

STRIVE

Report Series No.71

Composition and Sources of Particulate Air Pollution in a Port Environment, Cork, Ireland

STRIVE

Environmental Protection
Agency Programme

2007-2013

Environmental Protection Agency

The Environmental Protection Agency (EPA) is a statutory body responsible for protecting the environment in Ireland. We regulate and police activities that might otherwise cause pollution. We ensure there is solid information on environmental trends so that necessary actions are taken. Our priorities are protecting the Irish environment and ensuring that development is sustainable.

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EPA STRIVE Programme 2007–2013

Composition and Sources of Particulate Air Pollution in a Port Environment, Cork, Ireland

**Air Pollution in Cork Harbour, Ireland:
Environmental Linkages of In-Port Ship Emissions of Particulate
Matter, their Chemical Analysis and Effects on Health (ELIPSE)**

(2006-EH-MS-49)

STRIVE Report

Prepared for the Environmental Protection Agency

by

University College Cork

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The EPA STRIVE 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

This report provides the Environmental Protection Agency with quantitative assessments for the various source contributions of airborne particulate matter (PM) to the Port and Harbour of Cork regions during the 2007/2009 period.

The study was based on three main foundations:

1. A 28-month PM, aerosol and trace gas monitoring programme was performed at two selected sites, one in the Upper Harbour (Tivoli Docks and Estates) and the other Mid-Harbour (located at the Naval Base on Haulbowline Island).
2. A chemical analysis programme was mounted suitable for the measurement of inorganic and organic compounds as well as real-time parameters such as elemental carbon levels and the efficiency of oxidation of gaseous sulfur compounds to particulates.
3. Statistical treatments of the obtained analytical data were performed in order to provide source apportionment assessments of the contrasting origins of the measured PM.

Understanding the composition and sources of particulate matter such as $PM_{2.5}$ ¹ is important for evaluating its effects on health and thereby establishing national and international policies for reducing its emissions. Ambient concentration is the current metric used in legislative instruments for limiting airborne particulates but it has become increasingly clear with reference to a variety of international scientific co-operations (e.g. COST ACTION 633 Particulate Matter: Properties Related to Health Effects) that it is also necessary to provide assessments of other particulate/aerosol parameters such as size distribution and particle number. These properties are especially relevant to health matters when considered alongside chemical composition studies. In this context, one relatively ignored source of PM has been that derived from ship emissions. The

results obtained in the ELIPSE² programme represent the first systematic study of the airborne pollution associated with ship traffic in an Irish harbour region and provide much novel data on the contributions of the various sources of airborne pollution in the Port of Cork environs.

Five inter-linked topics were studied within the ELIPSE programme, which provide the first 'snapshot' picture of airborne pollution associated with a busy Irish Harbour location:

1. An aerosol time-of-flight mass spectrometer and a particle-number counter were co-located with a suite of real-time monitoring instrumentation at the Tivoli Docks in the Port of Cork, Ireland. The data provided novel evidence for a unique ship exhaust class containing internally mixed elemental carbon/organic carbon, sodium, calcium, iron, vanadium, nickel and sulfate. The measurements indicated that the vast majority of freshly emitted ship exhaust particles lie in the ultrafine mode (<100 nm diameter). Subsequent source apportionment analysis showed that the measured shipping traffic contributes only 1.5% to the ambient $PM_{2.5}$ mass collected but 18% to the total number of particles detected. This value is second only to road traffic (with a contribution of 42%). Thus, it appears that local shipping traffic can contribute significantly to local ambient particle number in the inhalable, deep-penetrating, 20- to 600-nm size range.
2. Domestic solid-fuel burning was found to comprise an important contribution to Harbour airborne pollution even in the summer period. The data showed that the organic composition of the collected aerosols was mainly associated with anthropogenic and biogenic emissions from local sources.

2. ELIPSE, Environmental Linkages of In-Port Ship Emissions of Particulate Matter, their Chemical Analysis and Effects on Health.

1. $PM_{2.5}$, PM with diameter less than 2.5 μm .

3. On average, approximately 50% by mass of the chemical content of PM_{2.5} was unambiguously identified in this study. The major inorganic constituents identified in the PM were sulfate, ammonium, nitrate, chloride and sodium ions, which were mainly attributable to sea salt and secondary inorganic aerosols from regional sources.
4. By scrutinising the data sets gathered at Tivoli Docks and Haulbowline Naval Base using various independent source apportionment techniques, the existence and location of a specific sulfate source was established, which appears to be located east-south-east and south-east of the receptor site. In this general direction lies the industrialised Little Island, the ESB power plant located at Aghada, and the Whitegate oil refinery.
5. Mostly all elements detected exhibit higher ambient concentration levels at Tivoli Docks than

at Haulbowline Naval Base – in line with a general dilution pattern of pollution sources generally observed across the Harbour. However, the average ambient concentrations for chromium and cadmium were higher at Haulbowline Naval Base than at Tivoli Docks. Chromium and cadmium were also found to be strongly correlated, which would indicate a common source. The findings indicate a possible contribution from re-suspended waste material associated with a disused steel manufacturing facility located on the island. It is important to note that although chromium and cadmium metals are clearly present in PM_{2.5} of the ambient air at the Haulbowline Naval Base receptor site, their concentrations are detected only at levels associated internationally with rural/urban background monitoring sites as opposed to heavily industrialised locations.

1 Introduction

The development of national and international policy on air quality issues related to the protection of human health and climate change effects on our environment is underpinned by systematic research on ambient air particulate pollution. Knowledge based on reliable data collection for airborne particulate matter (PM), the identification of specific particles that are hazardous to the quality of life and also the chemical processing of atmospheric aerosols are essential in order to service our abilities to devise and draft fair and appropriate legislative instruments. Hence, the main aims of the ELIPSE¹ programme were to chemically characterise airborne particulate matter (PM_{10-2.5}, PM_{2.5} and other)² present in the Port of Cork and its Harbour and to compare the results obtained with those determined in other locations. The specific driving force for the studies was based on the worldwide recognition that ship emissions comprise a major, relatively unmeasured, source of pollution with potentially adverse effects on human health.

1.1 Particulate Matter

Airborne PM is a mixture of solid and liquid particles suspended in the atmosphere, often referred to as aerosols. The chemical and biological content of PM in aerosols can be complex and varies spatially between urban and rural and continental and marine environments (Finlayson-Pitts and Pitts, 2000). These particles are important both in terms of their impact on the global environment and also on public health. Indeed, it is now well established that exposure to PM_{2.5} can lead to significant impacts on human health and it has been directly linked to cardiopulmonary morbidity and mortality (Pope and Dockery, 2006). Currently, PM_{2.5} is thought to pose potential health risks at all levels of exposure although it is not established how differences in chemical composition might affect thresholds. In this regard, many data have

been collected on the toxicological mechanisms that could relate the effects of chemical composition to cellular oxidant generation (Pourazar et al., 2005; Kelly and Mudway, 2007). Links to adverse human health concerns have thereby been developed using a variety of methodologies (Wessels et al., 2010). For example, it has been estimated that life expectancy in Europe is reduced by an average of 9 months as a result of exposure to anthropogenic fine particles (Amann et al., 2005). Given such concerns, which have been raised increasingly by chemists, toxicologists and epidemiologists, it is clear that any meaningful reduction in adverse population exposure, both episodic and chronic, to ambient PM can only be achieved cost-effectively if the sources of ambient PM are first identified and their impacts then classified.

1.2 Pollutant Sources

A requirement clearly exists for researchers and responsible authorities to create local and regional inventories of pollutant emissions and to link these data to sources. Such an approach is an important prerequisite if future European Union (EU) limits set from a variety of directives are to be met. However, quantifying emissions and most especially linking those emissions to sources, even at a local or regional scale, is a difficult task requiring a mixture of monitoring approaches (both real time and traditional), accurate chemical analysis and chemometric techniques to be employed. Harbour areas are particularly difficult to assess because they are generally dynamic areas housing industry, power-generation sites and other socio-economic drivers alongside a wide variety of transport modes, domestic residential inputs and natural marine emissions. Disentangling the respective sources in a modern port/harbour is therefore complex but can be approached using as its foundation a combination of continuous and intensive field campaigns. The results from these activities can then be used to produce extensive data sets of pollutant temporal and meteorological behaviour that can be treated using a

1. Environmental Linkages of In-Port Ship Emissions of Particulate Matter, their Chemical Analysis and Effects on Health.
2. PM_{2.5}, PM with diameter less than 2.5 µm; PM₁₀, PM with diameter less than 10 µm.

variety of source apportionment modelling methods. (Bruno et al., 2001).

1.3 Legislation

The Clean Air for Europe (CAFÉ) Directive (EP and CEU, 2008), which was published in 2008, superseded the Air Framework Directive and the first three Daughter Directives (First Daughter Directive 1999/30/EC, Second Daughter Directive 2000/69/EC, and Third Daughter Directive 2002/3/EC) and came into effect in June 2010. The standards set down in Irish air quality legislation correspond to the limits set down in the above Directive and in the Fourth Daughter Directive (2004/107/EC) which is concerned with heavy metals and polycyclic aromatic hydrocarbons (PAHs). The CAFÉ Directive (EP and CEU, 2008) sets an annual mean limit value for $PM_{2.5}$ of $25 \mu g/m^3$. Limit values, target values, together with upper and lower assessment thresholds, are set for individual pollutants including sulfur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3), carbon monoxide (CO), the heavy metals lead (Pb), cadmium (Cd), arsenic (As), nickel (Ni) and also benzene (C_6H_6).

1.4 Shipping

Identification of the various sources of anthropogenic PM in urban environments has received considerable attention, with traffic, biomass burning and industrial processes typically contributing significantly to mass concentration. However, there is a specific lack of data available regarding particulate emissions from ships and emissions inventories at harbour/port locations (Eyring et al., 2009). Information regarding size distributions of particles emitted from ship engine exhaust is sparse although it is expected that, in common with most large diesel engines, >80% of emitted PM will be PM_{10} or less with a significant proportion of these in the fine fraction, $PM_{2.5}$. Data on the chemical composition, other than sulfur content, is also relatively sparse (Swedish NGO Secretariat on Acid Rain, 2004) although much more was known in 2010 than in 2005 when the ELIPSE project commenced. One of the driving forces behind all the recent research programmes in harbour areas is the recognition that shipping emissions do contribute significantly, and in an adverse way, to pollution in coastal communities (Li et al., 2002; Endresen et al.,

2003). For example, international shipping has recently been linked with increased mortality in coastal regions, with an estimated 60,000 deaths from cardiopulmonary and lung cancer per annum attributed to emissions from ship exhaust (Corbett et al., 2007; Lubick, 2007). Particulate shipping emissions also contribute to the Earth's radiation budget due to their physical and optical properties (Corbett et al., 2007; Lack et al., 2009).

1.5 Aims of the ELIPSE Study

The main aims of the ELIPSE programme were to characterise the size and chemical composition of freshly emitted individual ship exhausts monitored in the Port of Cork and to estimate the contribution of individual sources, including transport and domestic solid-fuel (DSF) burning to air quality in Cork Harbour. The aims were achieved using the following set of objectives based on a combined monitoring and modelling approach:

- To conduct a 28-month continuous airborne monitoring programme for PM. This campaign included the collection of PM at two sites within Cork Harbour – Haulbowline Naval Base (Mid-Harbour) and Tivoli Docks and Estates (Upper Harbour). Two independent collection campaigns were conducted at each of these sites, providing a combined collection period of 28 months.
- To perform a detailed chemical analysis of the inorganic metal and ion content present in the fine fraction of the collected PM.
- To characterise the organic carbon (OC) content of the collected PM with a particular view to identifying distinguishing chemical tracers for domestic combustion products.
- To investigate the size and chemical composition of freshly emitted individual ship exhaust using a TSI 3800 Aerosol Time-of-Flight Mass Spectrometer (ATOFMS).
- To accumulate an extensive set of real-time data from a suite of instruments selected to measure trace gases – nitrogen oxides, ozone, sulfur dioxide, and particulate sulfate ion (SO_4^{2-}) during two intensive campaigns.

- To perform a preliminary source apportionment study using the data obtained from the off-line inorganic and organic analysis of aerosols in order to assess the contribution of major individual sources to ambient $PM_{2.5}$ levels.
- To use other real-time parameters, e.g. elemental and organic carbon (EC/OC) splits, S(IV)–S(VI)³ oxidation, and trace gas measurements, with a view to adding to the robustness of the developed source apportionment models.

3. Sulfur having an oxidation state of +4 to an oxidation state of +6.

2 Monitoring Methodologies

2.1 Sampling Campaign and Instrumentation

2.1.1 Locations

Two sampling sites were selected to represent environments with local pollutant sources that included shipping contributions. The City of Cork houses the second biggest port in Ireland, being located in one of the largest natural harbours in the world. The Port of Cork controls a number of facilities situated in the Harbour. Of these, Tivoli Docks and Estates located in the Upper Harbour and Ringaskiddy Deep Water Port located in the Mid-Harbour are the most commercially important. A detailed description of these sites is given below ([Fig. 2.1](#)).

2.1.1.1 Haulbowline Naval Base ($51^{\circ} 50' 30''$ N, $8^{\circ} 18' 25''$ W)

This sampling site ([Fig. 2.2](#)) was established at the end of 2006 and is located on grounds belonging to the Irish Naval Services. Particulate matter collections (105 individual samples) were made here between

April 2007 and May 2008 using a high-volume cascade impactor (HVCi). An automated weather station (Casella Nomad) was co-located with the HVCi to record meteorological parameters.

This site is located approximately 1.75 km north-east of Ringaskiddy Deep Water Port and approximately 1 km south of the Port of Cork's cruiser berthing at Cobh. Every ship entering the terminals at Tivoli Docks and City Quays further up the Harbour have to pass within 200–300 m of the sampling site. It is surrounded by the satellite towns of Carrigaline, Cobh, Ringaskiddy and Crosshaven. The whole region is influenced by industrial activities, including power plants (Aghada and Whitegate operated by the ESB and Bord Gáis, respectively, both located east-south-east of the site), production facilities centred around a cluster of industrial pharmaceutical companies based in and around the Mid-Harbour area to the south and south-west of the site, various transport modes and, finally, domestic heating sources.

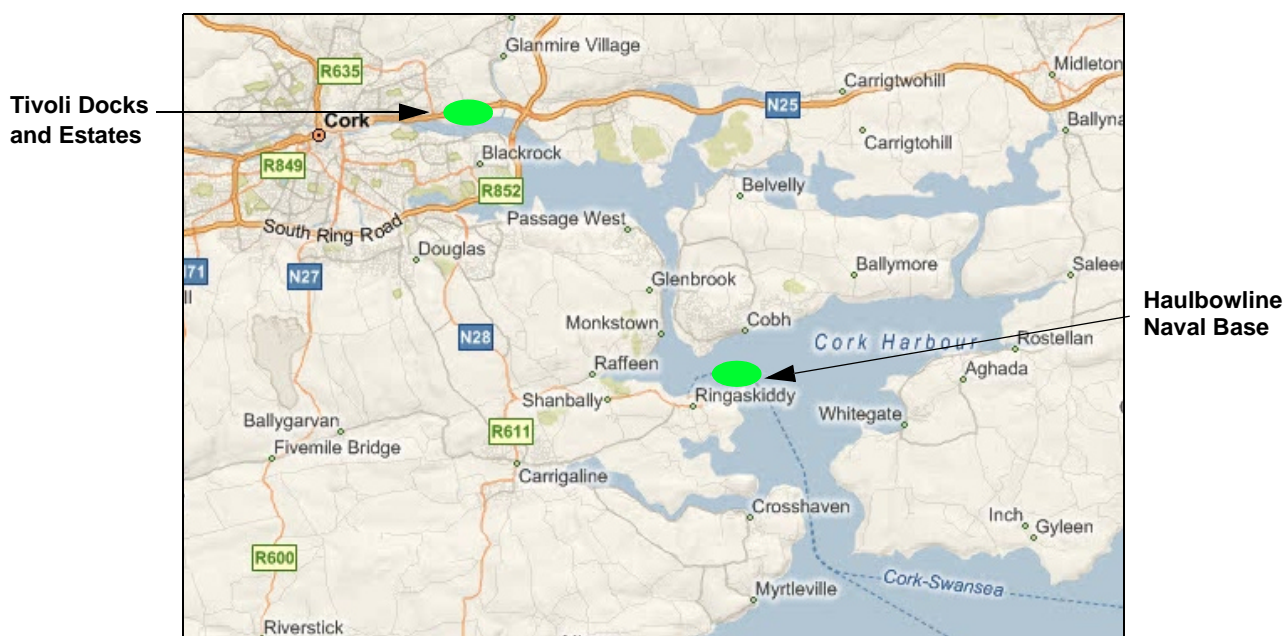


Figure 2.1. Geographical locations of sampling sites.



Figure 2.2. An aerial photograph of Haulbowline Naval Base. The location of the monitoring site is highlighted in green.

2.1.1.2 Tivoli Docks and Estates ($51^{\circ} 54' 05''$ N, $8^{\circ} 24' 38''$ W)

This location (Fig. 2.3) was the principal monitoring site for the ELIPSE research study. Tivoli Docks is the main container-handling terminal belonging to the Port of Cork and is located approximately 2.7 km due west of Cork City centre. This site is also approximately 200 m to the north-east of four shipping berths, including a liquid bulk tanker facility. The prevailing winds in Cork are from the south-west; hence, the predominant wind is from the direction of the main container berth and liquid bulk jetty of the Port of Cork. This site was

established in October 2007 and monitoring was carried out here from January 2008 to May 2009. A HVCi collected PM over this period and, in total, 133 collections were made. The Lower Glanmire Road, a busy access route into Cork, is located approximately 400 m north of the site and runs parallel to the Docks. Hence, this receptor site is situated in a complex environment supporting a variety of industrial and domestic activities. The port facility at Tivoli does not encompass a direct rail link; therefore, all transport of containers and goods is via vehicles. Consequently, there are many and varied factors operating locally that

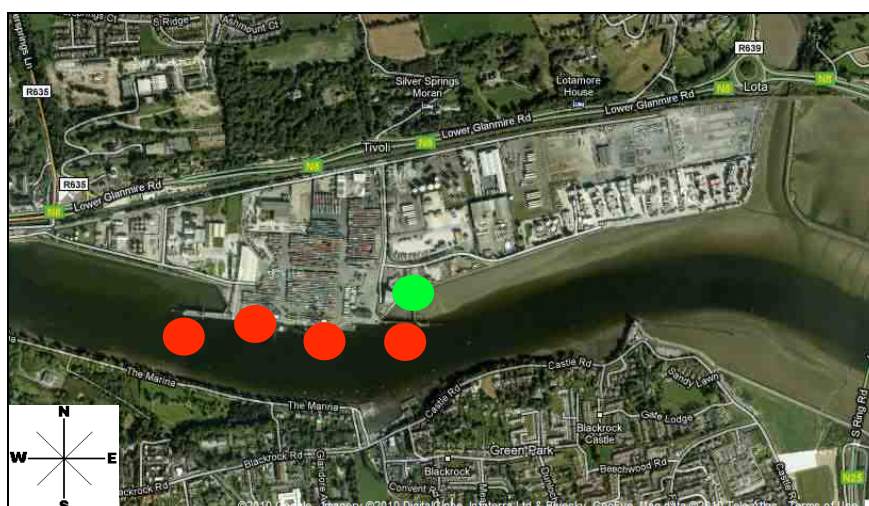


Figure 2.3. Aerial photograph of the Tivoli Docks monitoring centre (green) showing the shipping berths (red).

are likely to influence the air quality at this location, as well as regional and longer-range influences.

Because of its higher relevance both in terms of shipping emissions and in terms of ambient air quality (nearby high-density population centres), Tivoli Docks was designated as the exclusive site for performing intensive monitoring campaigns using real-time instrumentation to sample gases such as ozone and materials such as elemental carbon.

2.1.2 Instrumentation: a summary

- A HVCI (ChemVol 2400) operating at a flow rate of 900 l/min. Samples were collected on polyurethane foam (PUF) substrates on a biweekly basis. The resulting weekday (Monday–Friday) and weekend (Friday–Monday) collections were resolved into two size fractions: PM_{10–2.5} (coarse) and PM_{2.5–0.1} (fine).
- Trace gas analysers (Thermo Electron) for monitoring ozone, nitrogen oxides and sulfur dioxide in real time (at 1-min time resolution).
- A Thermo Electron SPA 5020 instrument for continuous, real-time monitoring of ambient particulate sulfate (at 10-min time resolution).
- A semi-continuous EC/OC analyser (Sunset Laboratory Inc.) operating at a 2-h time resolution.
- An ATOFMS (TSI model 3800), fitted with an aerodynamic lens (TSI model AFL100) for the measurement of particles in the size range 100–3,000 nm in real time, was also used in order to characterise the chemical composition and internal mixing state of single airborne particles.
- A scanning mobility particle sizer (SMPS, TSI model 3081) collected particle number concentrations in the size range 20–600 nm (mobility diameter) every 3 min.
- A tapered element oscillating microbalance (TEOM, Thermo Electron model 1400a) was also located on-site for the measurement of PM_{2.5} mass concentrations (averaged every 30 min).
- During the Tivoli Docks winter campaign, PM_{2.5} aerosol samples were collected on quartz-fibre

filters (Pallflex 150-mm diameter) using a high-volume (Digitel) sampler with a flow rate of 500 l/min in order to determine the specific organic components.

- An automated weather station (Casella Nomad) recording all essential meteorological parameters such as temperature, wind direction/speed, relative humidity, etc., at 5-min intervals.

2.1.3 Ambient air sampling methodologies

2.1.3.1 PM sample collection using a HVCI

Samples were collected twice weekly using PUF substrates, weekday collections beginning from early Monday morning and lasting until late on Friday night were followed by weekend collections beginning from late on Friday night and lasting until early on Monday morning. The HVCI, ChemVol 2400 designed by Harvard University, collected PM in sufficient quantities for both chemical and later toxicological studies. Using this collection system, PM is size-segregated by means of sequential stages containing a series of nozzles and slits prior to impaction and is then collected on the PUF substrate (Fig. 2.4).

