011) and during nights with cooler temperatures has been also been observed (Angelino *et al.*, 2001; Qin *et al.*, 2012). From Figure 3.14, it is apparent that neither air temperature nor relative humidity had a clear, consistent effect on processed, amine-containing particle mass concentrations. Wind speed may have influenced the detection of these particles during the Killarney campaign, with the highest mass concentrations observed during the periods of lowest wind speed (it generally affected local versus regional particle mass concentrations). The highest mass concentrations of processed combustion particles did coincide with the periods of lowest wind speed during both the Enniscorthy campaign (22 January 2015) and the Birr campaign (6 December 2015), but this effect was not as striking as that observed during the Killarney campaign.

3.4 Source Apportionment

Source apportionment was performed using version 5.0 of the PMF multivariate factor analysis tool, provided by the US EPA (Norris *et al.*, 2014). Two model approaches were employed. In model 1, averaged hourly data from all of the online instruments were used, while model 2 also incorporated the ATOFMS particle classes as particle counts per hour. Model 1 contains a much smaller number of parameters and only a limited number of factors (and hence sources) are likely to be identified. However, because the measured parameters (EC, OC, BC, etc.) are very relevant to combustion sources such as SFB and vehicle emissions, it is expected that a reasonable first approximation of the SCEs can be obtained from this limited dataset. The incorporation of the ATOFMS particle types into model 2 provides highly unique markers of specific sources, and it is expected that the SCEs will be vastly improved compared with the simpler models and the "sample" numbers can be adjusted to the highest appropriate temporal resolution. The results from both models are presented in three parts: (1) a factor fingerprint, which shows the number of factors (sources) and the relative contribution that every factor makes to each measured parameter; (2) a temporal profile of the identified factors; and (3) a pie chart showing the SCEs for the factors.

3.4.1 Killarney

Results from the PMF analysis performed using model 1 are presented in Figure 3.15. A three-factor solution was generated. The first factor (SF1) is dominated by OC and BC_{SF} and has a clear night-time peak, pointing to residential SFB as the source. The second factor (SF2) has a very similar temporal profile but is dominated by the particle number categories. A third factor (traffic) accounts for a large portion of the BC_{Tr} and most of the nitrogen dioxide. It peaks during morning and evening hours and is therefore attributed to a traffic source. The SCEs shown in the pie chart indicate that residential SFB accounts for just over 75% of the $PM_{2.5}$ mass concentration, with the remainder attributed to traffic. Note that, while the SF2 factor is part of the solution, i.e. it is required to explain the variance in the data, its contribution to the $PM_{2.5}$ mass concentration is negligible.

When including the ATOFMS particle classes in the model (model 2), several interesting solutions are possible, and more than one solution is able to explain the data. However, common to all solutions – whether they involve four, five or six factors – is a dominant factor characterised by strong contributions to carbonaceous aerosol and particle numbers. In the four-factor solution presented in Figure 3.16, this factor is labelled SF1 because of the composition and temporal profile. Another factor (traffic) is associated with BC_{Tr}, as well as the EC-traffic and K-Ca particle types, and shows a temporal profile typical for traffic. The two other factors (mixed and aged) have a mixture of components and a non-specific temporal profile. They are assigned to mixed or aged combustion particles. Despite the added complexity in this model, the SCE for residential SFB still remains around 70%.