The HVCI located at both sampling sites were fitted with a sampling inlet designed to collect two distinct aerosol size fractions, PM_{10–2.5} (coarse) and PM_{2.5–0.1} (fine), based on particle aerodynamic diameter lying between (i) 10 µm and 2.5 µm and (ii) 2.5 µm and

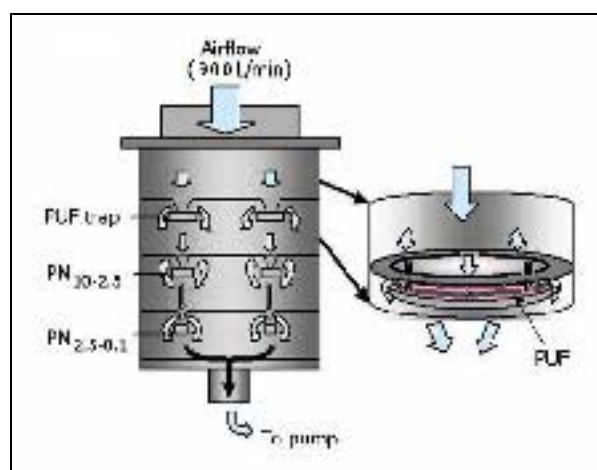


Figure 2.4. Two-stage high-volume cascade impactor showing three platforms for size fractionation of particles.

0.1 μm (Demokritou et al., 2002; Moreno et al., 2004; Jones et al., 2006).

It is important to note that this collection mechanism when used as part of a system for the measurement of ambient concentrations of PM_{10} and $\text{PM}_{2.5}$ tends to underestimate ambient mass concentrations compared with the standard reference methods EN12341 and EN14907. The HVCI has a collection sampling head system (ChemVol 2400) involving a series of collection stages that allows for the collection of PM of different size fractions. This impaction-type system collects coarse and fine PM simultaneously. Therefore, separate PM mass measurements for $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5-0.1}$ are made using this system. Collection of PM below an aerodynamic diameter of 0.1 was not made; hence, the ambient concentrations reported here are almost certainly an underestimate. The uncertainty associated with gravimetric determination of collected PM is ± 0.2 mg per collection, or $0.02 \mu\text{g}/\text{m}^3$, with a 95% confidence interval around the mean, allowing for an error of 10% in the sample volume.

2.1.3.2 PM sample collection using a Digital DHA-80 High-Volume Sampler

A Digital DHA-80 High Volume Sampler with a flow rate of 500 l/min was used to collect $\text{PM}_{2.5}$ aerosol samples. The head of the collection system is designed with a series of nozzles that accelerate sample airflow to allow particles with aerodynamic diameters larger than $2.5 \mu\text{m}$ to impact onto a grease-trap platform. Particles with diameters less than $2.5 \mu\text{m}$ continue with the airflow and are embedded onto a filter. Particulates were collected on Pallflex quartz-fibre filters (150-mm diameter, pre-fired for 24 h at 580°C).

2.1.3.3 Nitrogen oxides monitoring

Ambient concentrations of nitric oxide and nitrogen oxides were monitored using a conventional, chemiluminescence instrument (Thermo Electron 42i-TL Trace Level NO_x Analyser).

2.1.3.4 Ozone monitoring

Ambient concentrations of ozone were monitored using a conventional ultraviolet photometer (Thermo Electron 49i Ozone Analyser).

2.1.3.5 Sulfur dioxide monitoring

Ambient concentrations of sulfur dioxide were monitored using a pulsed-fluorescence gas analyser (Thermo Electron 43i Sulfur Dioxide Analyser), which measures the fluorescence of sulfur dioxide molecules induced by ultraviolet excitation.

2.1.3.6 Real-time sulfate monitoring

Total suspended particulate sulfate was monitored using a modified pulsed-fluorescence sulfur dioxide analyser (Thermo Electron 5020 SPA Sulfate Particulate Analyser), which effectively determines ambient sulfate concentrations by measuring the amounts of sulfur dioxide formed following the volatilisation and catalytic reduction of atmospheric sulfate material sampled through a high-temperature converter ($1,000^\circ\text{C}$). Integrated measurements are averaged every 5 min and corrected for noise generated by other fluorescing species (excluding gas-phase sulfur dioxide, which is scrubbed from the sample by a denuder at the inlet stage) measured over the same duration.

2.1.3.7 Elemental and organic carbon

Mass concentrations of elemental and organic carbon were obtained using a semi-continuous, thermo-optical carbon aerosol analyser (Sunset Laboratory Inc.). Size-resolved atmospheric aerosol ($\text{PM}_{2.5}$) is collected on a quartz-fibre filter for 2 h and is subsequently analysed for its carbon content. Carbon measurements proceeded through a two-stage thermal analysis. During Stage 1, the filter is baked under an inert gas atmosphere (helium) causing the organic carbon to volatilise from the sample. Organics transported in the gas phase are catalytically converted to carbon dioxide (CO_2) and measured using infrared. During Stage 2, the filter is subjected to a second temperature ramp under oxidative conditions (helium/oxygen carrier gas), causing the remaining elemental carbon to evolve from the sample as carbon dioxide.

2.1.3.8 ATOFMS

The ATOFMS (TSI model 3800) was fitted with an aerodynamic lens (TSI model AFL100) for the measurement of particles in the size range 100–3,000 nm. The instrument is described in detail elsewhere (Dall'Osto et al., 2004). In short, particles are sampled

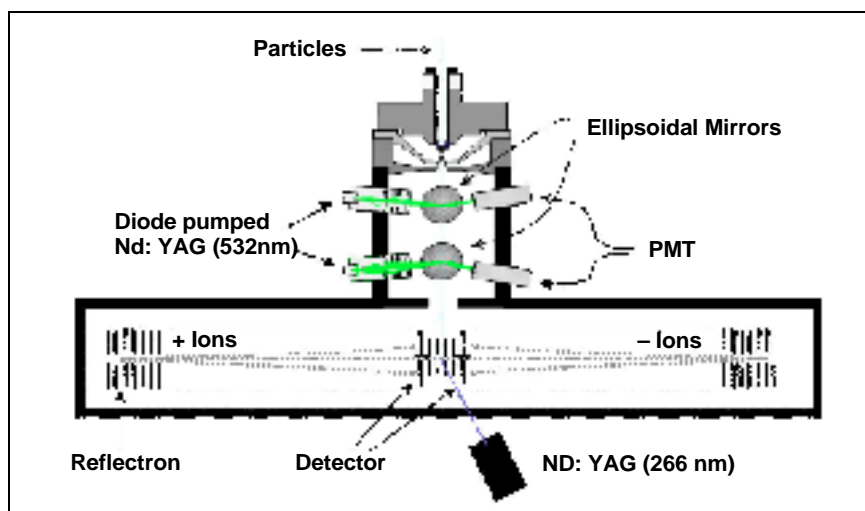


Figure 2.5. Schematic of aerosol time-of-flight mass spectrometer inlet, sizing and detection regions (source: Sodeman (2004)). Nd: YAG, neodymium-doped yttrium aluminium garnet; PMT; photomultiplier tube.

through an orifice and accelerated through the aerodynamic lens to the sizing region of the instrument (Fig. 2.5). Here, the aerodynamic diameter of particles is calculated based on their time of flight between two continuous sizing lasers (Nd:YAG⁴, 532 nm). Particles are then transmitted to the mass spectrometry region of the instrument and ionised using an Nd:YAG laser (266 nm). The resulting positive and negative ions are finally analysed using two collinear time-of-flight mass spectrometers.

The ATOFMS particle mass spectra were generated and subsequently imported into ENCHILADA (Environmental Chemistry through Intelligent Data Analysis), a freeware single particle data analysis software package (Gross et al., 2006; Snyder et al., 2009) and clustered into particle class using the *K*-means algorithm (MacQueen, 1967), (*K* = 50). Hourly summed particle counts of each final particle class were subsequently used for positive matrix factorisation (PMF).

2.2 Analytical Methods

2.2.1 Gravimetric analysis

The mass concentration of PM was determined by weighing filters using a Mettler Toledo microbalance

(AB265-S/FACT), with a readability of 1 µg and a precision of approximately 1 µg/m³. The PUF substrate was conditioned pre-collection at a relative humidity of 35–45% and at a temperature of 30 ± 3°C in a dedicated weighing room and post-collection was re-weighed under identical conditions.

In the case of the fine fraction (PM_{2.5-0.1}), after the overall PM mass had been measured, each ring of PUF was divided into six subsections of equal size and each subsection weighed in turn. The mass of PM present on each subsection (*m_S*) was determined by applying the following calculation:

$$m_S = r \cdot m_T \quad \text{Eqn 2.1}$$

where *r* is the ratio obtained from the mass of the subsection divided by the mass of the complete ring and *m_T* is the total mass of PM_{2.5-0.1} gathered during collection. This method relies on the assumption that PM coverage is uniform around the whole ring, which was validated by reproducibility tests conducted during chemical analysis when a series of two non-adjacent subsections were analysed and successfully compared.

2.2.2 Extraction of PM from substrate

Two extraction procedures (water-soluble extraction and acid digestion) were employed to recover the PM material from the PUF substrate. Water-soluble

4. Nd:YAG, neodymium-doped yttrium aluminium garnet (Y₃Al₅O₁₂) crystal used in the solid state laser.

extractions were effected by shaking and sonication of the samples for 2-h rotations, twice, after which the aqueous phase was recovered and filtered to remove any insoluble material (MilliQ water, designated as 18.2 Ω , was used for this process). To quantify the efficiency of the extraction protocol, recovery tests were performed on a series of 15 PUF samples spiked with known amounts of ionic analytes obtained from ion chromatography (IC) calibration standards (Dionex IC standards, traceable to the National Institute of Standards and Technology Standard Reference Materials). Recovery was found to be close to 100% for all cases. A microwave-assisted acid-digestion method was used to extract the totality of trace metals from the PM. A mixture of nitric acid (HNO₃, 69%, 2 ml), hydrofluoric acid (HF, 40%, 0.1 ml) and water (H₂O, distilled, 2 ml) achieved full digestion of PM. One reagent blank was also included in the analytical

procedure to assess any contamination associated with the process.

2.2.3 Inorganic chemical analysis of PM

The PM_{2.5-0.1} collections were characterised in terms of their inorganic composition using both IC (Dionex ICS-2000) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2000DV).

2.2.3.1 Chemical analysis of the inorganic ionic species

The water-soluble fraction of each sample was systematically analysed for 12 ionic components. The method detection limits (MDLs) are shown in [Tables 2.1–2.3](#). Among them, fluoride, nitrite and phosphate ions were consistently below their respective detection limit ([Table 2.3](#)). Consequently, ambient concentrations are reported here for nine ionic species: Cl⁻, Na⁺, Br⁻, K⁺, NH₄⁺, NO₃⁻, SO₄²⁻, Mg²⁺, and Ca²⁺.

Table 2.1. Method detection limits expressed in ng/ml for water-soluble metals.

Analyte	Lead	Iron	Aluminium	Manganese	Chromium	Magnesium	Calcium
	41.6	2.3	29.4	0.3	0.5	15.9	226.7
Analyte	Copper	Cadmium	Antimony	Barium	Nickel	Zinc	Vanadium
	0.6	0.5	12.7	0.8	1.5	5.9	1.5

Table 2.2. Method detection limits expressed in ng/ml for total metals (acid digestion extraction method).

Analyte	Lead	Iron	Aluminium	Manganese	Chromium	Magnesium	Calcium
	23.0	36.9	112.9	2.8	3.1	17.8	389.4
Analyte	Copper	Cadmium	Antimony	Barium	Nickel	Zinc	Vanadium
	1.2	0.5	13.0	1.8	3.3	17.9	3.3

Table 2.3. Method detection limits expressed in ng/ml for (water-soluble) ionic species.

Analyte	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Sulfate	Phosphate
	96.9	83.5	160.6	16.1	162.4	45.3	76.5
Analyte	Sodium	Ammonium	Potassium	Magnesium	Calcium		
	57.8	99.9	97.2	62.7	123.7		

Validation tests were performed to ensure the quality of this analytical method:

- Instrumental detection limits (IDLs) for each species were set as the standard deviation around 10 concentration measurements in the most diluted standard used for calibration purposes. Method detection limits for each species were determined using a series of 12 PUF field blanks. Each field blank was subjected to established extraction and analytical protocols. The MDL was set at three times the standard deviation around the average analyte concentration detected in the blank. When the analytical concentration of a species was found to lie below the MDL, it was replaced with half the MDL for that species.
- Reproducibility was assessed by repeating the extraction and analytical steps for half the collections. All repeated analytical values agreed within 10%, with the exception of the bromide ion for which significant discrepancies were observed. Because bromine was, consistently, the least concentrated of all ionic species considered, it is potentially more sensitive to analytical errors and uncertainties due to metal absorption on the IC column.
- For each collection, two filter sections were extracted and each of these extracts were analysed in duplicate. Combining the two instrumental values belonging to each of the two extracted samples allowed the final analytical concentrations to be determined using the average of four measurements with an associated uncertainty established at twice the standard deviation around that average ($\pm 2\sigma$).
- This analytical concentration was converted into ambient ionic concentrations ($\mu\text{g}/\text{m}^3$) for each collection by subtracting the average field blank contribution and factoring the proportion of sample analysed, the flow rate and sampling duration pertaining to each collection.

2.2.3.2 Chemical analysis of the trace metals

Both the water-soluble and the acid-soluble fractions of $\text{PM}_{2.5-0.1}$ were analysed for a selection of 21 transition metal and metalloid elements using ICP-OES. Only 14

of these were found to exhibit analytical concentrations above their respective MDL ([Tables 2.1 and 2.2](#)): Pb, iron (Fe), aluminium (Al), manganese (Mn), chromium (Cr), magnesium (Mg), calcium (Ca), copper (Cu), Cd, antimony (Sb), barium (Ba), nickel, zinc (Zn), and vanadium (V). Water-soluble extracts were acidified to match the 5% nitric acid matrix used in the calibration standards.

Validation tests were performed to ensure the quality of the analytical method:

- Instrumental detection limits for each element were set as the standard deviation around 10 concentration measurements using a reagent blank (5% nitric acid matrix). Method detection limits for each species were determined using a series of 12 PUF field blanks. Each field blank was subjected to the established extraction and analytical protocols. The MDL was set at three times the standard deviation around the average analyte concentration detected in the blanks. When the analytical elemental concentration was found to lie below the MDL it was replaced by half the MDL for that element.
- From each collection, three separate samples were extracted for which two instrumental readings were recorded. Analytical concentrations were calculated as the average of six separate measurements and the associated uncertainty set at twice the standard deviation around this average ($\pm 2\sigma$).
- Ambient concentrations for each element (ng/m^3) were reconstructed after subtraction of the field blank contribution by factoring the proportion of sample analysed, the flow rate and sampling duration pertaining to each collection.

2.2.3.3 Chemical analysis of organic component

This analysis was carried out on PM samples collected on quartz-fibre filters using a Digitel high volume system ([Section 2.1.3.2](#)). A section of the filter was spiked with internal recovery standards (0.5 μg methyl- β -D-xylanopyranoside (MXP) and 0.5 μg deuterated (D_4)-succinic acid and dried prior to extraction by solvent. The extraction process was performed three times with 20 ml of dichloromethane/methanol (80:20,

v/v) under ultrasonic agitation for 30 min. The extracts were combined, reduced in volume with a rotary evaporator (213 hPa, 30°C) to approximately 1 ml and filtered through a Teflon filter (0.45 µm). Thereafter, the filtrate was dried under nitrogen and dissolved in 200 µl of dichloromethane/methanol (50:50, v/v); a detailed description of the extraction procedure can be found in Kourtchev et al. (2005).

The GC/MS system used consisted of an Agilent 6890 N gas chromatograph system (Agilent Technologies, Palo Alto, CA, USA) coupled to an Agilent 5975 quadrupole mass selective detector. A cross-linked HP-5MS capillary column (5% phenyl, 95% methylpolysiloxane, 30 m × 0.25 mm i.d., 0.25 mm film thickness, J&W Scientific, Palo Alto, CA, USA) was used. The ion source was operated at electron energy of 70 eV at 230°C. The quadrupole temperature was maintained at 150°C. Helium was used as a carrier gas at a flow rate of 1.2 ml/min. The temperature programme of the column was: initial temperature at 50°C held for 5 min, a gradient of 3°C/min up to 200°C, held for 2 min, then 30°C/min to 310°C, held for 2 min.

2.2.4 Reference experiment for polar organic markers for combustion domestic solid fuels

Coal, 'smokeless' coal, peat and wood were burnt each in turn for approximately 1 h in an outdoor stove and the resulting fresh combustion particles monitored using the Sunset EC/OC analyser and the ATOFMS to obtain the associated mass-spectral signatures. Each fuel was purchased locally in order to be representative of typical domestic output in the area. Specifically, commercially available compacted peat briquettes, bituminous coal, smokeless coal and ash wood were used. Peat is commonly used in Ireland for domestic space heating. Ash wood was used as it is widely available for sale in retail outlets and service stations in Cork City. The mass spectra for coal, peat and wood-burning particles were sufficiently different to allow for the identification of individual single particle characterisation for each fuel type. These spectra were subsequently used to confirm the identification of classes in the ambient data set.

2.2.5 Source apportionment models

2.2.5.1 Principal component analysis approach

Principal component analysis (PCA) is a basic receptor modelling technique outlined in more detail below although a full description can be found in Hopke (2003b). Essentially the method can be used to determine the contributions made by various categories of pollutant sources to a location of interest (e.g. harbour, roadside or office). Details of this mathematical procedure and its application are given in Thurston and Spengler (1985) and Paatero et al. (2002).

The data used for PCA were pre-processed. The real-time data collected for elemental and organic carbon, nitrogen oxides and PM_{2.5} were averaged over periods corresponding to the sampling duration of individual filters. Notably, only the late autumn and winter campaigns involved filter sampling at temporal resolutions that allowed investigations into night and day variations in the concentrations of the organic marker compounds. The organic composition of the aerosols varied with the seasons and, consequently, the only species that were continuously determined above detection limits throughout all four campaigns were levoglucosan, mannosan, galactosan and 1,6-anhydro-β-D-glucofuranose (1,6-AGF). By carrying out multiple linear regressions of the obtained absolute principal component scores against measured values of organic carbon and PM_{2.5} (Thurston and Spengler, 1985), quantitative estimates were obtained for the contribution of each identified source category to the measured ambient concentrations of organic carbon and PM_{2.5}, respectively.

2.2.5.2 Positive matrix factorisation

The fundamental relationship between an emission source and receptor (sampling location) can be expressed as follows (Hopke, 2003a):

$$X = GF^T + E \quad (\text{Eqn 2.2})$$

where G is an $n \times p$ matrix representing source contributions to the samples, F^T is the transpose of an $m \times p$ matrix of source profiles, E is the matrix of residuals, n is the number of samples, p is the number of variables and m is the number of extracted components or source categories. Each sample is an

observation at a particular time, and thus G describes the temporal variation of the source contributions. The overall data set matrix is comprised of samples (rows) and variables (columns). A viable statistical solution to the expression is then sought, the aim of which is to minimise the residuals in E .

The PMF approach takes into account the uncertainties associated with each individual measurement, or data point (Paatero and Tapper, 1994; Hopke, 2003b; Ramadan et al., 2003). Hence, the variables are weighted by a measure of trust in the individual measurements and adjusted to their detection limits. 'Bad' samples can be down-weighted or excluded and the selected solution is based on goodness of fit. Results are also constrained to the non-negative to avoid sources providing negative contributions to concentrations measured at the receptor sites. This approach reduces the likelihood of misinterpreting factor profiles. The identification of factors can be improved by the inclusion of particle types that have been unequivocally assigned to a source through their unique mass spectra (Eatough et

al., 2008). As with the study of Eatough et al. (2008), the factorisation procedure has been applied to the previously clustered single particle mass spectra obtained by ATOFMS in this work. The clustering procedure provides hourly counts of identified particle types that are treated as independent variables alongside hourly averages of measured elemental and organic carbon, sulfate and $PM_{2.5}$ mass and SMPS particle number concentration. By combining this information, it is possible to apportion PM mass in a quantitative manner.

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 until the most reasonable results were obtained. Estimation of the contribution of each factor to the total $PM_{2.5}$ mass was subsequently performed by scaling the PMF factor contributions (in the G matrix of [Eqn 2.2](#)) against measured $PM_{2.5}$ mass by regression (Maykut et al., 2003; Shi et al., 2009).

3 Mass Concentrations and Chemical Compositions of PM_{2.5-0.1} in Cork Harbour

3.1 Tivoli Docks and Estates

Only the PM_{2.5-0.1} fraction was chemically characterised for the purposes of the ELIPSE study. Water-soluble species, both ionic and metal in nature, were extracted and quantified for the 133 PM collections made. Quantification of the total trace metals and water-soluble metals present was thereby achieved. Details on site, collection system used and analytical procedures employed are given in [Chapter 2](#).

3.1.1 Ambient mass concentrations

The PM_{10-0.1} ambient concentration average, over one calendar year within 2008 and 2009 at the Tivoli Docks location, was 14.2 µg/m³, as shown in [Table 3.1](#). This value is well below all limits set under EU Directive 2008/50/EC for the protection of human health ([Table 3.2](#)).

Table 3.1. PM_{10-0.1} mass concentration at Tivoli Docks for the period May 2008–April 2009.

Average (µg/m ³)	14.2
Median (µg/m ³)	12.4
Number of collections >30 µg/m ³	4
Number of collections >20 µg/m ³	20

Four exceedances were recorded during the campaign for the upper assessment limit related to the protection of human health; 20 exceedances were registered for the lower assessment threshold value (20 µg/m³ averaged over 24 h) ([Fig. 3.1](#)).

It was not possible to calculate exceedances for daily averages of PM concentration since the gravimetric measurements were made on samples collected for weekday and weekend periods. However, since the exceedances were recorded on samples collected over time periods longer than 24 h, it is likely that the total number of 24-h exceedances would be underestimated using this method.

High-volume samplers, similar to the impaction type system used in this study, can suffer artefacts linked to the bouncing and re-entrainment of impacted materials; they, therefore, fall short of the recommended standard evaluation methods (such as the low-volume Partisol instrument) for measurements of ambient PM mass loadings. However, comparison between integrated real-time data obtained from co-located instruments (Thermo SPA 5020 and an Aerodyne AMS) with the deployed HVCI collection device revealed that, in the case of the PM_{2.5-0.1} size fraction, the gravimetric measurements do not differ

Table 3.2. Outline of EU Directive 2008/50/EC on ambient air quality and the protection of human health.