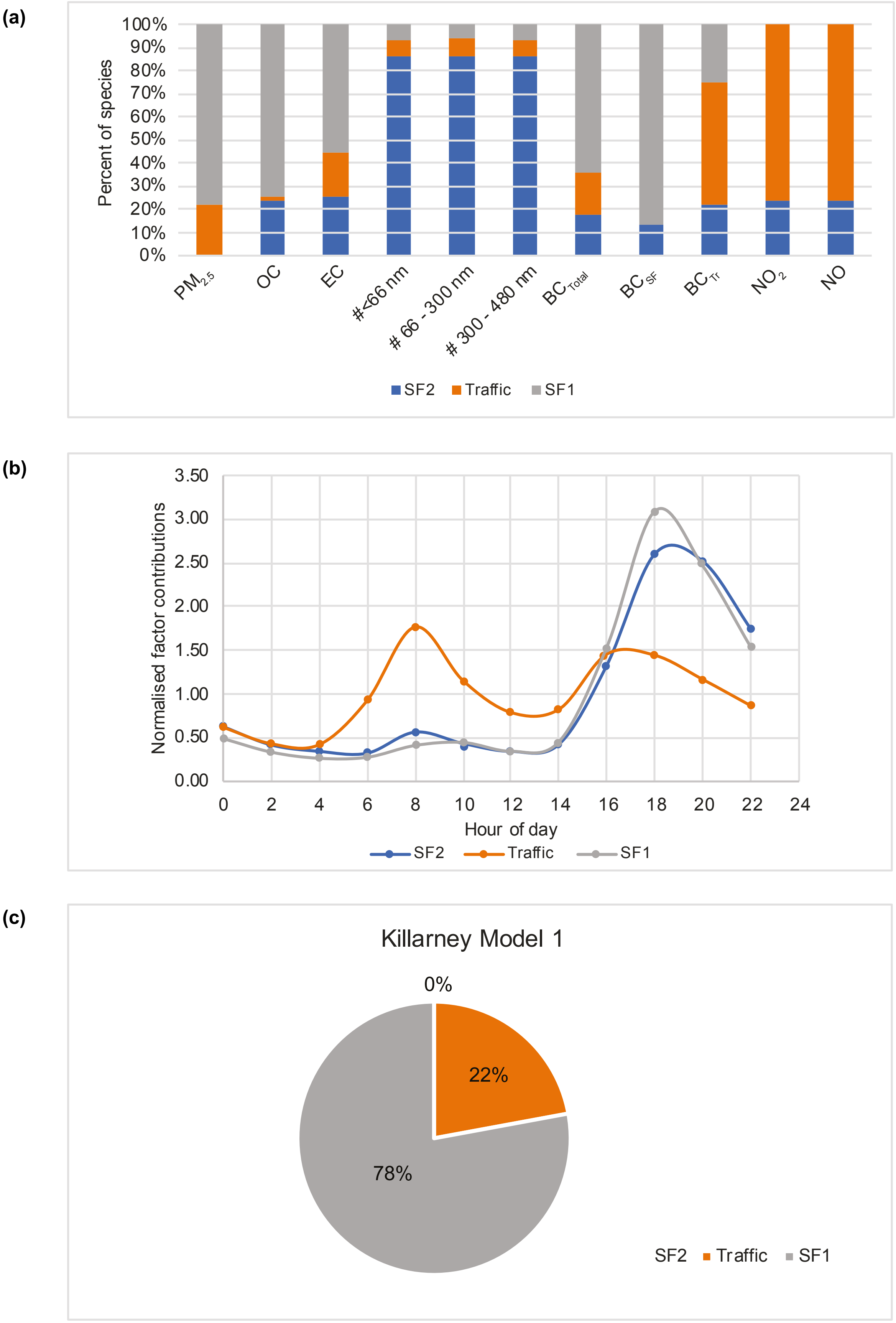


Figure 3.15. Results from PMF analysis of all online measurements, except the ATOFMS data (model 1), for Killarney: (a) factor fingerprint, (b) daily trend in factors and (c) SCEs for the factors.