Designation	Limit	Averaging period
24-h limit value for the protection of human health	50 µg/m ³ PM ₁₀ not to be exceeded more than 35 times in a calendar year	24 h
Annual limit value for the protection of human health	40 µg/m ³ PM ₁₀	Calendar year
Upper assessment threshold for the protection of human health	30 µg/m ³ PM ₁₀ not to be exceeded more than 35 times in a calendar year	24 h
Annual upper assessment threshold for the protection of human health	14 µg/m ³ PM ₁₀	Calendar year
Lower assessment threshold for the protection of human health	20 µg/m ³ PM ₁₀ not to be exceeded more than 35 times in a calendar year	24 h
Annual lower assessment threshold for the protection of human health	10 µg/m ³ PM ₁₀	Calendar year

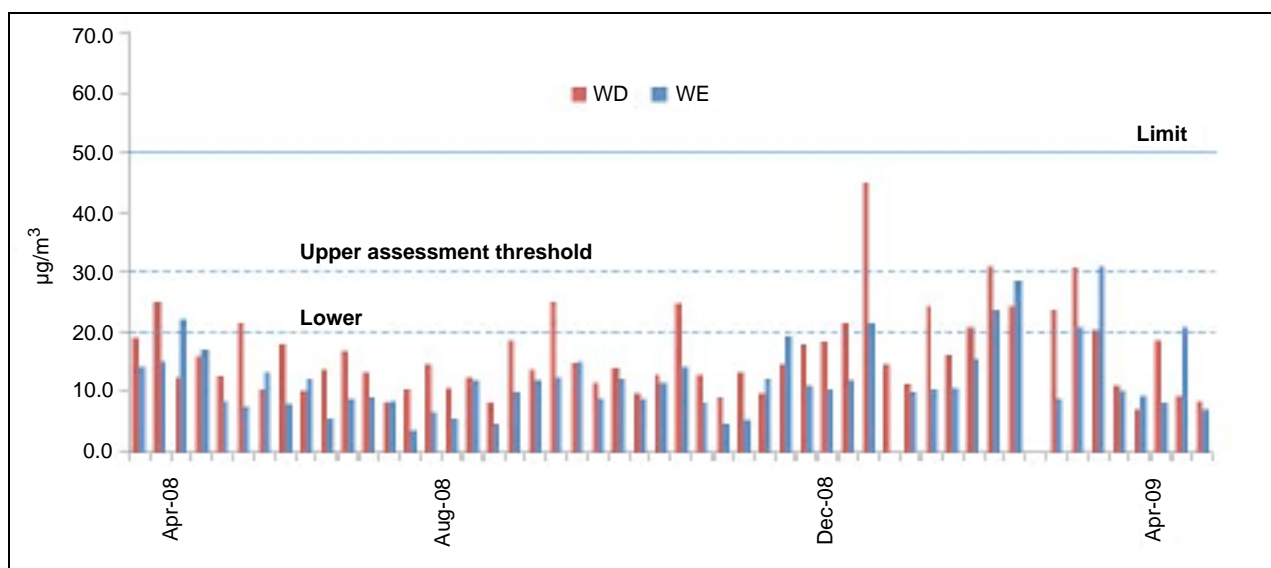


Figure 3.1. Ambient air concentration of $PM_{10-0.1}$ during collection April 2008 to May 2009 (WD, weekdays; WE, weekends).

significantly from the actual ambient concentrations. In order to put these gravimetric results in context, comparison was made with reference values obtained from a Partisol instrument operated by Cork City Corporation at its Old Station Road traffic emissions monitoring site (>3 km away from the Tivoli site). It was found that the measurements made at Tivoli differed by 14% for PM_{10} and by 35% in the case of $PM_{2.5}$. This is in line with the expected underestimation bias associated with high-volume samplers. However, it should also be noted that both sites are different in terms of pollution-source influence. Old Station Road operates as a roadside monitoring site next to a very busy traffic junction, which in itself could partly explain the higher concentrations of particles measured. As a consequence, it is not possible to determine a straightforward correction factor based on this comparison.

Certainly, because of the 0.1- μm cut-off point for the fine fraction, the HVCI sampler is missing the contribution of ultrafine particles with an aerodynamic diameter of 0.1 μm or under. However, this contribution is expected to be negligible in terms of mass, whatever the number density in this size range might be. It should also be emphasised that the choice of the Old Station Road data set was dictated by availability and

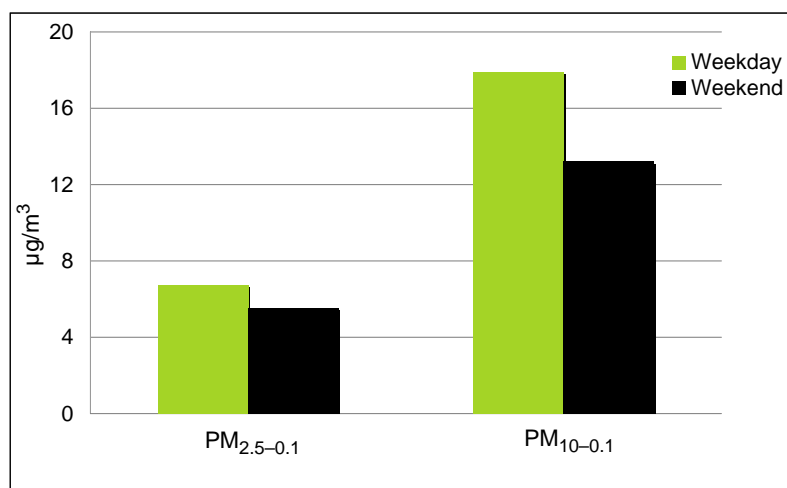
is essentially a city-centre roadside sampling site. It is therefore liable to be exposed to high PM mass loadings at certain times of the day. In these circumstances, it seems reasonable to assume that the results obtained using the HVCI sampler sited at Tivoli Docks represent an underestimation of the 'true' values.

The average value for $PM_{10-0.1}$ concentration made during the measurement campaign, $15.4 \mu g/m^3$, was well below the annual limit value for the protection of human health ($40 \mu g/m^3$) and the average $PM_{2.5-0.1}$ concentration ($6.3 \mu g/m^3$) also compares very favourably with the target value of $25 \mu g/m^3$ set under Directive 2008/50/EC ([Table 3.3](#)).

On average, over the course of the four seasons for which there were continuous and uninterrupted collections made, weekday collections were shown to exhibit higher ambient PM mass loading than their weekend counterparts in both the fine and the coarse size fractions ([Fig. 3.2](#)). This 30% difference in the PM_{10} mass loadings reflects the impact of anthropogenic emissions linked to economic activity, which is typically reduced at weekends. Natural inputs are not expected to be tied into any identifiable weekly patterns.

Table 3.3. Ambient mass concentration of particulate matter ($\mu\text{g}/\text{m}^3$) at Tivoli Docks for the period April 2008–April 2009.

	PM _{10-0.1}			PM _{2.5-0.1}		
	Overall	Weekday	Weekend	Overall	Weekday	Weekend
Average	15.4	17.9	12.9	6.3	6.8	5.7
Median	13.3	15.8	11.8	5.0	5.2	4.5

**Figure 3.2. Weekday and weekend splits for the mass concentrations of both PM_{2.5-0.1} and PM_{10-0.1} size fractions at Tivoli Docks.**

3.1.2 Major ionic components

Unsurprisingly, the correlation matrix constructed between ions for the total period (Table 3.4) shows two distinct, unambiguous groupings:

1. Sodium and chloride ions, indicative of the marine contribution to the PM_{2.5} sampled at the monitoring site; and
2. Ammonium, nitrate and sulfate ions characteristic of a component typically associated with combustion processes.

Both groupings also appear to be anti-correlated with one another, possibly as they originate from different locations and the detection of one is controlled by the occurrence of winds blowing from specific directions, at the expense of the other.

The results are of particular interest when seasonal variations are considered. Hence, the summer 2008 (June–August) data set stands out as being very different in many respects when compared with the

rest of the year. The PM_{2.5-0.1} mass loading is almost halved during this period (Fig. 3.3), with a summer mean of 3 $\mu\text{g}/\text{m}^3$ compared with 7 $\mu\text{g}/\text{m}^3$ for the rest of the year. This feature is presumably due to some reduction in the volume of traffic present during the holiday months and also as a result of the lower level of energy demand required for space heating purposes. When weather conditions were considered for summer 2008, it was noted that temperature records for 2008 show that, in the summer months, the average temperature was 4–5°C higher than during spring and autumn that year (14.4°C compared with 9.2°C and 10.7°C, respectively).

The ionic mass fraction accounts for about half the PM_{2.5-0.1} mass collected at Tivoli; the values range from 60% in spring 2008 to 40% in autumn 2008. The ionic species therefore display a seasonal trend similar to that observed for their particulate core. Most of the species exhibit a yearly low in ambient concentration in the summer and recover during the colder months (Fig. 3.4).

Table 3.4. Bivariate correlations between ionic species measured in PM_{2.5-0.1} at Tivoli Docks. Values in bold and highlighted in green show strong bivariate correlations (>0.70), while anti-correlated (highest negative values) values are highlighted in pink.

	Chloride	Bromide	Nitrate	Sulfate	Sodium	Ammonium	Potassium	Magnesium	Calcium
Chloride	1.00								
Bromide	0.37	1.00							
Nitrate	-0.01	-0.02	1.00						
Sulfate	-0.14	-0.06	0.84	1.00					
Sodium	0.86	0.11	-0.13	-0.18	1.00				
Ammonium	-0.09	0.04	0.94	0.92	-0.19	1.00			
Potassium	0.56	0.27	0.50	0.48	0.39	0.47	1.00		
Magnesium	0.52	0.07	0.00	-0.04	0.48	-0.14	0.31	1.00	
Calcium	0.14	0.12	0.33	0.31	0.01	0.23	0.45	0.34	1.00

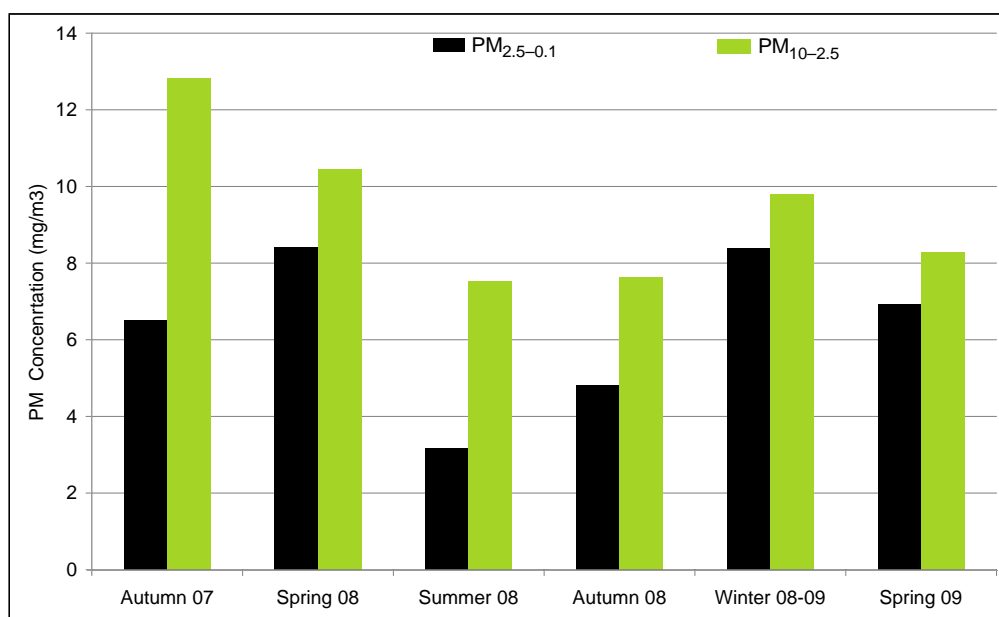


Figure 3.3. Particulate matter (PM) mass loading ($\mu\text{g}/\text{m}^3$) measured at Tivoli Docks averaged over individual seasons.

A more spectacular seasonal difference is displayed by [Fig. 3.5](#) which shows the relative concentration, using units of micrograms of ions per gram of PM_{2.5}, for each of the significant ionic species, averaged over the relevant periods. The singularity of the summer data is again made evident, especially by the fact that the relative contribution of sulfate to the PM_{2.5-0.1} chemical composition not only reaches a maximum during this season, but also because this maximum is not met by any increase in the ammonium or nitrate ion

concentrations. All of the acidic and alkaline species are expected to be correlated and exhibit a high degree of covariance as is likely for the other seasons. Quite the opposite is true in the summer, when the highest relative contribution for sulfate coincides with the lowest for nitrate and a low contribution for ammonium ions as well.

[Figure 3.6](#) further illustrates how markedly different the summer samples are when compared with the rest of the year, in terms of the PM_{2.5} ionic composition

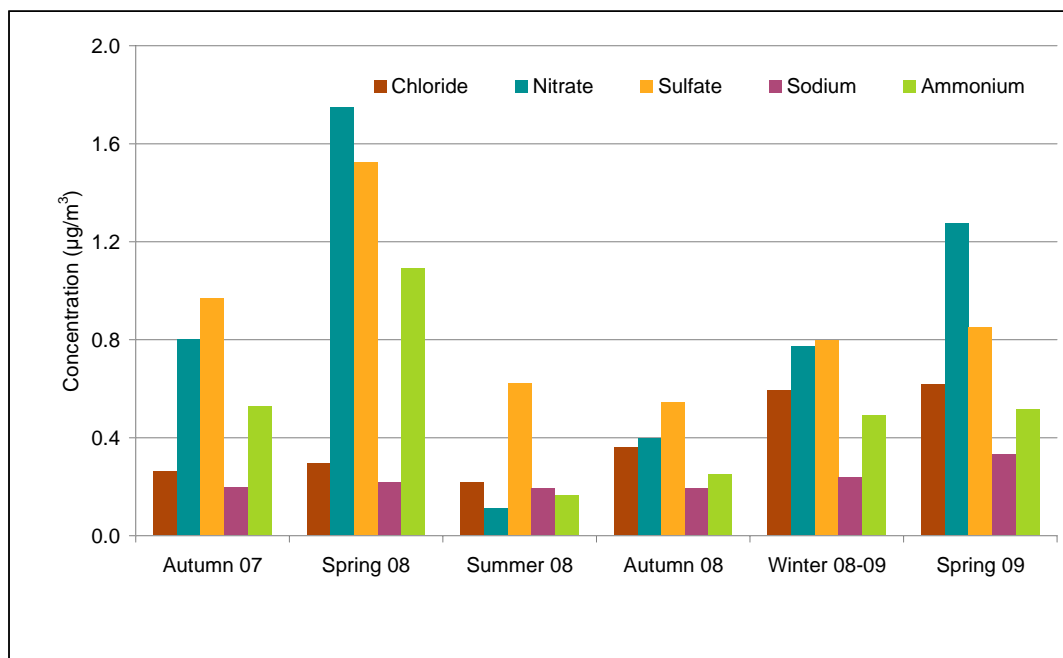


Figure 3.4. Ambient concentrations ($\mu\text{g}/\text{m}^3$) of ionic species measured in $\text{PM}_{2.5}$ at Tivoli Docks, averaged for each season.

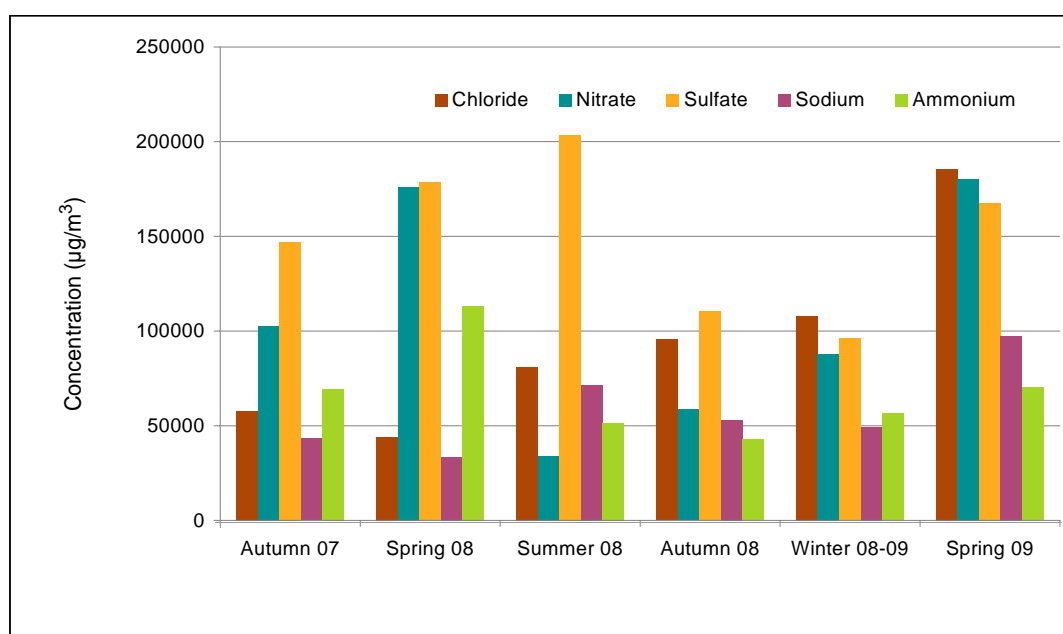


Figure 3.5. Relative concentrations (μg of ions per g of $\text{PM}_{2.5}$) of ionic species measured at Tivoli Docks, averaged for each season.

profile. As previously mentioned, $\text{PM}_{2.5}$ mass loading at Tivoli is at its lowest in the summer and this decrease in ambient concentration affects all ionic species, although not equally: sulfate remains at 73%

of its annual average, while ammonium finds its annual concentration reduced to a third, and nitrate – with a summer concentration only one sixth of its annual average value – is the most affected.

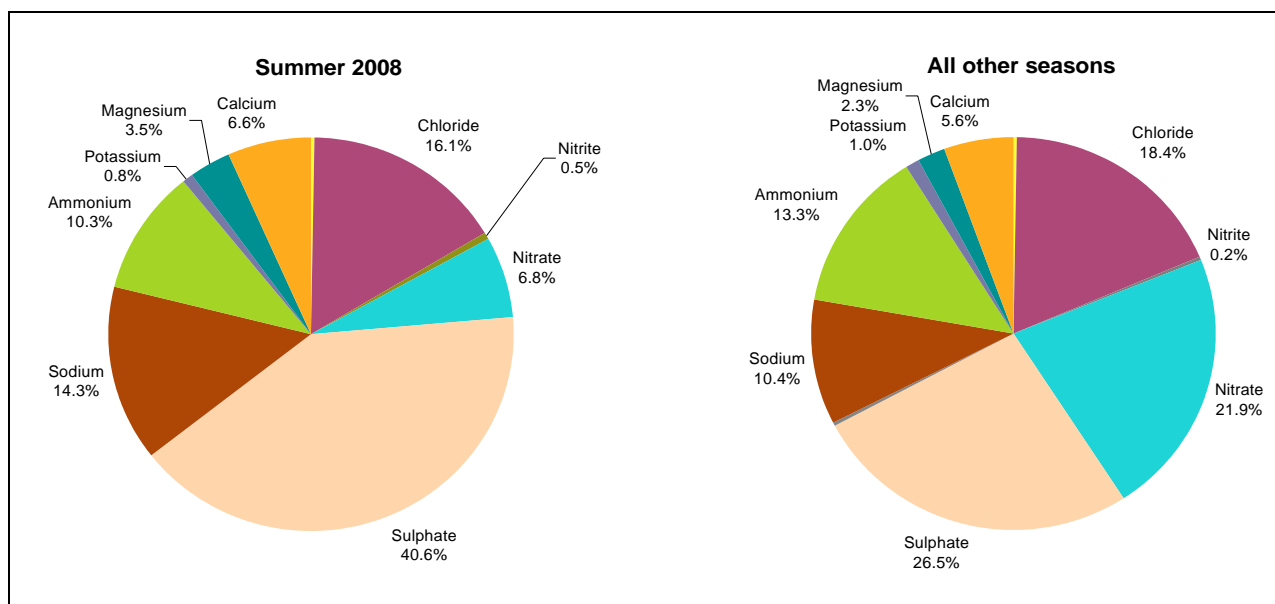


Figure 3.6. Comparison of individual contributions (%) of ionic species to overall ionic mass fraction measured in PM_{2.5} sampled at Tivoli Docks: Summer is compared with rest of the year.

The ammonium to sulfate ions ratio ($[\text{NH}_4^+]/[\text{SO}_4^{2-}]$) (based on molar equivalents derived from ambient concentrations) represents an important parameter and is a good indicator of the sulfate speciation in the particles. Thus, if $[\text{NH}_4^+]/[\text{SO}_4^{2-}] > 2$, it is likely that most sulfate is present in the form of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and that the aerosol is considered neutralised in terms of its acidity; it is deemed only partially neutralised for $2 > [\text{NH}_4^+]/[\text{SO}_4^{2-}] > 1.5$, as sulfate will be present as a mixture of ammonium sulfate and ammonium bisulfate ($(\text{NH}_4)\text{HSO}_4$). For $[\text{NH}_4^+]/[\text{SO}_4^{2-}] < 1.5$, the aerosol is considered acidic as the deficit in ammonium means that most of the sulfate will be present as sulfuric acid. Consequently, the ammonium to sulfate ratio was calculated for each of the PM_{2.5} collections gathered at Tivoli Docks and the results, averaged for each sampling season, are summarised in [Table 3.5](#).

Summer exhibits the lowest average ammonium to sulfate ratio, well below the acidity threshold of 1.5, while all other seasons present neutralised values. This result is clearly indicative of a change in sulfate speciation between ammonium sulfate for most of the year and sulfuric acid in summer, during which time close to 75% of the collections are considered acidic.

Table 3.5. Averaged ammonium to sulfate ratio ($[\text{NH}_4^+]/[\text{SO}_4^{2-}]$) in PM_{2.5} sampled at Tivoli Docks. Acidic collections refers to the proportion of samples for which $[\text{NH}_4^+]/[\text{SO}_4^{2-}] < 1.5$.

	$[\text{NH}_4^+]/[\text{SO}_4^{2-}]$	Acidic collections (%)
Overall	2.40	33.6
Autumn 2007	2.36	23.5
Spring 2008	3.26	11.8
Summer 2008	1.25	73.1
Autumn 2008	2.02	46.2
Winter 2008	3.25	7.7
Spring 2009	2.38	29.4

This finding is most arresting because aerosol acidity is linked – directly or indirectly – with health effects induced in humans by PM inhalation. Further proof of the predominance of sulfuric acid is given by the apparent chloride ion deficit observed during summer with a chloride to sodium mass ratio of 1.15 against a ratio of 1.80 (the conventional sea-salt value) for the rest of the year. Reaction between sulfuric acid and sodium chloride resulting in the formation of volatile hydrochloric acid is the most likely reason for this loss of chloride to the gas phase.

The sulfate finding in Cork Harbour is not altogether uncharacteristic. In fact, an increase in particulate sulfate concentrations is often observed in the summer as its formation depends on the oxidative capacity of the atmosphere to convert sulfur dioxide, by both homogeneous and heterogeneous oxidation pathways. These are sped up in summer because of the higher rate of oxidant formation (OH, H₂O₂, O₃). Such chemistry could explain why the sulfate concentrations measured in the PM_{2.5} samples at Tivoli – even though the lowest in absolute terms – remain strong in relative terms during the summer months.

In the presence of ammonia, an acid–base reaction can ensue leading to the formation of ammonium sulfate in the condensed phase. In the Tivoli samples, both the ammonium ion ambient concentration and the ammonium to sulfate ratio are at their lowest during the summer months, indicating that particulate sulfate did not encounter any ammonia-rich air mass as it travelled to the receptor site from its origin.

Conspicuously, both ambient and relative concentration values for particulate nitrate at Tivoli Docks are at their lowest in the summer. Fine fraction nitrate ion is expected to enter the condensed phase through the reaction between ammonia and nitric acid. The propensity of ammonium nitrate to decompose in a reversal of this acid–base reaction during the warm season means that nitrate concentrations in PM_{2.5} tend to be higher in the colder months than in the summer. It could well be the case, even though the average temperature recorded during summer 2008 was rather low (14.4°C), that the 4–5°C shift from the spring and autumn mean values is enough to account for the low nitrate levels as the thermal instability of ammonium nitrate sends ammonia and nitric acid back into the gas phase. Nonetheless, the released ammonia should react with the excess sulfate present in the form of sulfuric acid. Indeed, in the atmosphere, ammonia reacts preferentially with sulfuric acid. When nitric acid is also present and competing for ammonia, sulfate should be fully neutralised before ammonia is available to react with nitrate. In the summer, when the ammonium to sulfate ratio was at its lowest, this did not occur. Therefore, thermal decomposition can be ruled out as the main cause for the low level of particulate

nitrate measured in the summer. Instead, it reinforces the hypothesis that PM sampled during that period at the monitoring site had travelled over regions with very low ammonia concentrations, insufficient to achieve acid sulfate neutralisation (acidic particles). The materials were consequently unable to bring any significant amount of nitrogen oxides or nitric acid (potentially emitted by the same source(s) as the sulfate) into the condensed phase as nitrate.

Emissions of ammonia might be expected to peak during the spring as fertiliser is applied and they remain high during the comparatively hotter summer months because the decomposition of urea is thermally enhanced. The contrasting decrease in ammonium concentration associated with the summer months should therefore provide some clue as to the geographical origin of particulate sulfate sampled during that period. Vast areas of farmland start immediately beyond the city limits to the west and north of the sampling site. To the east and south, however, most of the region is occupied by the Harbour Basin, with very little agricultural land surface encountered between Tivoli Docks and the open sea. This sector is consequently likely to exhibit low levels of ammonia and it is probable that the acidic sulfate sampled here in the summer originates from this general direction.

3.1.3 Trace metal analysis

Aerosol acidity is not the only factor determining the impact of atmospheric particles on human health. For example, the presence of a variety of transition metals internally mixed within PM has been shown to trigger adverse physiological reactions. Acidity (and sulfate levels) exacerbates these effects by enhancing the solubility of the trace metals and their assimilation within the body following inhalation. It was therefore important to complement the results obtained regarding sulfate speciation with additional elemental composition information in order to assess potential health hazards associated with PM emissions in Cork Harbour.

[Table 3.6](#) outlines the ambient air concentrations of ‘total metal’ species (soluble and insoluble) and also shows the major water-soluble ionic species found in PM_{2.5–0.1}. [Table 3.7](#) outlines the water-soluble metal species for PM_{2.5–0.1}.

Table 3.6. Summary of ambient concentration (ng/m³) of total metal and ionic species for Tivoli Docks. SD, standard deviation; %BDL, percentage of collections below method detection limit ([Tables 2.1 and 2.3](#)) for individual elements/ions.

	Average	Median	Minimum	Maximum	SD	%BDL
Lead	2.23	1.75	0.57	12.65	1.74	38
Iron	39.36	30.26	5.17	375.81	43.01	2
Aluminium	24.22	18.24	3.60	89.90	19.02	17
Manganese	1.74	0.96	0.07	14.17	2.25	11
Chromium	0.24	0.17	0.07	0.90	0.19	55
Magnesium	63.02	46.26	5.70	499.60	62.24	1
Calcium	171.27	107.38	12.50	863.41	166.81	13
Copper	1.22	1.08	0.03	4.59	0.92	6
Cadmium	0.07	0.03	0.01	0.74	0.10	49
Antimony	0.67	0.48	0.31	3.36	0.46	73
Barium	0.97	0.89	0.09	3.37	0.60	2
Nickel	0.60	0.45	0.09	2.86	0.49	18
Zinc	7.25	5.04	0.87	37.93	6.59	7
Vanadium	0.96	0.69	0.08	5.25	0.90	16
Chloride ion	405.88	329.60	32.64	1,854.02	300.87	0
Bromide ion	1.54	0.98	0.41	6.00	1.32	55
Nitrate ion	811.62	299.15	4.43	6,603.45	1,163.32	8
Sulfate ion	840.84	634.17	200.48	3,216.74	642.43	0
Sodium ion	229.59	183.64	35.28	1,009.20	157.45	0
Ammonium ion	480.31	213.44	3.12	2,727.82	594.82	2
Potassium ion	24.80	19.95	3.84	92.47	15.75	5
Magnesium ion	57.40	41.87	2.54	321.62	51.73	2
Calcium ion	151.92	108.21	4.85	614.29	134.71	3

Table 3.7. Summary of ambient concentration of water-soluble metals for Tivoli Docks. SD, standard deviation; %BDL, percentage of collections below method detection limit ([Table 2.2](#)) for individual elements/ions.

	Average	Median	Minimum	Maximum	SD	%BDL
Lead	1.23	0.89	0.54	7.34	1.01	83
Iron	2.38	1.28	0.09	19.92	3.05	1
Aluminium	4.87	1.81	0.42	43.91	7.82	39
Manganese	1.32	0.64	0.01	10.00	1.84	6
Chromium	0.03	0.01	0.01	0.26	0.04	63
Magnesium	63.87	45.18	5.99	414.22	56.22	0
Calcium	163.08	113.35	14.14	631.01	132.44	0
Copper	0.32	0.23	0.01	2.78	0.37	21
Cadmium	0.05	0.04	0.01	0.36	0.06	45
Barium	0.50	0.42	0.05	2.32	0.34	1
Nickel	0.33	0.26	0.02	1.57	0.29	18
Zinc	6.60	4.27	0.09	69.84	8.65	2
Vanadium	0.70	0.60	0.02	2.37	0.57	15

The monitoring of lead concentrations in ambient air has been generalised since the adoption of the European Directive 1999/30/EC. Under the Fourth Daughter Directive 2004/107/EC, polycyclic aromatic hydrocarbons and certain metals (As, Cd, mercury (Hg), Ni) present at trace levels in ambient air were designated as harmful to human health and specific target values introduced for each of these.

Of the suite of trace metals analysed in ELIPSE, only lead, cadmium and nickel are subject to legal monitoring requirements. It is clear from the data presented in [Table 3.8](#) that the average concentrations monitored at Tivoli Docks were well below the appropriate lower assessment threshold.

In a comparison of weekend with weekday splits, it is evident that the average elemental composition profiles of mid-week collections compared with weekend ones for the data sets give a preliminary insight as to how elements might be grouped into common emission sources. In absolute terms, weekend ambient concentrations were consistently lower for all elements – on average 20% lower – in line with what was observed in terms of ambient PM_{2.5} mass loading as a whole, which reflects the impact of economic activity on air quality in the area. Examining the respective weekend/weekday relative concentrations (micrograms of analyte per gram of PM) proved informative, providing some initial groupings as shown in [Fig. 3.7](#).

In relative terms, species with a weekend to weekday ratio below unity are more prominent during weekdays and are likely to be linked with socio-economic activity and its weekly cycle; they could therefore be considered as the direct products of anthropogenic emissions. Conversely, species with a weekend to weekday ratio >1 can be regarded as background

components whose emission profile is sustained throughout the week or whose intensity is simply independent of any day of the week. Among these background sources, natural (marine or otherwise) as well as anthropogenic emissions such as shipping traffic (random) or energy generation (sustained intensity) would be expected to be found.

[Figure 3.7](#) allows two elemental groupings to be distinguished, based on their weekend to weekday ratios. According to the above criteria, iron, aluminium, manganese, magnesium, calcium, copper, barium and zinc fall within the first category, i.e. as emanating from anthropogenic sources affected by a weekly cycle. Some of these elements, such as iron, aluminium or calcium, are clearly crustal and possibly indicate the non-exhaust contribution of traffic in the form of re-suspended dust. This hypothesis is strengthened by their association with metals characteristic of vehicle wear and tear such as zinc, barium and copper present in tyre and brake dust. Lead, chromium, cadmium, antimony, nickel and vanadium constitute a second grouping, displaying a reverse trend in their weekend/weekday pattern as the mass fractions of these elements appear to be either constant throughout the week (Pb, Cr) or reinforced at weekends as a result of the reduced contribution of the traffic-related sources during the corresponding period. The prominence of nickel and vanadium unmistakably links this group to heavy fuel combustion. Lead is another common petroleum fuel combustion marker along with antimony, while chromium and also antimony would be more characteristic of coal-burning emissions. The tentative assignment of this second grouping to fuel combustion sources is reinforced by the fact that the secondary inorganic ions (NO_3^- , SO_4^{2-} and NH_4^+) display the same weekend/weekday pattern.

Table 3.8. Comparison of ambient levels of important metals.

	Target value	Tivoli Docks May 2008–April 2009	Lower assessment threshold	Averaging period
Lead (ng/m³)	500	2.1	250	One calendar year
Cadmium (ng/m³)	5	0.1	2	One calendar year
Nickel (ng/m³)	20	0.6	10	One calendar year

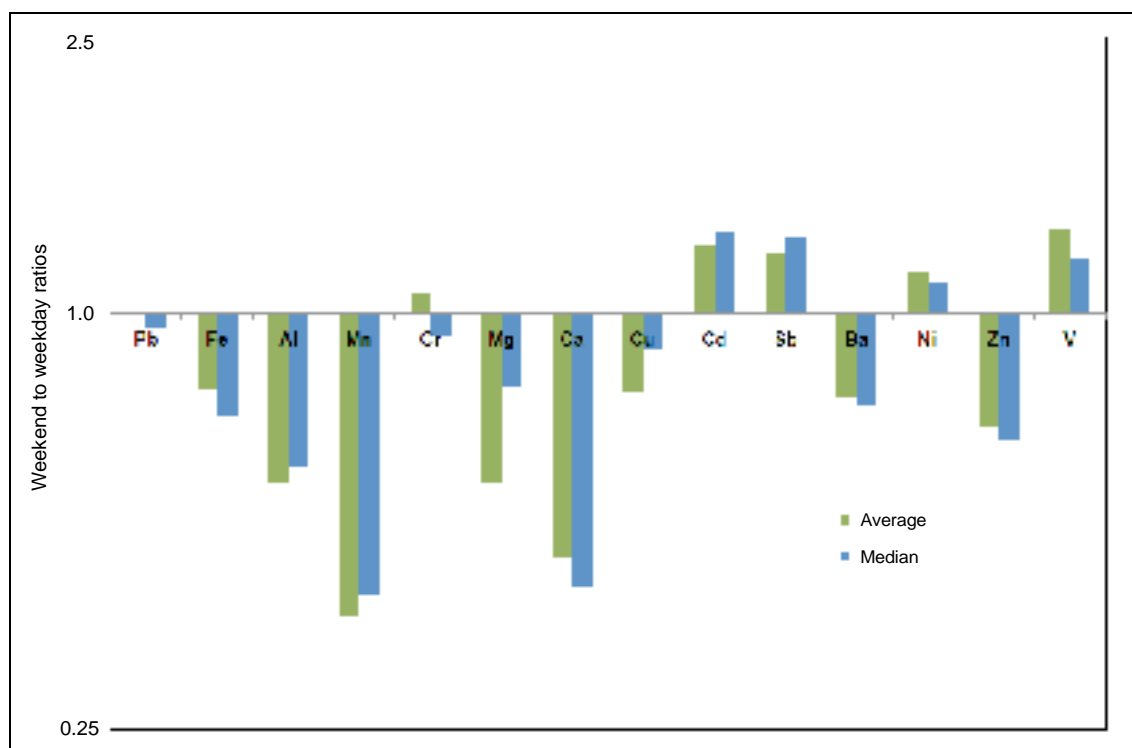


Figure 3.7. Weekend to weekday ratios of relative concentrations (elemental mass fraction in $\mu\text{g/g}$) for trace metals detected in $\text{PM}_{2.5}$ at Tivoli Docks. Yearly average and median values were used. The vertical axis has a log scale in order to highlight the pivotal quality of a ratio of 1 (see text for details).

By considering trace metals (soluble and insoluble) together with the water-soluble fraction of the fine $\text{PM}_{2.5-0.1}$ sampled at Tivoli Docks, it is possible to make an appraisal of their bioavailabilities, which are closely linked to the solubility of individual metals.

In the chemical make-up of the fine aerosol cores, trace metals such as iron, aluminium, copper and chromium appear to be bound in mostly non-soluble forms, while elements such as zinc, vanadium and manganese display the opposite trend and are bound to readily soluble compounds (Fig. 3.8).

Applying the weekend/weekday split to the water-soluble data set and the same grouping approach described above, it is possible to group elements based on their weekend to weekday relative concentration ratios (Fig. 3.9). Two groupings emerge (Mn, Mg, Ca, Zn) characterised mostly by crustal elements with higher relative contributions to the water-soluble chemical make-up of the fine aerosols sampled during weekdays than during weekends. These are possibly largely present through re-

suspension by traffic. Conversely, the second group (Pb, Fe, Al, Cr, Cu, Cd, Sb, Ba, Ni, Zn, V) would be considered as a combination of background natural sources and sustained anthropogenic emissions unaffected by any weekly pattern. The presence of oil markers, such as the nickel and vanadium pair, points to oil fuel combustion as the origin of the anthropogenic contribution to this second group.

What is of interest is the mean weekend to weekday ratios obtained for both the total and water-soluble metal measurements. Figure 3.9 shows that the relative concentrations of certain trace metals, such as iron, aluminium, copper and barium, exhibit weekly temporal trends that are diametrically opposed when measured as part of the water-soluble fraction or as part of the total metal fraction. This is an indication that – at least in the case of these particular elements – trace metals are present as part of ambient $\text{PM}_{2.5}$ sampled at Tivoli Docks in two or more chemical forms emitted directly or resulting from the atmospheric

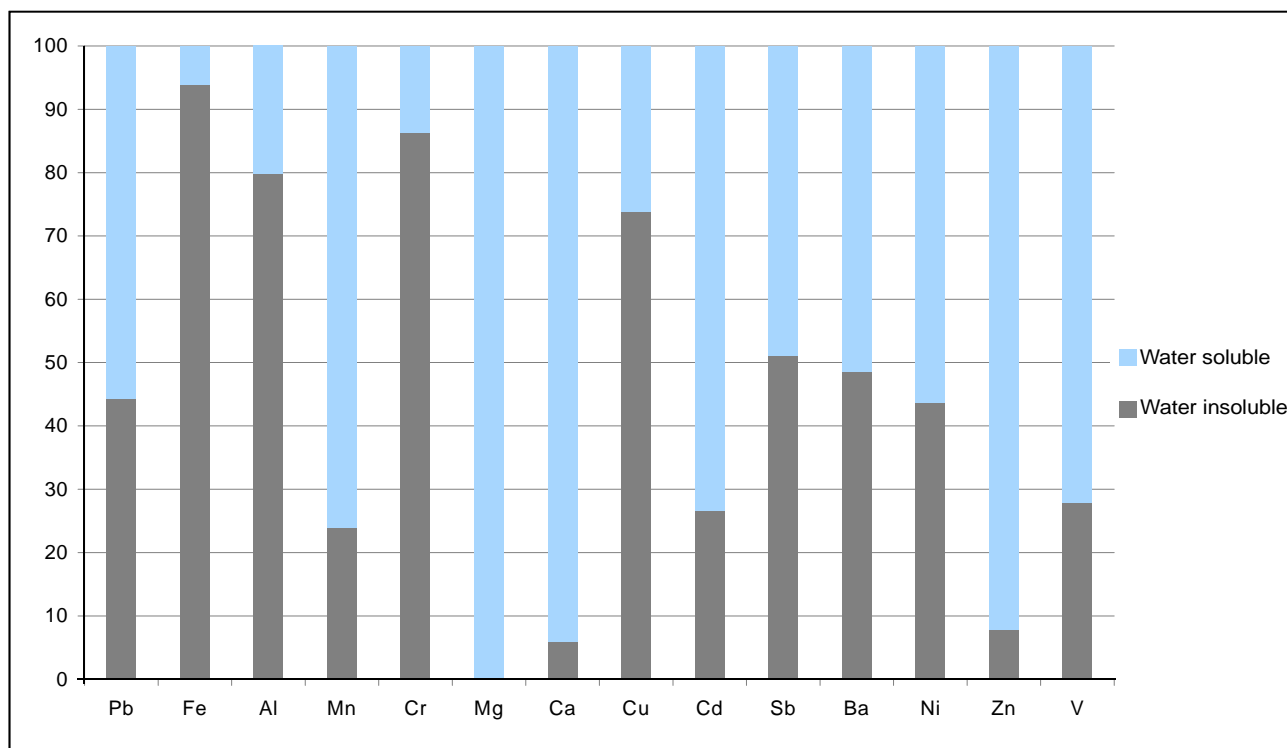


Figure 3.8. Solubility of trace metals present in the PM_{2.5-0.1} sampled at Tivoli Docks.

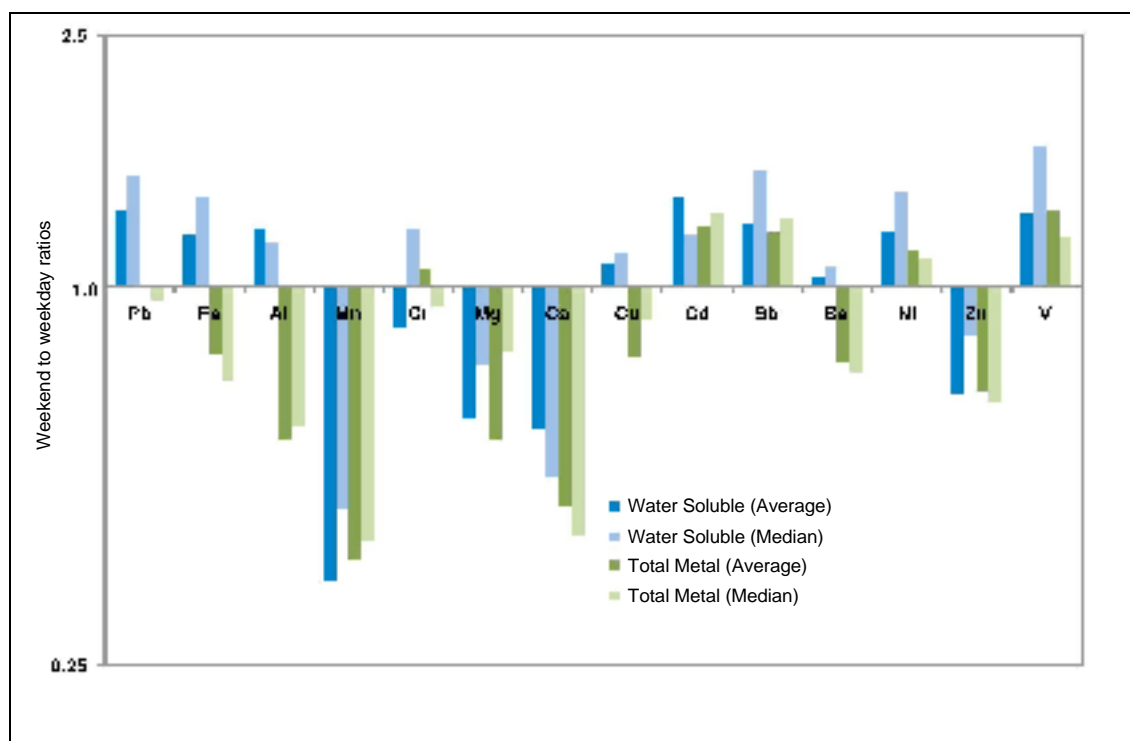


Figure 3.9. Weekend to weekday ratio of relative concentration (elemental mass fraction in µg/g) for trace metals detected in PM_{2.5} at Tivoli Docks. Comparison between soluble and insoluble metal (green) and water soluble (blue) fractions. Annual average and median were used.

processing of emissions by two or more sources with distinct temporal trends.

3.2 Haulbowline Naval Base

Water-soluble species were extracted and quantified for the 105 collections of $PM_{2.5-0.1}$ made. Details on the exact site, collection system used, and analytical procedures employed are outlined in [Chapter 2](#). Over the duration of the sampling campaign at Haulbowline Island, referred to as Haulbowline Naval Base because of its location at the Naval Base, the samples were collected representing four full seasons: spring 2007, summer 2007, autumn 2007 and winter 2007–2008.