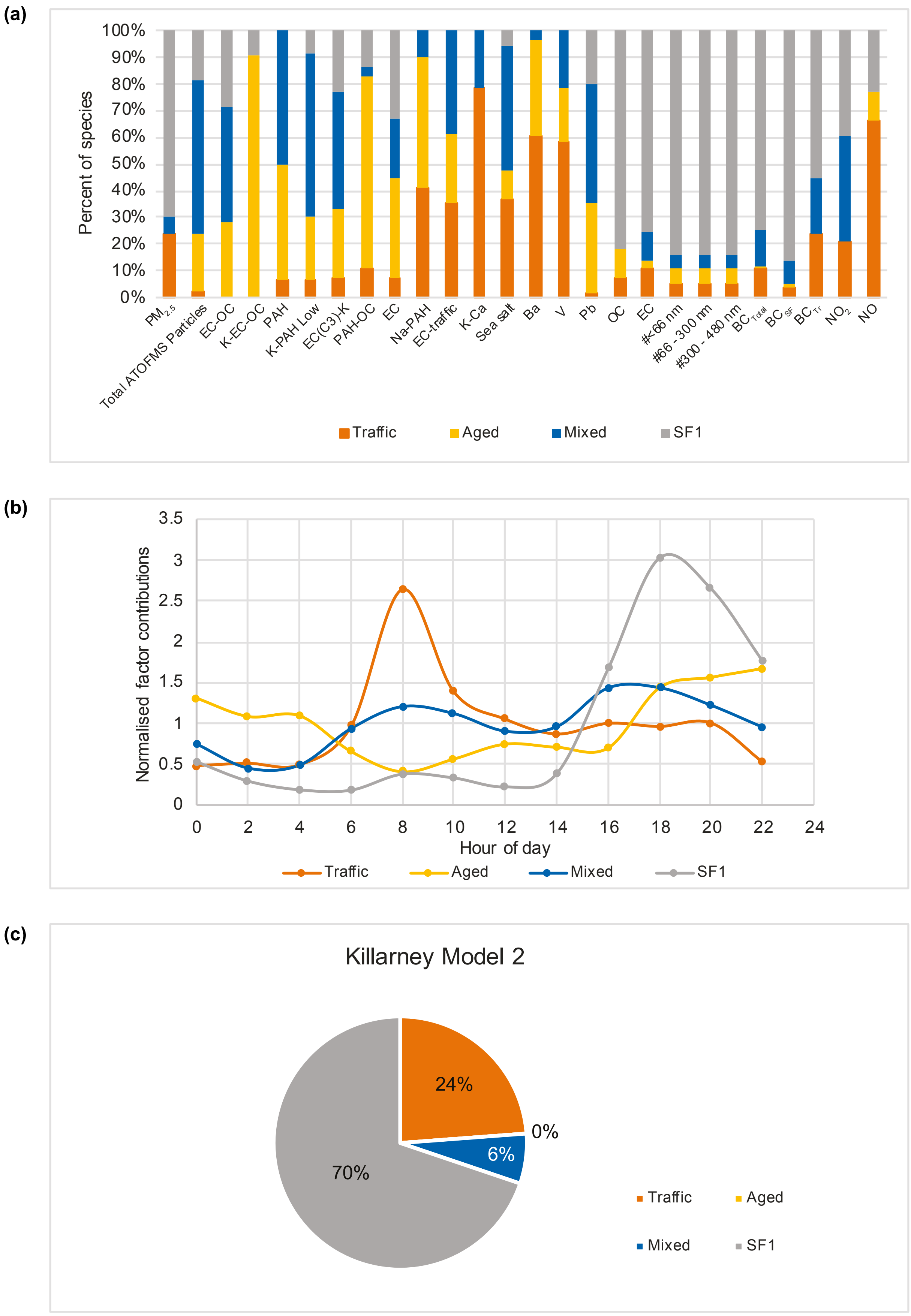


Figure 3.16. Results from PMF analysis of all online measurements, including the ATOFMS data (model 2), for Killarney: (a) factor fingerprint, (b) daily trend in factors and (c) SCEs for the factors.

3.4.2 Enniscorthy

Results from the PMF analysis performed using model 1 on the Enniscorthy data also generated a three-factor solution, as shown in Figure 3.17. There are two clear factors associated with residential SFB (SF1 and SF2) that have slight differences in temporality. The first factor (SF1) is dominated by small particle numbers, while SF2 is very strongly associated with BC_{SF}, OC, EC and larger particle sizes. Both of these factors have a very similar temporal profile with a clear night-time peak, pointing to residential SFB as the source. The third factor (traffic) accounts for all of the BC_{Tr}. Overall, residential solid fuel combustion represents 75% of the $PM_{2.5}$ mass concentration, while traffic contributes 25%.

The corresponding results for model 2 are shown in Figure 3.18. A four-factor solution was obtained, with SF1 as the dominant factor, which was strongly associated with OC, BC and other carbonaceous components. The traffic factor accounts for half of the BC_{Tr} and EC, although the temporal profile is not as convincing as in model 1. Two other carbonaceous factors, labelled “aged” and “mixed”, make up the remainder. Overall, the three combustion factors make up 80% of the $PM_{2.5}$ mass, with traffic remaining at 20%. It therefore appears that the main impact of adding the ATOFMS particle types is to break down the combustion factor into several components, without significantly changing the contribution to the $PM_{2.5}$ mass concentration.

3.4.3 Birr

The results for Birr are very similar to those obtained at the other sites. A three-factor solution is obtained using both model 1 and model 2, as shown in Figures 3.19 and 3.20, respectively. In both models, two SFB factors are obtained, which account for 92% of the $PM_{2.5}$ mass concentration, with traffic contributing 8%.