3.2.1 Ambient mass loadings

The $PM_{10-0.1}$ ambient concentration average over one calendar year is $4.6 \mu\text{g}/\text{m}^3$ ([Table 3.9](#)), which is well below all limits set under EU Directive 2008/50/EC for the protection of human health. Indeed no

exceedances were recorded during the whole campaign and the lower assessment threshold value ($20 \mu\text{g}/\text{m}^3$ averaged over 24 h) was also not exceeded ([Fig. 3.10](#)). However, the collection system used tends to provide an underestimation of ambient concentrations as referred to in [Section 3.1](#). An estimate of the likelihood of any exceedances (24 h) based on these measurements is not possible.

The $PM_{2.5}$ average ambient concentration measured here during 2007–2008 is less than half the value obtained at Tivoli Docks ($2.8 \mu\text{g}/\text{m}^3$ versus $6.2 \mu\text{g}/\text{m}^3$) during 2008–2009 ([Table 3.10](#)). The same factor of difference was observed when directly comparing 20 collections made at each site at the same time. These measurements indicate that Haulbowline Naval Base is exposed to much less $PM_{2.5}$ emissions. Its Mid-Harbour location with an increased proximity to the open sea clearly contributes to the dilution of $PM_{2.5}$ concentrations likely transported downwind from the more polluted areas west of the receptor site.

The weekend to weekday difference in PM_{10} concentration is low at Haulbowline Naval Base (8%) and certainly not as significant as that observed at Tivoli Docks (28%). Weekday concentration values remain slightly more elevated than their weekend

Table 3.9. $PM_{10-0.1}$ mass concentration at Haulbowline Naval Base, April 2007–April 2008.

Average ($\mu\text{g}/\text{m}^3$)	4.6
Median ($\mu\text{g}/\text{m}^3$)	3.8
Number of collections $>20 \mu\text{g}/\text{m}^3$	0

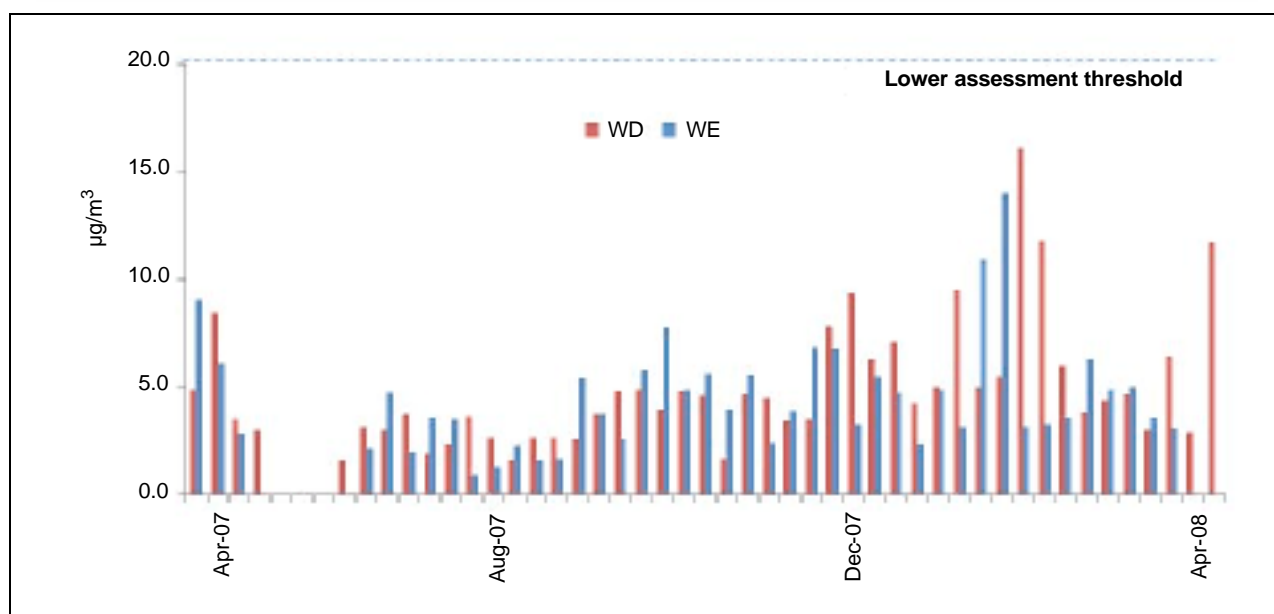


Figure 3.10. Ambient air concentration of $PM_{10-0.1}$ during the collection period April 2007–April 2008 at Haulbowline Naval Base (WD, weekday; WE, weekend).

Table 3.10. Ambient mass concentration of particulate matter (PM) ($\mu\text{g}/\text{m}^3$) at Haulbowline Naval Base, showing weekend and weekday breakdown from April 2007 to May 2008.

	PM _{10-0.1}			PM _{2.5-0.1}		
	Overall	Weekday	Weekend	Overall	Weekday	Weekend
Average	4.7	4.9	4.5	2.8	2.9	2.7
Median	3.9	4.3	3.8	2.1	2.1	2.0

counterparts (Fig. 3.11), indicating an impact from anthropogenic emissions linked with the weekly socio-economic cycle. However, the Haulbowline Naval Base location in the Mid-Harbour region appears less directly affected by these factors and more influenced by either sustained anthropogenic or natural sources.

3.2.2 Major ionic compounds

Correlations were made between the analyte ions and revealed groupings that were similar to those highlighted in the Tivoli data set, namely marine aerosol (Na^+ , Cl^-) and combustion particles (NH_4^+ , NO_3^- , SO_4^{2-}). Most ambient concentrations of the ions analysed for were found to be lower at Haulbowline Naval Base than at the Tivoli receptor site, which would indicate that PM sampled in Mid-Harbour had undergone a degree of 'dilution' through deposition or mixing with cleaner air masses. As highlighted previously, this trend is valid for PM_{2.5} mass loading as a whole, with an average of $2.8 \mu\text{g}/\text{m}^3$ measured at

Haulbowline Naval Base against an average of $6.2 \mu\text{g}/\text{m}^3$ reported in Tivoli Docks the following year. One notable exception is the sodium ion, which exhibits an average ambient concentration equal to or slightly higher than its Tivoli counterpart. The Haulbowline Naval Base site appears, therefore, to be more directly affected by a marine influence, which is to be expected considering location. In terms of anthropogenic influence, both sites are likely to be affected by the same combustion sources. The dilution/deposition pattern would indicate that Tivoli is closer to these sources and that PM collected at Tivoli comes predominately from local sources.

Further interesting information gained from analysis of the Haulbowline Naval Base data set is the confirmation that the pronounced seasonal trend in sulfate speciation, identified in Tivoli and discussed above, is also present here. During the summer months of 2007, the same sharp increase in the

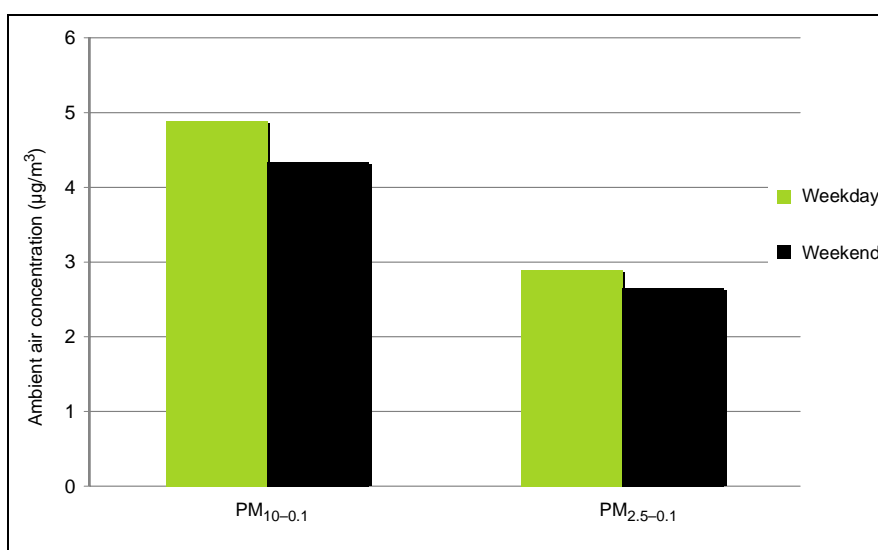


Figure 3.11. Weekday and weekend splits for the mass concentrations of both PM_{10-0.1} and PM_{2.5-0.1} size fractions at Haulbowline Naval Base.

relative mass fraction of sulfate in the PM fine fraction was detected, resulting in potentially strongly acidic particle formation during this period. Based on the seasonal breakdown of the ammonium to sulfate ions ratio, the sulfate speciation is seen to shift clearly to sulfuric acid in the summer (using an ammonium to sulfate ratio of 1.5 as a threshold value). In this season, 83% of the collections made at the Haulbowline Naval Base site can be considered acidic ([Table 3.11](#)).

Note that the average ammonium to sulfate ions ratio is constantly lower for the Haulbowline Naval Base site when compared with the corresponding season at the Tivoli Docks site, leading to comparatively more frequently acidic collections being sampled at Haulbowline Naval Base. This feature could be a consequence of the availability of lower amounts of ammonium ions due to the Haulbowline Naval Base site being situated further away from rural sources of ammonia (e.g. fertiliser). In this regard, it is of interest that only 29% of the collections are acidic in spring, when agricultural use of fertiliser is at its highest.

The contrast in seasonal acidity is mainly attributable to the increase in the ionic mass fraction of sulfate during the summer months during which it scales up to 45% compared with an average of 25% for the rest of the year. The observation is similar to that observed at the Tivoli site. However, while the sulfate mass fraction increases mainly at the expense of nitrate and ammonium ions at Tivoli Docks, it is compensated at

Haulbowline Naval Base by a concomitant decrease in the chloride ion mass fraction. As this does not affect the sodium mass fraction, it can be surmised that the chloride ion depletion occurs as a result of its displacement into the gas phase as hydrochloric acid following in situ reactions between sulfuric acid and sodium chloride. The increased intensity of this chloride displacement is an indirect indication that particulate sulfate in ambient air is more acidic in the Mid-Harbour (Haulbowline Naval Base site) than in the Upper Harbour area (Tivoli Docks site) not only during the summer months but all year round as shown in [Table 3.12](#).

Given the 13% fluctuation across the five monitored seasons ([Table 3.13](#)), the seasonal variability of sulfate is the smallest monitored for all the ionic ambient concentrations, making sulfate emissions the most stable contributors to the major ionic components of PM_{2.5} at Haulbowline Naval Base; the value compares with a 37% variability for sodium. By contrast, the most stable ionic contributors to the fine PM fraction collected at Tivoli Docks are sodium, magnesium and calcium (seasonal variability of 23%, 20% and 27%, respectively), which is indicative of the sustained influences of marine aerosols and soil dust re-suspended by local transport activity all year round. The ambient sulfate concentration at Tivoli Docks exhibits a seasonal variability of 39%, an indication of the multiplicity of the sources monitored at this particular receptor site. Of course the intensity of some

Table 3.11. Averaged ammonium to sulfate ions ratio ($[\text{NH}_4^+]/[\text{SO}_4^{2-}]$) in PM_{2.5} sampled at Haulbowline Naval Base. Acidic collection refers to the proportion of samples for which $[\text{NH}_4^+]/[\text{SO}_4^{2-}] < 1.5$.

	$[\text{NH}_4^+]/[\text{SO}_4^{2-}]$	Acidic collection (%)
Overall	1.60	53
Spring 2007	2.28	29
Summer 2007	0.92	83
Autumn 2007	1.48	50
Winter 2007–2008	2.09	42
Spring 2008	1.65	43

Table 3.12. Comparison of average seasonal chloride to sodium ions mass ratio obtained at the Tivoli Docks and Haulbowline Naval Base sites. The theoretical chloride to sodium ratio for sea salt is 1.8. The high winter value at Tivoli Docks indicates additional contributions from domestic solid fuel near Cork City.

	Chloride to sodium ratio	
	Haulbowline Naval Base	Tivoli
Spring	1.3	1.61
Summer	0.89	1.12
Autumn	1.24	1.61
Winter	1.71	2.51

Table 3.13. Seasonal variability of major ionic species sampled in the PM_{2.5} collections at Haulbowline Naval Base and Tivoli Docks, expressed as the standard deviation of the ambient concentration for each season relative to the yearly average for each species.

	Seasonal variability (%)	
	Haulbowline Naval Base	Tivoli Docks
Chloride	58	44
Nitrate	72	69
Sulphate	13	39
Sodium	37	23
Ammonium	51	64
Magnesium	48	20
Calcium	46	27

sulfate contributors, such as domestic heating in Cork City, is expected to vary greatly during the year. Again, by contrast, Haulbowline Naval Base appears to be exposed to sources with a more constant yearly emission profile as regards ambient sulfate levels ([Fig. 3.12](#)).

3.2.3 Trace metals

The water-soluble fraction of the Haulbowline Naval Base PM samples was analysed for trace metals. Analyses of acid-extracted metals (total metals) were

not conducted on samples from Haulbowline Naval Base due to a lack of time and resources; it is envisioned that at least some of the sample set will be analysed for 'total metal' content in the future. Therefore, it is not possible to come to any definitive conclusions regarding the ambient concentrations of the three metals (Pb, Cd, Ni) in the ELIPSE database that are subject to limits and target values under European Directive 1999/30/EC and the Fourth Daughter Directive 2004/107/EC. However, given the ambient PM levels monitored at Haulbowline Naval

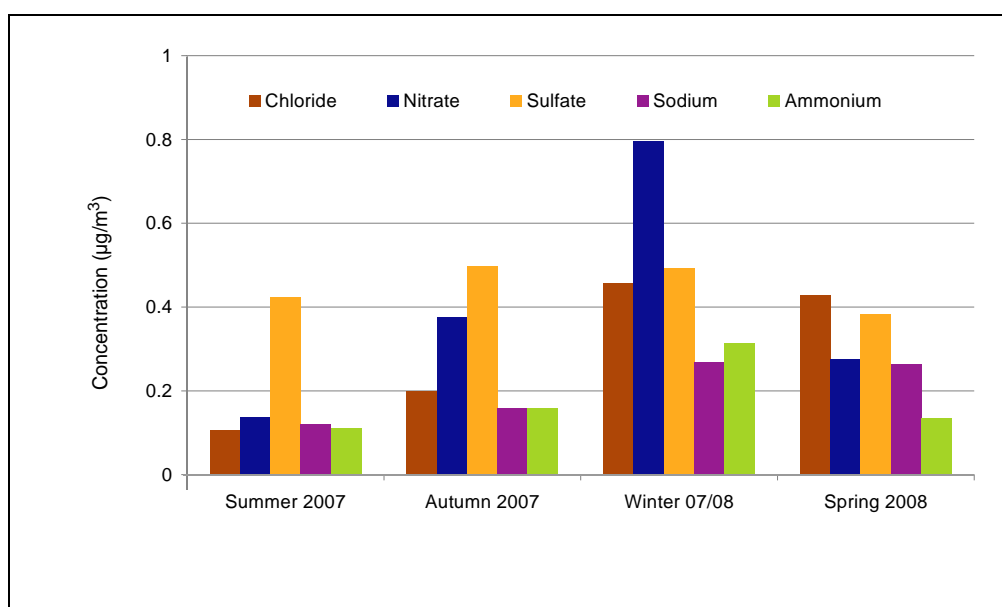


Figure 3.12. Ambient concentrations (µg/m³) of major ionic species measured in PM_{2.5} at Haulbowline Naval Base, averaged for each season.

Base compared with Tivoli Docks and in view of solubility considerations (Fig. 3.8), the ambient concentrations of lead, cadmium and nickel at Haulbowline Naval Base almost certainly lie safely below their respective lower assessment thresholds for the protection of human health (Table 3.14). The annual ambient concentrations of all trace metals detected at Haulbowline Naval Base appear very low in comparison with studies made in Spain (including a harbour area), where in one study the mean ambient levels of lead, cadmium and nickel in PM₁₀ were measured as 12, 4 and 6 ng/m³ respectively, while chromium levels at a harbour site were 4 ng/m³ in PM₁₀ (Alastuey et al., 2007).

In terms of PM_{2.5}, the levels found in Cork Harbour appear to be in line with mass loadings detected at rural/urban background sites in another study from

Spain (Querol et al., 2007). Few studies have in fact been performed that can be directly compared with the ELIPSE study. However, for chromium belonging to PM_{2.5}, concentrations were found at 1–5 ng/m³ levels for a background site in the Querol et al. study. Furthermore, at their chosen steel site location, the level was found to be 15 ng/m³. Hence, in the ELIPSE study, the measured maximum of 0.25 ng/m³ for chromium falls well within the background site levels determined in Spain even allowing for the fact that only water-soluble chromium levels were determined. Likewise, this Spanish study found concentrations of 'total' cadmium at its background to be in the range of 0.2–0.4 ng/m³ compared with this ELIPSE study which found maximum water-soluble cadmium levels to have a mean of 0.06 ng/m³ and a median of 0.04 ng/m³. An estimate of the solubility of different metal species was

Table 3.14. Ambient concentration (ng/m³) of water-soluble ionic species and trace metals for PM_{2.5-0.1} for particulate matter collected at Haulbowline Naval Base, Mid-Harbour. SD, standard deviation; %BDL, percentage of collections below method detection limit (Tables 2.2 and 2.3) for individual elements/ions.

	Average	Median	Minimum	Maximum	SD	%BDL
Lead	1.01	0.73	0.30	13.75	1.48	78
Iron	1.23	0.60	0.03	9.14	1.79	4
Aluminium	4.82	3.75	0.39	20.52	4.25	1
Manganese	0.24	0.16	0.00	1.70	0.29	3
Chromium	0.06	0.03	0.00	0.25	0.06	27
Magnesium	30.38	26.88	2.32	84.59	19.65	0
Calcium	22.89	19.20	2.86	134.31	19.05	3
Copper	0.16	0.07	0.01	1.15	0.22	32
Cadmium	0.06	0.01	0.00	0.32	0.07	59
Antimony	0.22	0.21	0.10	0.99	0.11	91
Barium	0.15	0.10	0.01	0.94	0.16	16
Nickel	0.24	0.19	0.04	1.05	0.19	0
Zinc	2.80	1.44	0.11	19.63	3.57	1
Vanadium	0.40	0.21	0.02	3.08	0.55	22
Chloride ion	281.98	263.54	6.67	882.81	213.09	0
Bromide ion	0.81	0.74	0.18	2.66	0.62	38
Nitrate ion	451.19	174.32	23.87	4,878.08	816.92	0
Sulfate ion	467.18	322.26	67.68	2,207.34	384.49	0
Sodium ion	197.73	198.24	21.65	508.84	107.90	0
Ammonium ion	201.37	78.28	2.26	1,952.01	335.61	10
Potassium ion	16.53	14.44	2.23	61.49	9.97	8
Magnesium ion	25.16	22.88	1.04	72.98	17.42	1
Calcium ion	17.54	14.20	1.67	127.54	17.36	10

performed using both water-soluble and acid-digested ('total') measurement on data from Tivoli Docks and is outlined in [Section 3.1.3](#) and [Fig. 3.8](#).

3.2.4 Source apportionment studies: weekend/weekday splits

The weekend/weekday dichotomous approach described earlier in [Section 3.1](#) was applied to the water-soluble fraction of the Haulbowline Naval Base samples. From the weekend to weekday ratio data plotted in [Fig. 3.13](#), two broad groupings emerge:

1. Iron, aluminium, manganese, calcium, barium and zinc, with a dependence on the weekly economic cycle (ambient levels higher during weekdays, in relative terms); and
2. Lead, chromium, copper, cadmium, antimony, nickel and vanadium, whose emissions are sustained or independent of any weekly pattern.

The first group of metals is dominated by crustal elements and is certainly generated by dust re-suspension associated with road transport, which is more prominent during weekdays. The second group

is unambiguously associated with fuel combustion sources, with lead, nickel and vanadium as its key markers. However, antimony also occurs in soil while chromium and cadmium individually can be associated with several industrial activities including steel manufacturing. No steel manufacturing has been ongoing in Cork Harbour since the closure in 2001 of the Irish Steel facility situated on Haulbowline Island, yet some waste material resulting from activities for this facility remain on the Island. Re-suspension of materials from contaminated soil at the Irish Steel site may influence the elemental composition of naturally occurring wind-generated aerosol emissions in the area. Hence, this second elemental grouping appears to be the result of combined emissions from heavy oil combustion (power generation, shipping) and the wind-driven suspension of soil particles, neither component being tied to any cyclical weekly pattern. It is important to reaffirm that although the chromium and cadmium grouping of trace metals is present in the ambient air associated with the Haulbowline Naval Base receptor site, their concentrations are at levels found, internationally, at rural/urban background

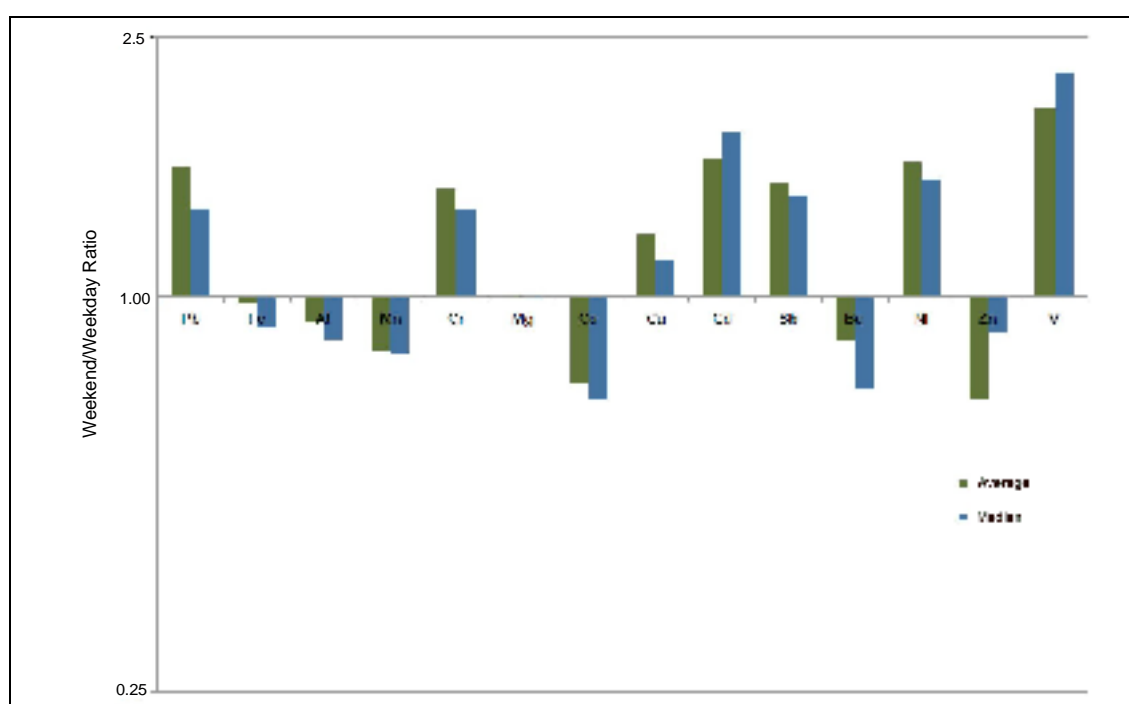


Figure 3.13. Weekend to weekday ratios of relative concentration (elemental mass fraction in $\mu\text{g/g}$) for trace metals detected in $\text{PM}_{2.5}$ at Haulbowline Naval Base. Yearly average and median were used. The vertical axis has a log scale in order to highlight the pivotal quality of a ratio of 1.

monitoring sites as opposed to industrial locations (Querol et al., 2007).