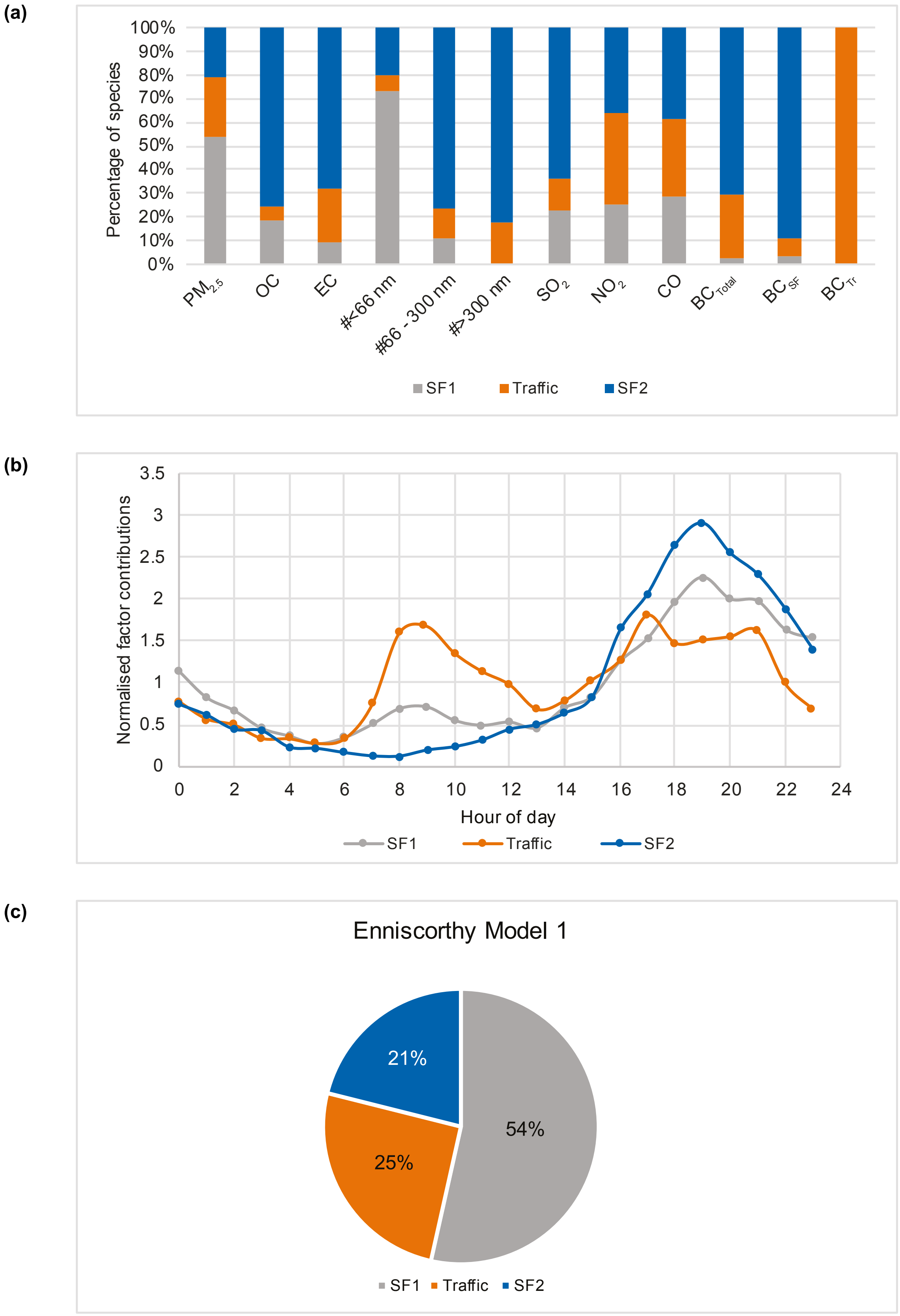


Figure 3.17. Results from PMF analysis of all online measurements, except the ATOFMS data (model 1), for Enniscorthy: (a) factor fingerprint, (b) daily trend in factors and (c) SCEs for the factors.

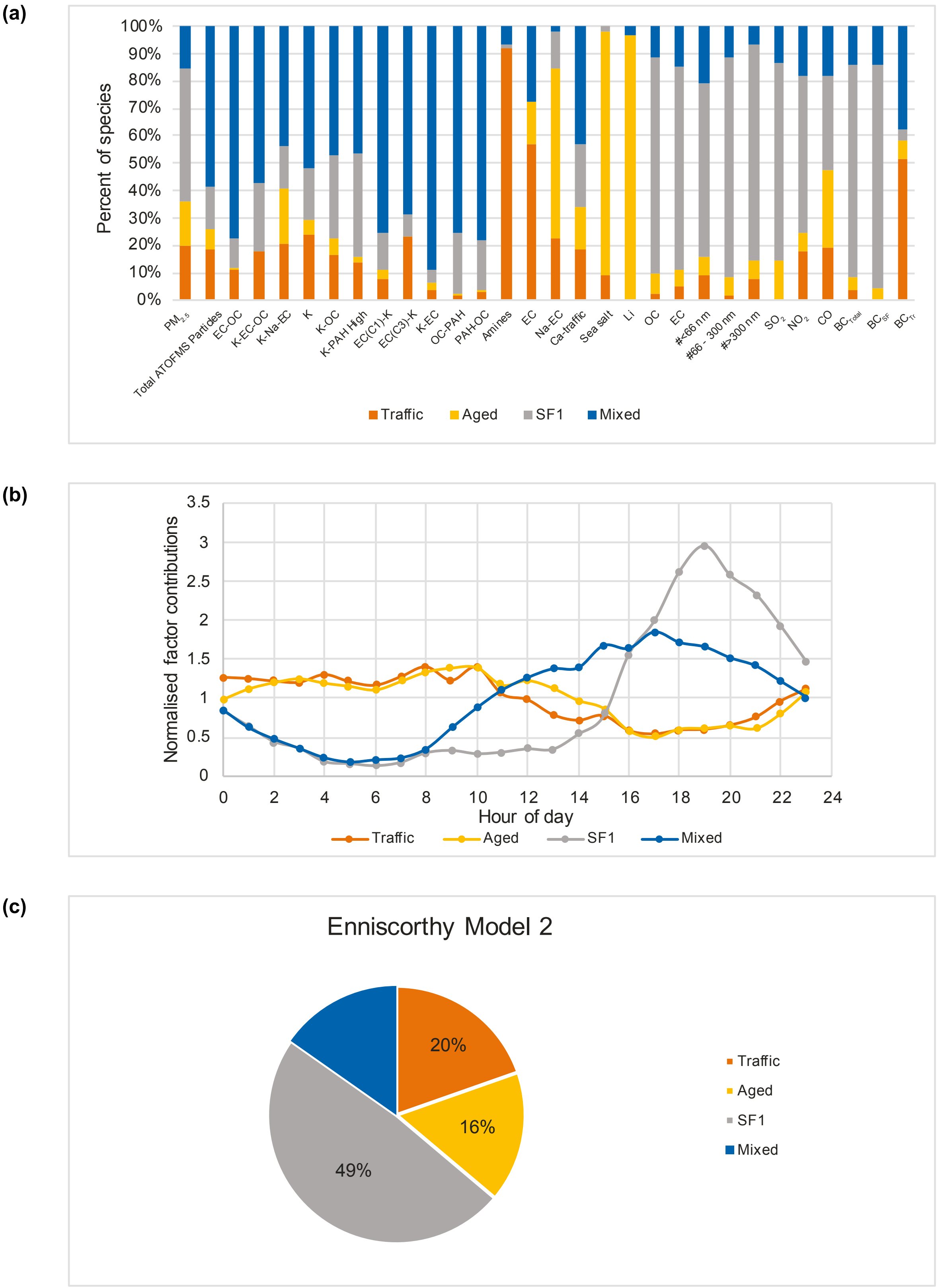


Figure 3.18. Results from PMF analysis of all online measurements, including the ATOFMS data (model 2), for Enniscorthy: (a) factor fingerprint, (b) daily trend in factors and (c) SCEs for the factors.