In the case of the Haulbowline Naval Base data set, the source identification was refined using PCA. This apportionment model identified three supplementary aerosol sources besides the obvious marine component (PC2), namely Combustion and Traffic Emissions (PC1), Road Dust (PC3) and Heavy Fuel (PC4). PC1 combined the secondary ions characteristic of combustion processes (NH_4^+ , NO_3^- and SO_4^{2-}), with trace metal markers such as zinc, iron and lead whose sources typically include vehicular tailpipe emissions, as well as industrial incineration and combustion processes. PC3 is characterised by calcium and aluminium and, hence, appears typically crustal. It is obviously influenced by the re-suspension of local material found on the island itself, which could explain why zinc and manganese are also associated with this component. PC4 is dominated by nickel and vanadium, associated with lead and zinc, all trace elements released in atmospheric PM by combustion of heavy oil such as ship bunker fuel. Results of the completed analysis of the Haulbowline Naval Base data set are shown in [Table 3.15](#).

Comparison of the metals in the water-soluble fraction for both sites shows that, similarly to the ion analyses, the ambient concentrations of the selected trace metals detected undergo systematic dilutions as they

travel from Tivoli Docks to Haulbowline Naval Base ([Table 3.15](#)). This observation again indicates that the former receptor site is closer to more pollution sources and leads to the conclusion that *most* of the trace metal emissions have their origin in the Upper Harbour area, close to the City Centre and its main traffic arteries. Ambient levels of manganese, barium, zinc and copper are significantly higher at the Tivoli Docks site ([Fig. 3.14](#)).

Two notable exceptions are evident from [Fig. 3.14](#), namely chromium and cadmium, whose average ambient concentrations measured in Mid-Harbour exceed their Tivoli equivalents. Given this finding and the existence of a strong correlation between chromium and cadmium at this receptor site ([Table 3.16](#)), the possibility could exist that these trace metal markers for stainless steel manufacturing are attributable to re-suspension of waste material from contaminated soil on the former steel plant on Haulbowline Island. However, as stated above, the ambient concentrations of all trace metals detected, are relatively low compared to those found, internationally, in industrialised regions. It is not possible, from the ELIPSE study, to conclude if the detection of chromium and/or cadmium is due to re-suspension of waste material from soil on the former Irish Steel site facility on the Island as, at the levels detected, such concentrations could be attributable to re-suspension of natural crustal material.

Table 3.15. Comparison between averages and medians of concentrations of the water-soluble metal fraction of $\text{PM}_{2.5}$ from Tivoli Docks and Haulbowline Naval Base.

	Tivoli Docks				Haulbowline Naval Base			
	Average (ng/m^3)	Median (ng/m^3)	Minimum (ng/m^3)	Maximum (ng/m^3)	Average (ng/m^3)	Median (ng/m^3)	Minimum (ng/m^3)	Maximum (ng/m^3)
Lead	1.23	0.89	0.54	7.34	1.01	0.73	0.30	13.75
Iron	2.38	1.28	0.09	19.92	1.23	0.60	0.03	9.14
Aluminium	4.87	1.81	0.42	43.91	4.82	3.75	0.39	20.52
Manganese	1.32	0.64	0.01	10.00	0.24	0.16	0.00	1.70
Chromium	0.03	0.01	0.01	0.26	0.06	0.03	0.00	0.25
Copper	0.32	0.23	0.01	2.78	0.16	0.07	0.01	1.15
Cadmium	0.05	0.04	0.01	0.36	0.06	0.01	0.00	0.32
Barium	0.50	0.42	0.05	2.32	0.15	0.10	0.01	0.94
Nickel	0.33	0.26	0.02	1.57	0.24	0.19	0.04	1.05
Zinc	6.60	4.27	0.09	69.84	2.80	1.44	0.11	19.63
Vanadium	0.70	0.60	0.02	2.37	0.40	0.21	0.02	3.08

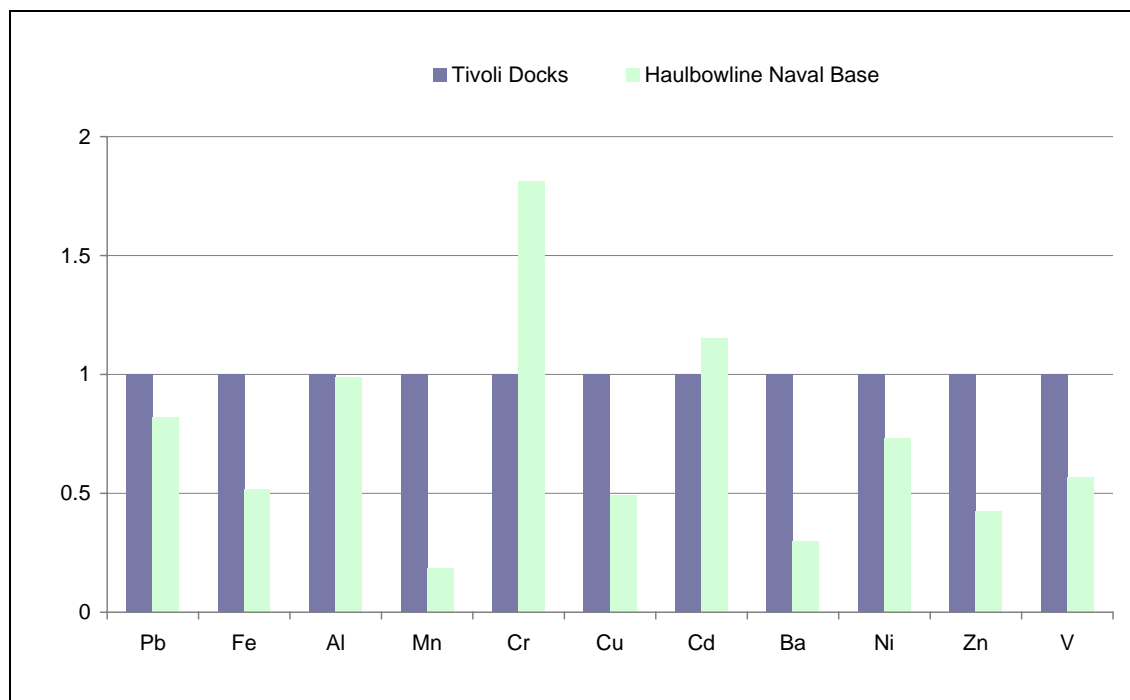


Figure 3.14. Annual ambient concentration of trace metals detected in PM_{2.5} (water-soluble fraction) at Haulbowline Naval Base (green) normalised for equivalent concentration (water-soluble fraction) measured at Tivoli Docks (blue). Ratio of metal concentrations used in order to compare all metals irrespective of actual magnitude of concentration.

Table 3.16. Bivariate correlation between trace metals in PM_{2.5-0.1} sampled at Haulbowline Naval Base. Values highlighted in green show a significant degree of correlation (>0.7).

	Lead	Iron	Aluminium	Manganese	Chromium	Copper	Cadmium	Barium	Nickel	Zinc	Vanadium
Lead	1.00										
Iron	0.61	1.00									
Aluminium	0.39	0.55	1.00								
Manganese	0.47	0.90	0.54	1.00							
Chromium	0.24	0.39	0.41	0.56	1.00						
Copper	0.35	0.57	0.27	0.53	0.19	1.00					
Cadmium	0.20	0.31	0.32	0.51	0.96	0.25	1.00				
Barium	0.16	0.39	0.39	0.59	0.69	0.37	0.71	1.00			
Nickel	0.49	0.80	0.61	0.78	0.62	0.60	0.56	0.50	1.00		
Zinc	0.37	0.69	0.49	0.70	0.27	0.42	0.23	0.35	0.63	1.00	
Vanadium	0.41	0.63	0.37	0.57	0.31	0.84	0.32	0.31	0.79	0.47	1.00

4 Results from the Tivoli Docks Intensive Campaigns

Two intensive measurement campaigns at Tivoli Docks were made, each for 1-month duration, as part of the overall programme. A summer month (August 2008) and a winter month (February 2009) were chosen as clear contrasts and the entire suite of monitoring instruments available to ELIPSE were deployed. The objectives for performing such a set of measurements were as follows:

- To determine the chemical compositions and size distributions of the collected PM that originates from shipping emissions;
- To determine the chemical compositions, by measurement of known pollutant markers, of the other major sources of emissions in Cork Docks/Harbour; and
- To estimate the relative contribution of shipping emissions to overall airborne pollution in the Harbour area, both in terms of the percentage of total PM and the percentage of total particle number present.

4.1 Characterisation of Single Particles Originating from In-Port Ship Emissions

A unique mass spectral signal giving the internal mixing state of single particles freshly emitted from ships was made using an ATOFMS (TSI model 3800) fitted with an aerodynamic lens (TSI model AFL100) during the August 2008 campaign. The results are novel and have been confirmed in a later study on shipping emissions performed in the USA (Ault et al., 2009).

Hence, analysis of the particles in the 100- to 3,000-nm size range allowed for the identification of a mass spectral signature for locally emitted (fresh) ship exhaust particles. The signature contains contributions from internally mixed organic carbon (m/z 12, $[C]^+$, 27, $[C_2H_3]^+$, 36, $[C_3]^+$, 37, $[C_3H]^+$), elemental carbon (m/z -12, $[C]^-$, -24, $[C_2]^-$, -36, $[C_3]^-$, -48, $[C_4]^-$), sodium (m/z 23, $[Na]^+$), calcium (m/z 40, $[Ca]^+$), iron (m/z 56,

$[Fe]^+$), vanadium (m/z 51, $[V]^+$, 67, $[VO]^+$), nickel (m/z 58, $[Ni]^+$), cyanide (m/z -42, $[CN]^-$), and sulfate (m/z -64, $[SO_2]^-$, -80, $[SO_3]^-$, -81, $[HSO_3]^-$, -97, $[HSO_4]^-$) (Fig. 4.1).

Each of the components observed in the mass spectra can be attributed to the combustion of marine residual fuel oil typically burned by ships at sea and in port. Contaminants that do not distil during refining are concentrated into the residual fraction, including both water- and oil-soluble ions such as sodium, calcium, iron, vanadium and nickel (Moldanová et al., 2009). Sulfate is known to be formed rapidly in ship stacks from gas-particle conversion of sulfur dioxide (Hobbs et al., 2000; Murphy et al., 2009). The presence of the cyanide ion does not necessarily indicate that cyanide is present in the particles but does indicate that carbon and nitrogen are internally mixed, probably in the form of nitrogen-containing organic compounds (Silva et al., 1999). Organic and elemental carbon have also been previously directly observed in ship plumes using an AMS (aerosol mass spectrometer) and a particle soot absorption photometer (Lu et al., 2006; Murphy et al., 2009). More recently, sodium, calcium and vanadium have all been observed in ship exhaust particles using off-line energy-dispersive X-ray spectroscopy (EDS) and two-step laser mass spectrometry (L2MS) (Moldanová et al., 2009; Murphy et al., 2009). Moldanová et al. (2009) observed four distinct ship exhaust particle types:

1. Soot-type particles (approximately 50 nm mean diameter) containing vanadium/nickel/sulfur;
2. Carbonaceous char particles (200–5,000 nm in diameter) containing vanadium/calcium/nickel/iron;
3. Mineral/Ash particles containing lime, calcite and nickel sulfide; and
4. Organic particles containing semi-volatile species (approximately 100 nm diameter).

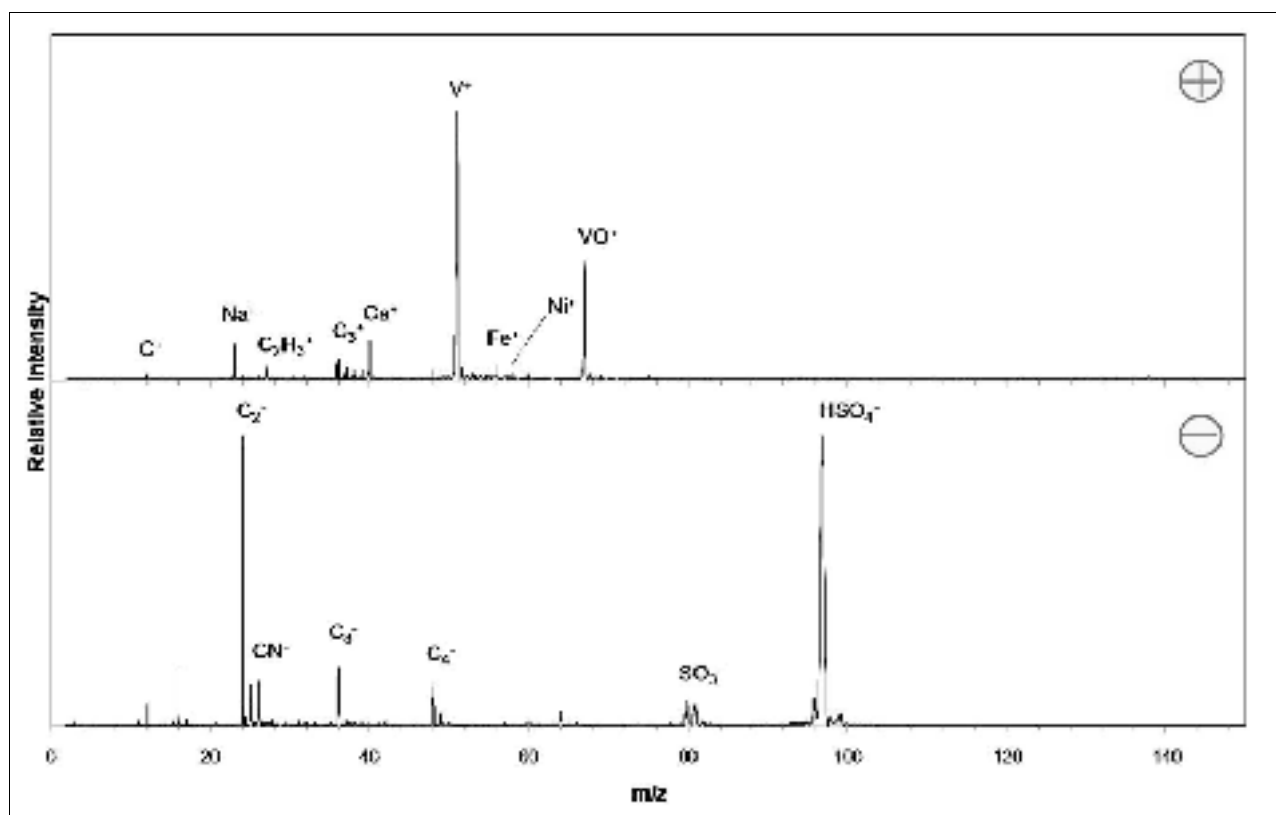


Figure 4.1. Typical positive and negative ion mass spectra for 200-nm shipping emission particles (sizes correspond to aerodynamic diameter).

In this study, internally mixed particles (OC/EC/Na/Ca/V/Ni/Fe/SO₄) were found and are thus most likely freshly emitted carbonaceous char based on their size and composition. The nitrate content is almost certainly of secondary origin, while the sulfate may be primary or secondary based on the high sulfur content of residual fuel oil. The water-soluble ions, sodium and calcium, are also internally mixed with vanadium and iron. The relatively small size and chemical composition of the particles detected by ATOFMS here suggest a local freshly emitted ship exhaust source, and this conclusion is supported by meteorological data, other real-time measurements and berthing records obtained from the Port of Cork as outlined in subsequent sections of this report (Fig. 4.2).

The temporal trend for the shipping emission particles is shown in Fig. 4.2, where 23 ‘sharp’ events were observed for assigned exhaust particles, typically lasting less than 30 min. When compared with shipping logs from the Port of Cork, each of these events was matched to the berthing/departure times of container

or liquid bulk ships. Gross tonnage for these ships was in the range 3,000–8,000 GT. No discernible difference was observed between mass spectra for each event indicating that each of the ships observed was burning residual fuel oil of similar composition. When coupled with wind direction data (temporal resolution of 1 h), a strong dependence on south-westerly and west-south-westerly wind was observed for particles of this type (Fig. 4.3). This measurement indicates that these particles were emitted from the nearby berths, probably while ships were running auxiliary engines and operating bow and stern thrusters (Cooper, 2003).

Several events were observed during the first and third week of the August 2008 campaign when the wind was predominantly from a west-south-westerly or south-westerly direction. Between 14 and 23 August, the wind was predominantly north-westerly, explaining the absence of ship exhaust events for this period. A slight dependence on an easterly wind was apparent, which is most likely due to ships passing the site from the

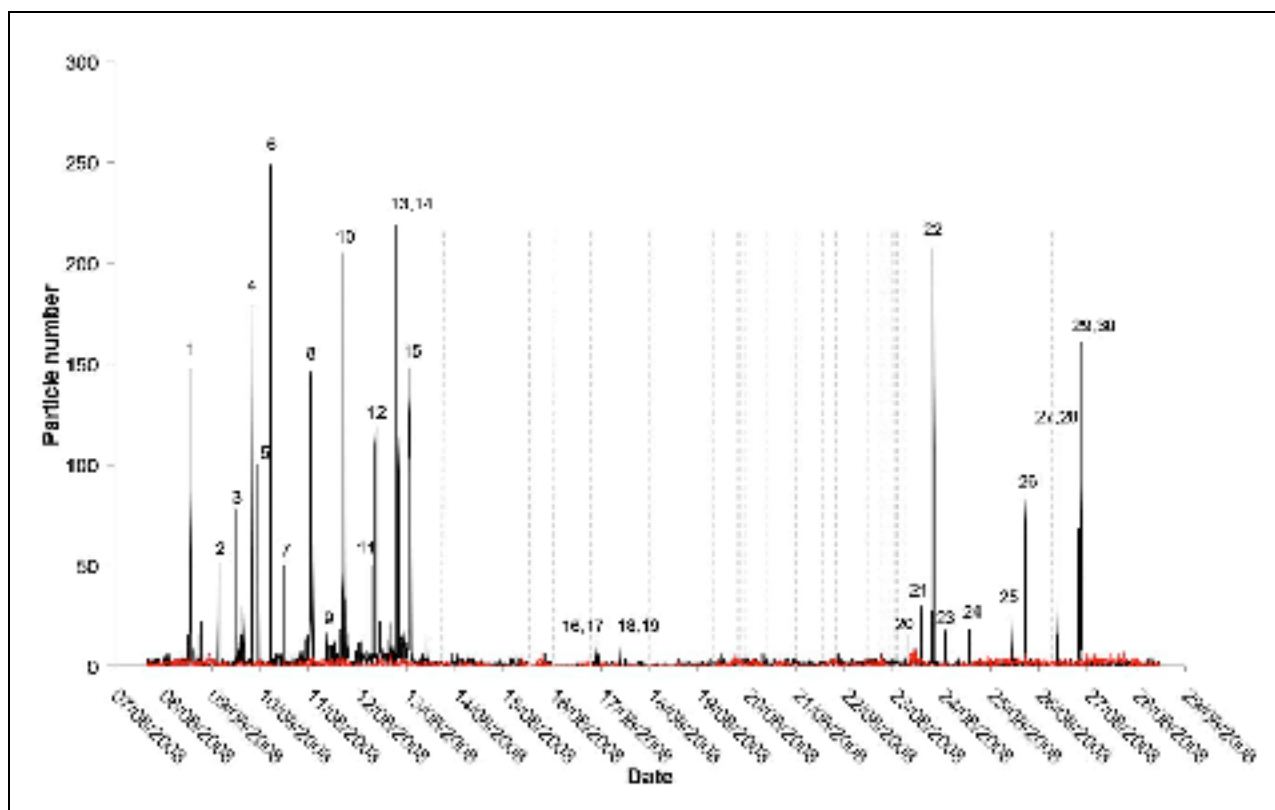


Figure 4.2. Temporal trends for ship exhaust particles (black) successfully sized and ionised by an aerosol time-of-flight mass spectrometer. Particle number is summed up to 10-min intervals. Each number represents an individual ship's berthing.

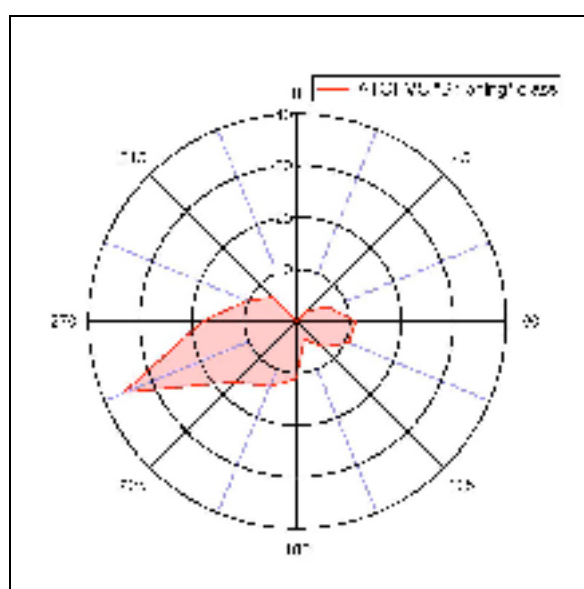


Figure 4.3. Dependence of the number of particles detected by an aerosol time-of-flight mass spectrometer on wind direction with a temporal resolution of 1 h. Particle number has been normalised based on wind direction. No hourly averaged wind values were observed from the north–north–west, north or north–north–east directions.

east as they approach the berths (see [Section 2.1.1.2](#), [Fig. 2.3](#)).