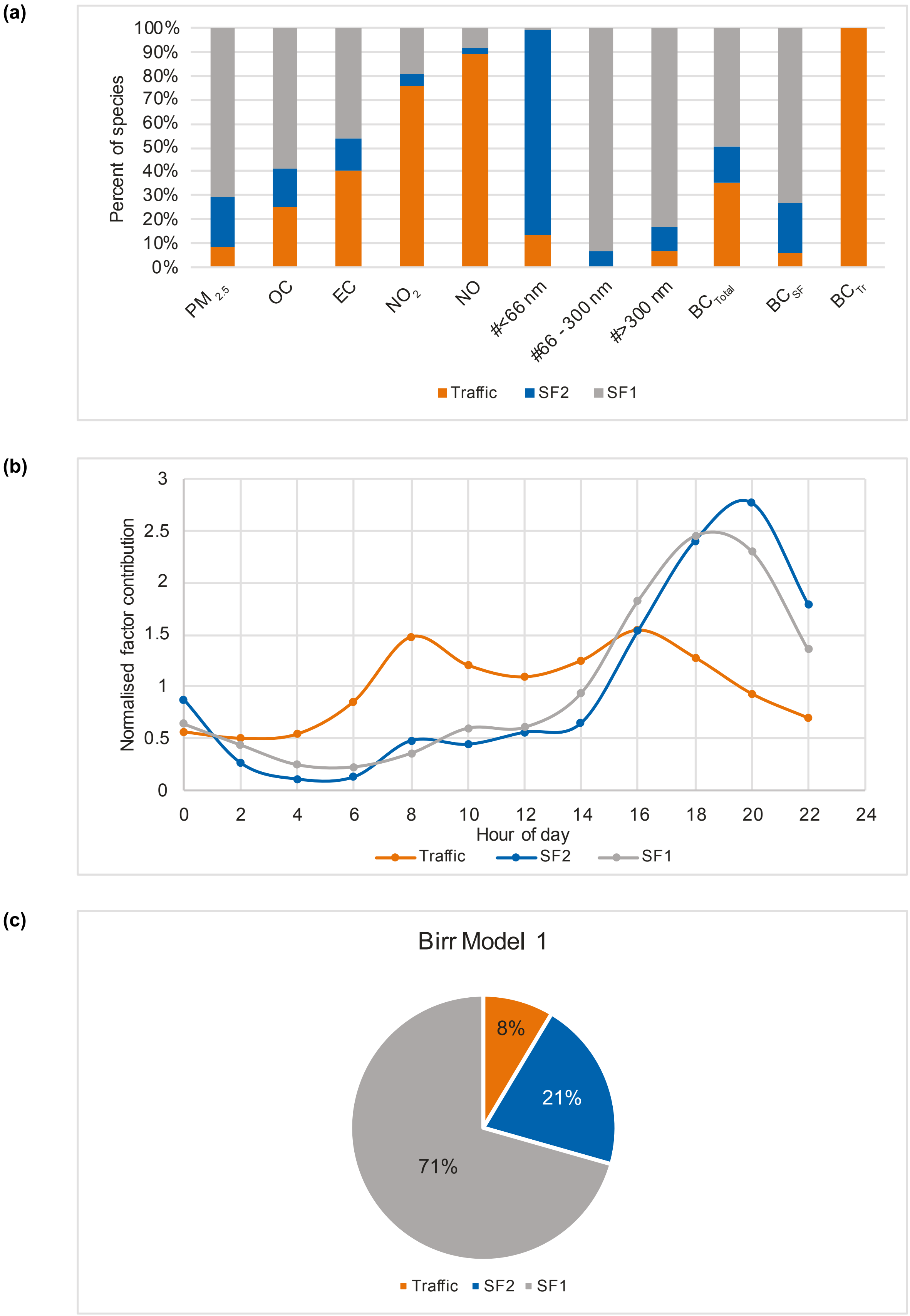


Figure 3.19. Results from PMF analysis of all online measurements, except the ATOFMS data (model 1), for Birr: (a) factor fingerprint, (b) daily trend in factors and (c) SCEs for the factors.

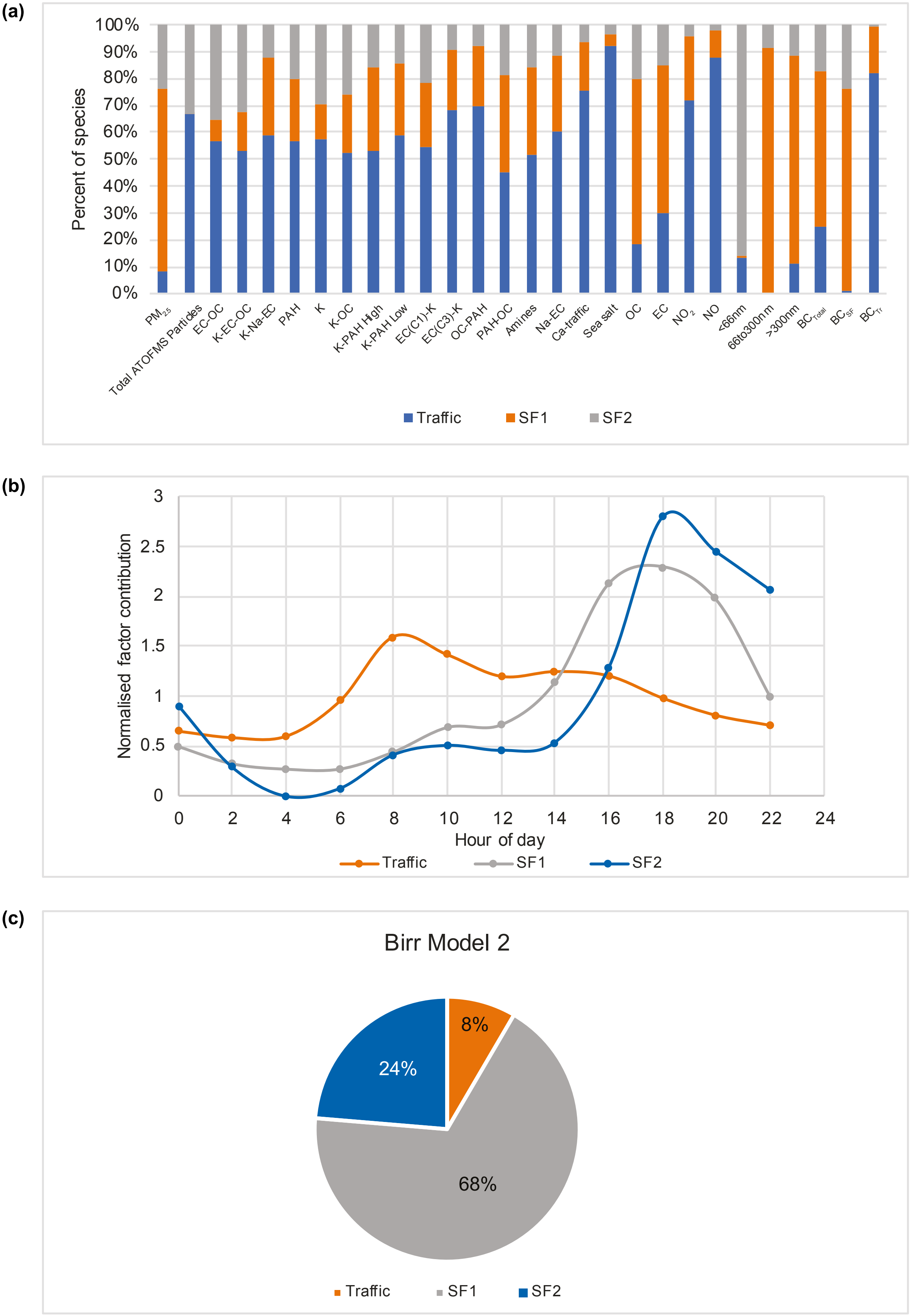


Figure 3.20. Results from PMF analysis of all online measurements, including the ATOFMS data (model 2), for Birr: (a) factor fingerprint, (b) daily trend in factors and (c) SCEs for the factors.

4 Conclusions and Recommendations

The sources of wintertime $PM_{2.5}$ in three rural Irish towns (Killarney, Enniscorthy and Birr) have been determined using a combination of field measurements and receptor modelling. Levels of $PM_{2.5}$ during evening hours were often an order of magnitude higher than those measured during the day, and huge spikes in pollution were regularly observed when wind speeds were low. Particulate pollution was highest in Enniscorthy, where $PM_{2.5}$ levels averaged 29.2 $\mu g/m^3$ and a high of 236.6 $\mu g/m^3$ was recorded. Furthermore, the WHO 24-hour mean guideline value of 25 $\mu g/m^3$ was exceeded on 42% of the days (16 out of 38), and on every one of these days the highest hourly average $PM_{2.5}$ was $> 50\ \mu g/m^3$. The same pattern was observed at the other sites, although the pollution levels were lower. Killarney experienced a mean $PM_{2.5}$ value of 15.3 $\mu g/m^3$ and four exceedances of the WHO 24-hour mean guideline value in 40 days. Birr was the least polluted site, with a mean $PM_{2.5}$ value of 7.9 $\mu g/m^3$ and no exceedances of the WHO 24-hour mean guideline value in 43 days.

Real-time monitoring of the PM chemical composition using a single-particle mass spectrometer revealed nine major types of particles, which were assigned to specific sources using a “fingerprinting” approach. The dominant source category at all three monitoring locations was residential SFB, which accounted for 72%, 82% and 60% of $PM_{2.5}$ measured in Killarney, Enniscorthy and Birr, respectively. The two other sources of $PM_{2.5}$ identified at these sites were traffic and sea spray.

A considerable contribution to $PM_{2.5}$ mass during each campaign (approximately 5%) consisted of chemically processed combustion particles. These were characterised by a peat-like combustion particle containing TMA, ammonium and ammonium nitrate. TMA and ammonium are present as gases in the atmosphere and they probably originated from agricultural activities in the surrounding areas. This important result indicates that agricultural emissions can combine with combustion emissions to further particle growth and increase levels of $PM_{2.5}$.

State-of-the-art receptor modelling approaches were used to confirm that SFB was the major source of $PM_{2.5}$ at each site. The receptor models also identified traffic, sea spray and mixed agricultural/combustions as contributors to $PM_{2.5}$.

Importantly, the mass spectrometer “fingerprinting” approach was able to distinguish between combustion particles produced from the main solid fuels – coal, peat and wood. Peat particles accounted for 31%, 27% and 26% of the $PM_{2.5}$ mass in Killarney, Enniscorthy and Birr, respectively. Wood was the second most dominant combustion source (17%, 21% and 23%, respectively), followed by coal (16%, 17% and 5%, respectively). Based on Irish census data, all three fuels appear to be popular choices for domestic space heating in Killarney, while coal dominates in Enniscorthy and peat is most common in Birr. However, the results presented here indicate that particles from the combustion of all three fuel types were present in all three towns. As there was no one clearly dominant solid fuel combustion emissions source, measures such as a smoky or low-smoke coal ban in these areas may be only partly successful in reducing $PM_{2.5}$ concentrations. Future efforts to improve air quality in these towns, and others like them, will need to address how domestic residences are heated in general, rather than attempting to discourage the use of one specific fuel.

If measures such as a nationwide ban on the use of smoky coal are implemented, it is recommended that a follow-up study is conducted in these three towns to assess their impact on air quality. Future research in this area could also involve more detailed molecular characterisation of the organic components in $PM_{2.5}$, to better elucidate the sources and toxic effects of SFB emissions.

This research clearly showed the benefits of deploying state-of-the-art instrumentation for the real-time monitoring of chemical composition in order to deliver highly time-resolved information on the sources of $PM_{2.5}$. It is therefore recommended that further investment is made in this area, with efforts focusing on expanding the source apportionment capabilities across the national air quality monitoring network. One cost-effective way of doing this could be through the deployment of aethalometers, which were shown to be very effective in apportioning BC to solid fuel and traffic sources in near real time. Further research on BC is also recommended, as reductions in this pollutant would have co-benefits for both air quality and climate.