Some types of particles, with similar composition but with larger size distribution, did not exhibit an obvious dependence on wind direction ([Fig. 4.3](#)) and were not correlated with ship exhaust particles ($R^2 = 0.004$, 1 h temporal resolution). The data suggest that the origin of such particles is possibly from the 'background' based on their similarity to those observed by Ault et al. (2009). They contain elemental and organic carbon most likely coming from various combustion processes ongoing in the Cork Harbour region.

Simultaneous SMPS measurements at the site demonstrate that ship exhaust particle number distributions in the size range 20–600 nm (mobility diameter) are characterised by an ultrafine mode with a maximum at approximately 50 nm that coincides with ATOFMS-labelled particle events ([Fig. 4.4](#)). The highest ultrafine particle number concentration (mobility diameter 20–100 nm) observed during a ship exhaust event was 212,564 particles/cm³ coinciding

with Event 22 in [Fig. 4.2](#). Based on mobility diameter, the analysis of Moldanová et al. (2009) suggests that these are soot-type particles. These particles lie outside the range of the ATOFMS as the photomultipliers used for optical sizing have a lower aerodynamic diameter detection limit of approximately 100–150 nm due to the limited amount of light scattered. Furthermore, the aerodynamic lens is limited to the transmission of particles in the 100- to 3,000-nm size range (aerodynamic diameter). Thus, 50-nm particles are detected by the SMPS but not by the ATOFMS. Murphy et al. (2009) report a class of ship exhaust nanoparticles between 5 and 8 nm in diameter and Fridell et al. (2008) report a coarse mode approximately 8 μm in diameter arising from re-entrainment of soot particles from the stack walls; however, both of these modes lie outside the measurement range of the particle-measuring instruments used in ELIPSE. Thus, the ATOFMS analysis technique does miss a significant portion of the overall ship exhaust particle distribution.

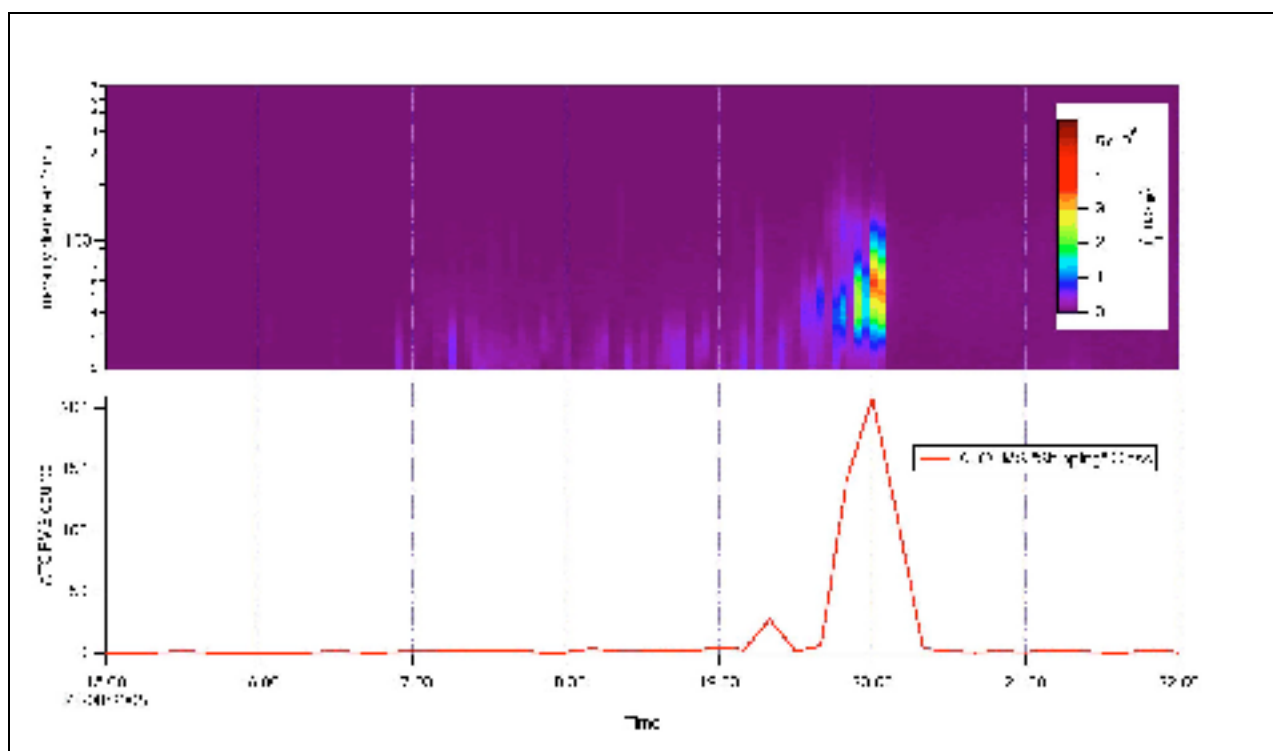


Figure 4.4. Contour plot of a scanning mobility particle sizer particle mobility diameter and number for two ship plume events on 23 August 2008. The plumes coincide with Events 16 and 17 in [Fig. 4.2](#).

The majority of particle events associated with shipping emissions were also characterised by simultaneous increases in sulfate and elemental carbon mass concentrations, and also slight increases in $PM_{2.5}$ mass concentrations. The maximum mass concentrations observed during these events for sulfate, elemental carbon and $PM_{2.5}$ were 2.57 (Event 22, Fig. 4.2), 5.95 (Event 10, Fig. 4.2) and 22.6 (Event 17, Fig. 4.2) $\mu\text{g}/\text{m}^3$, respectively. It should be noted that these sulfate, elemental carbon and $PM_{2.5}$ mass concentrations represent 10-min, 1-min and 30-min averaged values, respectively. In fact, only three of the shipping emission particle events exhibit a coincident increase in sulfur dioxide mixing ratios above background levels. These observations can best be explained by rapid processing events in which sulfur dioxide is converted to sulfate particulate on ship exhaust particles themselves (Hobbs et al., 2000; Murphy et al., 2009). The maximum sulfur dioxide mixing ratio (1-min average) associated with a particle event was 8.2 ppb (Event 13/14, Fig. 4.2).

During the intensive campaign conducted in August 2008, 558,740 mass spectra were generated by the ATOFMS. Following the *K*-means analysis, one cluster in particular, which was clearly related to shipping-emission-type particles, exhibited very sharp temporal trends with no dependence on time of day and exhibited aerodynamic diameters in the 150- to 900-nm range (Fig. 4.5). The precise assignment of this grouping to a particular chemical class will need further data to be collected from other campaigns.

4.2 Source Apportionment of $PM_{2.5}$ in Cork Harbour

4.2.1 Discriminating between particle classes using ATOFMS

The ATOFMS was co-located with a suite of semi-continuous instrumentation for the quantitative measurement of elemental and organic carbon, particulate sulfate, particle number and $PM_{2.5}$ mass at Tivoli Docks, Ireland, for 3 weeks in August 2008. Off-line analysis of polar organic markers was also performed for samples collected over the same period

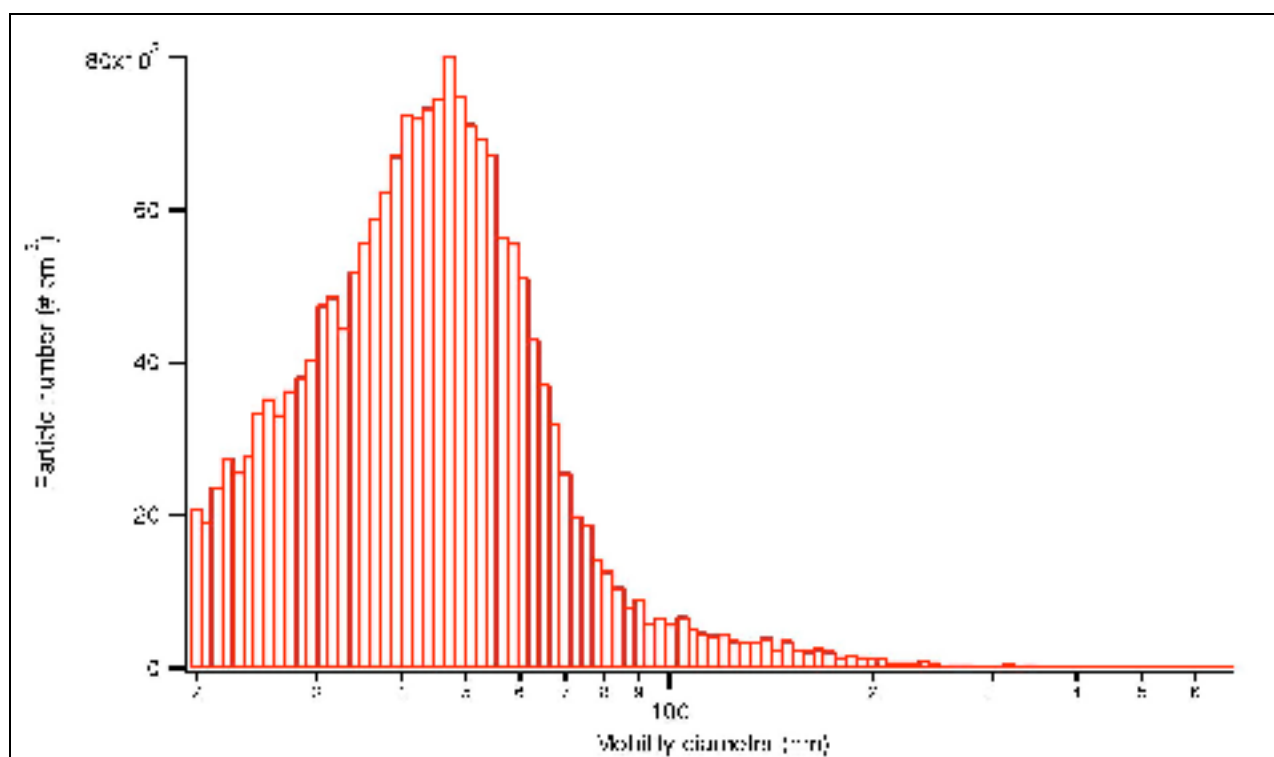


Figure 4.5. Size distribution of ship exhaust particles ionised by an aerosol time-of-flight mass spectrometer.

of time. The data obtained were used to identify and source-apportion local and regional sources of the airborne PM_{2.5}. Over 550,000 ATOFMS particle mass spectra were generated and classified using the *K*-means algorithm. The vast majority of particles ionised by the ATOFMS could be attributed to local sources. The temporalities associated with the ambient ATOFMS particle classes identified were subsequently used in conjunction with the semi-continuous measurements in order to apportion PM_{2.5} mass data using the PMF technique. Six factors were obtained, corresponding to vehicular traffic, marine, long-range transport, power generation, domestic solid-fuel combustion and shipping traffic. A breakdown of the contribution of these factors, which represent local, regional and long-range sources, is outlined in [Table 4.2](#). For the purposes of this report, two of the ATOFMS classes and two of the PMF-derived factors are discussed – domestic solid-fuel combustion and shipping traffic. (For full details of the source apportionment methods applied refer to Healy et al., 2010.)

4.2.1.1 Shipping

Shipping particles exhibited a very strong dependence on west–south-westerly wind direction, as discussed in [Section 4.1](#), but little or no dependence on time of day; they accounted for approximately 4% of the particles ionised. These particles were observed in short, sharp events and were attributed to ships entering and departing from the nearby shipping berths. This hypothesis was confirmed through comparison with the Port of Cork shipping logs. The full details are outlined in an article published as a result of this study (Healy et al., 2009) and are also described in [Section 4.1](#) of this report.

4.2.1.2 Coal, peat and wood

Coal, peat and wood particles accounted for 41%, 10% and 9%, respectively, of the total particles successfully ionised and detected by the ATOFMS; they were observed almost exclusively in the submicron size range. The results indicate that, even during the summer months, domestic solid-fuel combustion is an important source of PM_{2.5} in Cork Harbour. The clustering procedure used in this study allowed for the separation of freshly emitted and aged combustion particles into subclasses. These subclasses were then

recombined for PMF as they originate from the same source type.

Controlled combustion experiments were therefore undertaken in order to generate ‘fresh’ fuel particles, which could be identified by their ATOFMS signature and then compared with the ambient sampling results. Average dual-ion mass spectra for freshly emitted ambient ‘coal-fresh’, ‘peat-fresh’ and ‘wood-fresh’ clusters were compared with those generated during the controlled laboratory experiments (see Healy et al. (2010) for detailed description of this chemical comparison).

Although none of these ions are individually unique to the combustion of coal, there is a very strong similarity in the relative ion intensities of freshly emitted coal combustion particles and the ambient ‘coal-fresh’ particles. Strong signals for sulfate were consistently observed even for freshly emitted coal combustion particles. ‘Peat-fresh’ particles are characterised by much higher signals for sodium (m/z 23, [Na]⁺) and potassium (m/z 39, 41, [K]⁺) which dominate the positive ion mass spectra, although similar carbon and hydrocarbon fragments to those observed for coal are also present.

Spectra generated from wood-burning particles during the controlled combustion experiment exhibit almost identical positive ion mass spectra to those observed in the ambient data set; they also share many of the same ions in the negative ion mass spectra. However, the particles generated during the combustion experiment contain much higher signals at m/z –43 and –59, which probably correspond to the oxidised organic carbon fragments C₂H₃O[–] and CH₃COO[–], respectively.

The average dependence of the various coal, peat and wood subclasses on time of day is shown in [Fig. 4.6](#). The average diurnal profile for the three freshly emitted particle types is very similar, increasing sharply between 18:00 and 21:00 h, and decreasing sharply after 22:00 h. The periods of increasing and decreasing particle number can be explained by the lighting of fires and their eventual extinction.

All three domestic combustion particle classes are very well correlated with each other ($R^2 > 0.90$, least

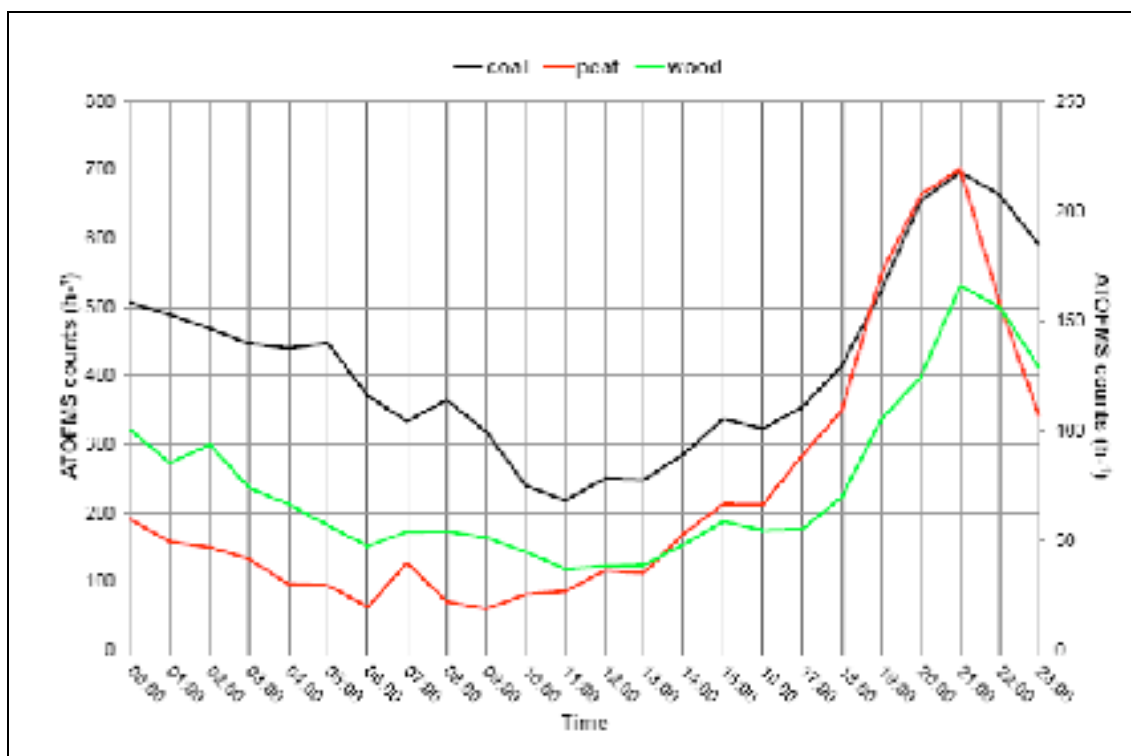


Figure 4.6. Average diurnal trends for coal (top), peat (middle), and wood (bottom) subclass particle counts. The ‘coal-fresh’ particle number has been multiplied by a factor of 5 for clarity. The vertical axes have units of an aerosol time-of-flight mass spectrometer (ATOFMS) particle counts per hour.

squares linear regression), indicative of a single source as shown in [Table 4.1](#). Particle counts for these classes, when summed over 24-h intervals, are also well correlated with the 24-h resolution, off-line quantitative GC/MS measurements made for levoglucosan, mannosan and galactosan. These species arise from the thermal degradation of cellulose and are well-established markers for biomass burning (Pashynska et al., 2002; Simoneit et al., 2004; Kourtchev et al., 2008).

Also, contributions of individual sources to the PM_{2.5} organic carbon were assessed using reported conversion factors for isoprene secondary organic aerosol (SOA), fungal spores and smoke from the combustion of cellulose-containing fuels. The latter factor was experimentally derived in a combustion study for a set of domestic solid fuels commonly used in Ireland, i.e. wood, peat, bituminous and smokeless coal. Polar organic markers were identified after analysis of PM collected on filters during the

Table 4.1. Correlation coefficient squared (R^2) values for the least squares linear regression of coal, peat and wood particle counts and galactosan, mannosan and levoglucosan mass concentrations ($n = 17$).

	Coal	Peat	Wood	Galactosan	Mannosan	Levoglucosan
Coal	1	0.91	0.92	0.68	0.57	0.82
Peat	0.91	1	0.9	0.59	0.53	0.82
Wood	0.92	0.9	1	0.56	0.46	0.81
Galactosan	0.68	0.59	0.56	1	0.9	0.79
Mannosan	0.57	0.53	0.46	0.9	1	0.75
Levoglucosan	0.82	0.82	0.81	0.79	0.75	1

combustion experiment; details of the experiment are given in [Chapter 2](#).

The contribution of domestic solid-fuel burning to the measured organic carbon mass concentration from the burning of peat, bituminous coal, wood and smokeless coal was estimated at 10.8%, 50%, 66.4% and 74.9% for summer, autumn, late autumn and winter periods, respectively (Kourtchev et al., 2011).

This study clearly demonstrates that, despite the ban on the sale of bituminous coal in Cork and other large urban areas in Ireland, domestic solid-fuel combustion is still the major source of organic carbon during autumn and winter periods and also makes a significant contribution to PM_{2.5} levels. The developed marker approach for estimating the contribution of domestic solid-fuel combustion to ambient organic carbon concentrations can, in principle, also be applied to other locations.

4.2.2 Source apportionment

Positive matrix factorisation analysis was performed using the ATOFMS particle classes and quantitative elemental and organic carbon, sulfate, particle number and PM_{2.5} data. A six-factor solution appears to be the most appropriate to describe the data as no useful information is gained by increasing the number of factors. The source categories identified by this six-factor solution can be described as: traffic, marine, long-range transport, power generation, domestic solid-fuel combustion, and shipping. The traffic source contributes an estimated 23%. The estimated

contributions (%) of each factor/source to the measured PM_{2.5} mass and each variable (EC mass, OC mass and SO₄ mass) are given in [Table 4.2](#). For each variable, the sum of all contributions from the factors accounts for 100% of the measured mass because the model is restricted to these six sources. On average during this period, the sum of the individual mass loadings for each of the measured variables (EC, OC, SO₄) only amounted to 67% of the total PM_{2.5} mass obtained from separate gravimetric measurements. Consequently, the contributions of each factor to the PM_{2.5} mass have been scaled to account for this fact.

4.2.2.1 Domestic solid-fuel combustion

This factor is characterised by contributions of 52%, 84% and 63% to the coal, peat and wood ATOFMS classes, respectively. The value for coal is lower than that for peat due to the input from power generation to the former. However, the contribution to the wood class is also relatively low when compared with peat, suggesting that either another unidentified source exists or some incorrect distribution among the other factors has occurred. High contributions to the elemental carbon domestic and oligomer particle classes are also observed (91% and 76%, respectively). The observations provide good support for the hypothesis that oligomers are present in relatively fresh domestic combustion particles. This factor contributes 21% and 20% to the organic and elemental carbon measured, and is estimated to contribute 5% to the measured PM_{2.5} mass.

Table 4.2. Percentage variable contributions to the six-factor positive matrix factorisation model and estimated percentage contribution of each factor to the measured ambient PM_{2.5} mass.

	Traffic	Marine	Long-range	Various combustion	Domestic combustion	Shipping	Total
Quantitative measurements							
Organic carbon mass	21	20	18	16	21	4	100
Elemental carbon mass	43	5	11	18	20	4	100
Sulfate mass	9	23	15	40	11	2	100
Particle number¹	42	6	7	13	14	18	100
PM_{2.5} (mass)	23	14	13	11	5	1	67

¹Mobility diameter range, 20–600 nm.

4.2.2.2 Shipping

The shipping factor was not identified in the initial study of Hellebust et al. (2010b) due to the absence of complementary ATOFMS data. However, with this input, a contribution of 100% is observed for the ATOFMS shipping class. This figure is expected, as these unique particles are emitted exclusively from container and liquid bulk vessels arriving and departing from the nearby shipping berths, with no input from other sources (Healy et al., 2009). Although shipping

traffic is estimated to contribute only 1.5% to the ambient PM_{2.5} mass collected during the sampling period, it contributes 18% to the total number of particles detected by the SMPS. This value is second only to road traffic (with a contribution of 42%). Thus, it appears that local shipping traffic can contribute significantly to the local ambient particle number in the 20- to 600-nm size range (mobility diameter) in Cork Harbour.