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Abbreviations

AMS	Aerosol mass spectrometer
ATOFMS	Aerosol time-of-flight mass spectrometer
BC	Black carbon
BC_{SF}	Solid fuel burning-related black carbon
BC_{Total}	Total measured black carbon mass
BC_{Tr}	Traffic-related black carbon
D_a	Aerodynamic diameter
EC	Elemental carbon
EPA	Environmental Protection Agency
HMS	Hydroxymethanesulfonate
MDL	Method detection limit
m/z	Mass-to-charge ratio
NO_X	Nitrogen oxides
OC	Organic carbon
OPS	Optical particle sizer
PAH	Polycyclic aromatic hydrocarbon
PCA	Principal component analysis
PM	Particulate matter
$PM_{2.5}$	Particulate matter with a diameter of less than 2.5 microns
PM_{10}	Particulate matter with a diameter of less than 10 microns
PMF	Positive matrix factorisation
SAPPHIRE	Source Apportionment of Particulate Matter in Urban and Rural Residential Areas of Ireland
SCE	Source contribution estimate
SFB	Solid fuel burning
SMPS	Scanning mobility particle sizer
TEOM	Tapered element oscillating microbalance
TMA	Trimethylamine
WHO	World Health Organization

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL

Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: *Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.*

Eolas: *Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.*

Tacaíocht: *Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.*

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:

- saoráidí dramhaíola *(m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola)*;
- gníomhaíochtaí tionsclaíocha ar scála mór *(m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta)*;
- an diantalmhaíocht *(m.sh. muca, éanlaith)*;
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe *(OGM)*;
- foinsí radaíochta ianúcháin *(m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha)*;
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil *(m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí)*.

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn *(m.sh. mórphleananna forbartha)*.

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol *(m.sh. Timpeall an Tí, léarscáileanna radóin)*.
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

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Source Apportionment of Particulate Matter in Urban and Rural Residential Areas of Ireland (SAPPHIRE)

Authors: John Wenger, Jovanna Arndt, Paul Buckley, Stig Hellebust, Eoin McGillicuddy, Ian O'Connor, John Sodeau and Eoin Wilson

epaResearch
Climate - Water - Sustainability
Identifying pressures • Informing policy • Developing solutions

Ireland is seeking to reduce levels of particulate matter with a diameter of less than 2.5 microns ($PM_{2.5}$) in order to protect human health and the environment. This goal can be achieved by developing and implementing policies that target reductions in the emissions of known sources of pollution. In this research project, the contribution of residential solid fuel burning to ambient levels of wintertime $PM_{2.5}$ was determined in the towns of Killarney, Enniscorthy and Birr. The results show that the burning of peat, coal and wood for home heating is by far the largest source of $PM_{2.5}$ air pollution in these locations.

Identifying Pressures

The European Environment Agency has identified air pollution as the single largest environmental health hazard in Europe. PM2.5 is the pollutant with the greatest impacts on human health, accounting for over 1100 premature deaths each year in Ireland. Detailed information on the composition and sources of $PM_{2.5}$ is required for establishing policies to reduce emissions and protect public health. Residential solid fuel burning is known to be a significant source of $PM_{2.5}$ in the main cities of Ireland; however, comparable information is not available for the many small towns across the country. In this project a combination of field measurements and source apportionment modelling was used to investigate the sources of $PM_{2.5}$ in Killarney, Enniscorthy and Birr. At each location, evening levels of $PM_{2.5}$ were often an order of magnitude higher than those during the day, and huge spikes in pollution were regularly observed when wind speeds were low. Real-time monitoring of the chemical composition of $PM_{2.5}$ showed that residential solid fuel burning was the dominant source category, accounting for 72%, 82% and 60% of $PM_{2.5}$ measured in Killarney, Enniscorthy and Birr, respectively. Using chemical fingerprints of particles generated from the combustion of different solid fuels, it was shown that burning of peat was the dominant source at each location, followed by burning of wood and then coal.

Informing Policy

The research findings show that new measures and policies are urgently needed to reduce harmful emissions from residential solid fuel burning across the country. As peat and wood were found by this study to be major contributors to $PM_{2.5}$, the introduction of a nationwide smoky coal ban is unlikely to lead to significant air quality improvements in small towns. Measures to reduce emissions from all solid fuels – peat, wood and coal – would be more successful in improving air quality for all urban centres including small towns. Future efforts will need to address how domestic residences are heated in general, rather than attempting to discourage the use of one specific solid fuel.

Developing Solutions

This research clearly showed the benefits of deploying state-of-the-art instrumentation for the real-time monitoring of chemical composition in order to deliver detailed information on the sources of $PM_{2.5}$. Source receptor modelling is also proven to be effective in identifying and quantifying the sources of air pollution. It is therefore recommended that further investment is made in this area, with efforts focusing on expanding the source apportionment capabilities across the national air quality monitoring network. The information generated by an enhanced network will inform the development of policies that not only are essential for the protection of health and the environment, but also help to mitigate the damage caused by climate change.

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