5 Conclusions

Ship exhaust particles collected in Cork Harbour have been identified and chemically characterised by their unique mass-spectral signature (OC/EC/Na/Ca/V/Ni/Fe/SO₄²⁻). Their temporal trends were shown to match the shipping logs from the Port of Cork and to coincide with increases in elemental carbon, particulate sulfate and PM_{2.5} mass concentrations. Ultrafine particle numbers were also observed to peak coincident with these emissions.

The contributions of various local and regional sources to ambient levels of PM_{2.5} mass in Cork Harbour have been estimated using PMF and PCA techniques. Following an intensive monitoring campaign during August 2008, specific sources were identified, accounting for an estimated 66% of the PM_{2.5} mass measured at Tivoli Docks. Local vehicular traffic was found to be the largest source contributing to ambient PM_{2.5} mass in Cork Harbour during the summer. Shipping traffic emissions were not a significant contributor to ambient PM_{2.5} mass, but were found to be an important contributor to particulate number when compared with other Harbour pollution sources. Considering that fresh ship exhaust particles reside predominantly in the ultrafine mode containing polycyclic aromatic hydrocarbons and transition metals with known toxicological effects, this source may have implications for human health in the area (Fridell et al., 2008; Healy et al., 2009; Murphy et al., 2009; Sodeau et al., 2009).

A second intensive Harbour monitoring campaign was conducted during February 2009. During the winter, domestic solid fuel became the single most important source of ambient particulate pollution in the region with an estimated contribution of 75% to organic carbon and 30% to PM_{2.5} mass. Particles emitted from individual fuel types such as coal, peat and wood were identified in the ambient data set by their mass spectra. These results were validated by ancillary reference combustion experiments using ATOFMS to monitor the emissions.

The distribution of the variable mass loadings of the ATOFMS particle classes across six factors provided information that could not have been ascertained without the use of models. Hence, domestic- and power-generation-related coal-burning events could be separated and the identification of a marine organic carbon contribution could be made. The results indicate that the temporality of these uniquely characterised ATOFMS particles can be used to efficiently separate local freshly emitted in-port shipping emissions from other local and regional sources, and thus estimate their contribution to air quality.

Analysis of the ionic composition of the fine particulate matter sampled in Cork Harbour over the duration of the project highlighted issues relating to sulfate speciation and the prominence of airborne acidic particles in the summer. The phenomenon appeared to be neither site specific nor dependent on the sampling year. It affects the greater Cork Harbour and exhibits a recurrent yearly pattern, which could have health implications as particle acidity has been linked with cell toxicity, particularly with regard to the bioavailability of associated trace metals. Seasonal sulfate variations hinted at the presence of a sustained source located south-east of the Harbour that impacted more directly and more strongly on particles sampled at Haulbowline Naval Base than on those collected at Tivoli Docks. The existence and probable location of this source, tentatively linked to power generation in the Whitegate–Aghada area, have also been confirmed following the analysis of real-time sulfate measurements made at Tivoli Docks (Hellebust et al., 2010b).

Analysis of the trace metal composition of the fine particulate matter sampled in the Harbour exposed an interesting pattern in the case of aluminium and chromium. Mostly all elements detected exhibit higher ambient concentration levels at Tivoli Docks than at Haulbowline Naval Base – in line with a general dilution pattern of pollution sources generally observed across the Harbour. However, the average ambient

concentrations for chromium and cadmium were higher at Haulbowline Naval Base than for Tivoli Docks. Chromium and cadmium were also found to be strongly correlated, which would indicate a common source. However, the concentrations of these two metals were relatively low (i.e. rural/urban background levels) when compared with similar field studies elsewhere. The concentration of water-soluble cadmium measured in Haulbowline Naval Base during the ELIPSE study has an average of 0.06 ng/m^3 , with a median of 0.01 ng/m^3 . The maximum concentration for cadmium for a single collection at Haulbowline Naval Base was 0.32 ng/m^3 as compared with the 5 ng/m^3 EU limit (24-h average) set out in Directives 2004/107/EC and 2008/50/EC.

Anthropogenic markers for domestic solid-fuel burning were observed throughout the sampling campaign. The data showed that the organic compositions of the collected aerosols were mainly associated with local anthropogenic sources and biogenic emissions. While biogenic marker compounds were detected only during the summer and early autumn seasons, the domestic solid-fuel contribution gradually increased to reach a maximum in the winter. The ELIPSE study clearly demonstrates that, despite the ban on the sale of bituminous coal in Cork, as well as in other large urban areas in Ireland, domestic solid-fuel combustion remains the major source of organic carbon during autumn and winter periods in Cork Harbour and makes a significant contribution to $\text{PM}_{2.5}$ levels.

References

- Alastuey, A., Moreno, N., Querol, X., Viana, M., Artýnano, B., Luaces, J.A., Basora, J. and Guerra, A., 2007. Contribution of harbour activities to levels of particulate matter in a harbour area: Hada Project – Tarragona Spain. *Atmospheric Environment* **41**: 6366–6378.
- Amann, M., Bertok, I., Cofala, J., Gyarfas, F., Heyes, C., Klimont, Z., Schöpp, W., and Winiwarter, W., 2005. *Baseline Scenarios for the Clean Air for Europe (CAFE) Programme*. Final Report B4-3040/2002/340248/MAR/C1, Laxenburg, Austria, 76 pp.
- Ault, A.P., Moore, M.J., Furutani, H. and Prather, K.A., 2009. Impact of emissions from the Los Angeles port region on San Diego air quality during regional transport events. *Environmental Science and Technology* **43**: 3500–3506.
- Bruno, P., Caselli, M., de Gennaro, G. and Traini, A., 2001. Source apportionment of gaseous atmospheric pollutants by means of an absolute principal component scores (APCS) receptor model. *Fresenius. Journal of Analytical Chemistry* **371**: 1119–1123.
- Cooper, D.A., 2003. Exhaust emissions from ships at berth. *Atmospheric Environment* **37**: 3817–3830.
- Corbett, J.J., Winebrake, J.J., Green, E.H., Kasibhatla, P., Eyring, V. and Lauer, A., 2007. Mortality from ship emissions: A global assessment. *Environmental Science and Technology* **41**: 8512–8518.
- Dall'Osto, M. and Harrison, R.M., 2006. Chemical characterisation of single airborne particles in Athens (Greece) by ATOFMS. *Atmospheric Environment* **40**: 7614–7631.
- Dall'Osto, M., Beddows, D.C.S., Kinnersley, R.P., Harrison, R.M., Donovan, R.J. and Heal, M.R., 2004. Characterization of individual airborne particles by using aerosol time-of-flight mass spectrometry at Mace Head, Ireland. *Journal of Geophysical Research – Atmospheres* **109**: (D21) (Article no. D21302).
- Demokritou, P., Kavouras, I.G., Ferguson, S.T. and Koutrakis, P., 2002. Development of a high volume cascade impactor for toxicological and chemical characterisation studies. *Aerosol Science and Technology* **36**: 925–933.
- Eatough, D.J., Grover, B.D., Woolwine, W.R., Eatough, N.L., Long, R. and Farber, R., 2008. Source apportionment of 1 h semi-continuous data during the 2005 study of organic aerosols in riverside (SOAR) using positive matrix factorization. *Atmospheric Environment* **42**: 2706–2719.
- Endresen, Ø., Sørsgård, E., Sundet, J.K., Dalsøren, S.B., Isaksen, I.S.A., Berglen, T.F. et al., 2003. Emission from international sea transportation and environmental impact. *Journal of Geophysical Research* **108**: 4560.
- EP and CEU (European Parliament and Council of the European Union), 2008. *Directive 2008/50/EC of 21 May 2008 on Ambient Air Quality and Cleaner Air for Europe*.
- Eyring, V., Isaksen, I.S., Berntsen, T., Collins, W.J., Corbett, J.J., Endresen, O., Grainger, R.G., Moldanová, J., Schlager, H. and Stevenson, D.S., 2009. Transport impacts on atmosphere and climate: shipping. *Atmospheric Environment* **44**: 4735–4771, doi: 10.1016/j.atmosenv.2009.04.059.
- Finlayson-Pitts, B.J. and Pitts, J.N., Jr., 2000. *Chemistry of the Upper and Lower Atmosphere*. Academic Press, New York, USA.
- Fridell, E., Steen, E. and Peterson, K., 2008. Primary particles in ship emissions. *Atmospheric Environment* **42**: 1160–1168.
- Gross, D.S., Schauer, J.J., Chen, L., Ramakrishnam, R., Ritz, A. and Musicant, D.R., 2006. Enchilada: a data-mining application for the analysis of atmospheric mass spectrometry data. *International Aerosol Conference*, St. Paul, MN, USA.
- Healy, R.M., O'Connor, I.P., Hellebust, S., Allanic, A., Sodeau, J.R. and Wenger, J.C., 2009. Characterisation of single particles from in-port ship emissions. *Atmospheric Environment* **43**: 6408–6414.
- Healy, R.M., Hellebust, S., Kourtchev, I., Allanic, A., O'Connor, I.P., Bell, J.M., Sodeau, J.R. and Wenger, J.C., 2010. Source apportionment of PM_{2.5} in Cork Harbour, Ireland. *Atmospheric Chemistry and Physics Discussions* **10**: 1035–1082.
- Hellebust, S., Allanic, A., O'Connor, I.P., Jourdan, C., Healy, D. and Sodeau J.R., 2010a. Sources of ambient concentrations and chemical composition of PM_{2.5-0.1} in Cork Harbour, Ireland. *Atmospheric Research* **95**: 136–149.
- Hellebust, S., Allanic, A., O'Connor, I.P., Wenger, J.C. and Sodeau J.R., 2010b. The use of real-time monitoring data to evaluate major sources of airborne particulate matter. *Atmospheric Environment* **44**: 1116–1125.
- Hobbs, P.V., Garrett, T.J., Ferek, R.J., Strader, S.R., Hegg, D.A., Frick, G.M., Hoppel, W.A., Gasparovic,

- R.F., Russell, L.M., Johnson, D.W., Dowd, C., Durkee, P.A., Nielsen, K.E. and Innis, G., 2000. Emissions from ships with respect to their effects on clouds. *Journal of the Atmospheric Sciences* **57**: 2570–2590.
- Hopke, P.K., 2003a. Recent developments in receptor modelling. *Journal of Chemometrics* **17**: 255–265.
- Hopke, P.K., 2003b. The evolution of chemometrics. *Analytica Chimica Acta* **500**: 365–377.
- Jones, T., Moreno, T., BeruBe, K. and Richards, R., 2006. The physicochemical characterisation of microscopic airborne particles in south Wales: a review of the locations and methodologies. *Science of the Total Environment* **360**: 43–59.
- Kelly, F. and Mudway, I., 2007. Particle-mediated extracellular oxidative stress in the lung (Chapter 5). In: Donaldson, K. and Borm, P. (Eds) *Particle Toxicology*. CRC Press, Boca Raton, FL, USA.
- Kourtchev, I., Ruuskanen, T., Maenhaut, W., Kulmala, M. and Claeys, M., 2005. Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiälä, Finland. *Atmospheric Chemistry and Physics* **5**: 2761–2770.
- Kourtchev, I., Warnke, J., Maenhaut, W., Hoffmann, T. and Claeys, M., 2008. Polar organic marker compounds in PM_{2.5} aerosol from a mixed forest site in Western Germany. *Chemosphere* **73**: 1308–1314.
- Kourtchev, I., Bell, J., Hellebust, S., O'Connor, I., Allanic, A., Healy, R.M., Healy, D., Wenger, J.C. and Sodeau, J.R., 2009. Organic composition of PM_{2.5} aerosols in Cork Harbour, Ireland. *European Aerosol Conference*. Karlsruhe, Germany, 2009.
- Kourtchev, I., Hellebust, S., Bell, J.M., O'Connor, I.P., Healy, R.M., Allanic, A., Healy, D., Wenger, J.C. and Sodeau, J.R., 2011. The use of polar organic compounds to estimate the contributions of domestic solid fuel combustion and biogenic sources to ambient levels of organic carbon and PM_{2.5} in Cork Harbour, Ireland. *Science of the Total Environment* **409**: 2143–2155.
- Lack, D.A., Corbett J.J., Onasch, T. et al., 2009. Particulate emissions from commercial shipping: Chemical, physical and optical properties. *Journal of Geophysical Research – Atmosphere* **114**: D00F04
- Lauer, A., Eyring, V., Corbett, J.J., Wang, C.F. and Winebrake, J.J., 2009. Assessment of Near-Future Policy Instruments for Oceangoing Shipping: Impact on Atmospheric Aerosol Burdens and the Earth's Radiation Budget. *Environmental Science and Technology* **43**: 5592–5598.
- Li, Q., Jacob, D.J., Bey, I., Palmer, P.I., Duncan, B.N., Field, B.D. et al. 2002. Transatlantic transport of pollution and its effects on surface ozone in Europe and North America. *Journal of Geophysical Research* **107(D13)**: 4166, doi:10.1029/2001JD001422.
- Lu, G., Brook, J.R., Alfara, M.R., Anlauf, K., Leaitch, R.W., Sharma, S., Wang, D., Worsnop, D.R. and Phinney, L., 2006. Identification and characterization of inland ship plumes over Vancouver, BC. *Atmospheric Environment* **40**: 2767–2782.
- Lubick, N., 2007. Death from shipping. *Environmental Science and Technology* **41**: 8206.
- MacQueen, J., 1967. Some methods for classification and analysis of multivariate observations. *Fifth Berkeley Symposium on Mathematical Statistics and Probability*. University of California Press, CA, USA. p. 281.
- Maykut, N.N., Lewtas, J., Kim, E. and Larson, T.V., 2003. Source apportionment of PM_{2.5} at an urban IMPROVE site in Seattle, Washington. *Environmental Science and Technology* **37**: 5135–5142.
- Moldanová, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccineto, A. and Focsa, C., 2009. Characterisation of particulate matter and gaseous emissions from a large ship diesel engine. *Atmospheric Environment* **43**: 2632–2641.
- Murphy, S.M., Agrawal, H., Sorooshian, A., Padro, L.T., Gates, H., Hersey, S., Welch, W.A., Jung, H., Miller, J.W., Cocker, D.R., Nenes, A., Jonsson, H.H., Flagan, R.C. and Seinfeld, J.H., 2009. Comprehensive simultaneous shipboard and airborne characterization of exhaust from a modern container ship at sea. *Environmental Science and Technology* **43**: 4626–4640.
- Moreno, T., Jones, T.P. and Richards, R.J., 2004. Characterisation of aerosol particulate matter from urban and industrial environments: examples from Cardiff and Port Talbot, South Wales, UK. *Science of the Total Environment* **334–335**: 337–346.
- Paatero, P. and Tapper, U., 1994. Positive matrix factorisation – a nonnegative factor model with optimal utilisation of error-estimates of data values. *Environmetrics* **5**: 111–126.
- Paatero, P., Hopke, P.K., Song, X.H. and Ramadan, Z., 2002. Understanding and controlling rotations in factor analytic models. *Chemometrics and Intelligent Laboratory Systems* **60**: 253–264.
- Pashynska, V., Vermeylen, R., Vas, G., Maenhaut, W. and Claeys, M., 2002. Development of a gas chromatographic/ion trap mass spectrometric method for the determination of levoglucosan and saccharidic compounds in atmospheric aerosols. Application to urban aerosols. *Journal of Mass Spectrometry* **37**: 1249–1257.
- Pope, C.A. and Dockery, D.W., 2006. Health effects of fine particulate air pollution: Lines that connect. *Journal of Air & Waste Management Association* **56**: 709–742.

- Pourazar, J., Mudway, I.S., Samet, J.M., Helleday, R., Blomberg, A., Wilson, S.J., Frew, A.J., Kelly, F.J., and Sandström, T., 2005. Diesel exhaust activates redox-sensitive transcription factors and kinases in human airways. *American Journal of Physiology – Lung Cellular and Molecular Physiology* **289**: L724–L730.
- Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., De La Rossa, J., Sanchez de la Campa, A., Artinano, B., Salavador, P., Garcia Dos Santos, S., Fernandez-Patier, R., Moreno-Grau, S., Negral, L., Minguillon, M., Monfort, E., Gil, J., Inaz, A., Ortega, L., Santamaria, J., and Zabalza, J., 2007. Source and origin of trace elements in PM from regional background, urban and industrial sites of Spain. *Atmospheric Environment* **41**: 7219–7231.
- Ramadan, Z., Eickhout, B., Song, X.H., Buydens, L.M.C. and Hopke, P.K., 2003. Comparison of positive matrix factorisation and multilinear engine for the source apportionment of particulate pollutants. *Chemometrics and Intelligent Laboratory Systems* **66**: 15–28.
- Shi, G.L., Li, X., Feng, Y.C., Wang, Y.Q., Wu, J.H., Li, J. and Zhu, T., 2009. Combined source apportionment, using positive matrix factorization-chemical mass balance and principal component analysis/multiple linear regression-chemical mass balance models. *Atmospheric Environment* **43**: 2929–2937.
- Silva, P.J., Liu, D.Y., Noble, C.A. and Prather, K.A., 1999. Size and chemical characterization of individual particles resulting from biomass burning of local Southern California species. *Environmental Science and Technology* **33**: 3068–3076.
- Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, K., Rushdi, A.I., Medeiros, P.M., Rogge, W.F., and Didyk, B.M., 2004. Sugars-dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. *Environmental Science and Technology* **38**: 5939–5949.
- Snyder, D.C., Schauer, J.J., Gross, D.S. and Turner, J.R., 2009. Estimating the contribution of point sources to atmospheric metals using single-particle mass spectrometry. *Atmospheric Environment* **43**: 4033–4042.
- Sodeau, J., Hellebust, S., Allanic, A., O'Connor, I., Healy, D.A., Healy, R. and Wenger, J., 2009. Airborne emissions in the harbour and port of Cork. *Biomarkers* **14**: 12–16.
- Sodeman, D.A., 2004. *Characterization of Ambient, Automobile, and Diesel Aerosols Utilizing Aerosol Time of Flight Mass Spectrometry*. A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Chemistry.
- Swedish NGO Secretariat on Acid Rain, 2004. *Air Pollution from Ships*. A briefing document by the European Environmental Bureau (EEB), European Federation for Transport and Environment (T&E) and Seas At Risk (SAR).
- Thurston, G.D. and Spengler, J.D., 1985. A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. *Atmospheric Environment* **19**: 9–25.
- Wessels, A., Birmili, W., Albrecht, C., Hellack, B., Jermann, E., Wick, G., Harrison, R.M. and Schins, R.P.F., 2010. Oxidant generation and toxicity of size-fractionated ambient particles in human lung epithelial cells. *Environmental Science and Technology* **44**: 3539–3545.
- Winebrake, J.J., Corbett, J.J., Green, E.H., Lauer, A. and Eyring, V., 2009. Mitigating the Health Impacts of Pollution from Oceangoing Shipping: An Assessment of Low-Sulfur Fuel Mandates. *Environmental Science and Technology* **43**: 4776–4782.

Project Outputs

Published Papers

Hellebust, S., Allanic, A., O'Connor, I.P., Wenger, J.C. and Sodeau, J.R., 2010. The use of real-time monitoring data to evaluate major sources of airborne particulate matter. *Atmospheric Environment* **44**: 1116–1125.

Hellebust, S., Allanic, A., O'Connor, I.P., Jourdan, C., Healy, D. and Sodeau, J.R., 2010. Sources of ambient concentrations and chemical composition of PM_{2.5-0.1} in Cork Harbour, Ireland. *Atmospheric Research* **95**: 136–149.

Healy, R.M., O'Connor, I.P., Hellebust, S., Allanic, A., Sodeau, J.R. and Wenger, J.C., 2009. Characterisation of single particles from in-port ship emissions. *Atmospheric Environment* **43**: 6408–6414.

Healy, R.M., Hellebust, S., Kourtchev, I., Allanic, A., O'Connor, I.P., Bell, J.M., Sodeau, J.R. and Wenger, J.C., 2010. Source apportionment of PM_{2.5} in Cork Harbour Ireland. *Atmospheric Chemistry and Physics Discussions* **10**: 1035–1082.

Kourtchev, I., Hellebust, S., Bell, J.M., O'Connor, I.P., Healy, R.M., Allanic, A., Healy, D., Wenger, J.C. and Sodeau, J.R., 2011. The use of polar organic compounds to estimate the contributions of domestic solid fuel combustion and biogenic sources to ambient levels of organic carbon and PM_{2.5} in Cork Harbour, Ireland. *Science of the Total Environment* **409**: 2143–2155.

Sodeau, J., Hellebust, S., Allanic, A., O'Connor, I., Healy, D., Healy, R. and Wenger, J., 2009. Airborne emissions in the harbour and port of Cork. *Biomarkers* **14**: 12–16.

Oral Presentations

Kourtchev, I., Bell, J., Hellebust, S., O'Connor, I., Allanic, A., Healy, R.M., Healy, D., Wenger, J.C. and Sodeau, J. R., 2009. Organic composition of PM_{2.5} aerosols in Cork Harbour, Ireland. Presented at *European Aerosol Conference*, Karlsruhe, Germany.

Healy, R.M., Hellebust, S., Kourtchev, I., Allanic, A., O'Connor, I., Bell, J., Dall'Osto, M., Ceburnis, D., Ovadnevaite, J., Berresheim, H., O'Dowd, C., Sodeau, J. and Wenger, J., 2010. Source apportionment of PM_{2.5} in Cork Harbour, Ireland using single particle mass spectrometry. Presented at *International Aerosol Conference*, Helsinki, Finland.

Healy, R.M., Hellebust, S., Kourtchev, I., Allanic, A., O'Connor, I., Bell, J., Dall'Osto, M., Ceburnis, D.,

Ovadnevaite, J., Berresheim, H., O'Dowd, C., Sodeau, J. and Wenger, J., 2010. Source identification and apportionment of sources of PM_{2.5} in Cork Harbour using single particle mass spectrometry. Presented at *Transboundary Research Workshop*, Galway, Ireland.

Bell, J.M., Kourtchev, I., O'Connor, I.P., Hellebust, S., Allanic, A., Healy, R.M., Healy, D., Sodeau, J.R. and Wenger, J.C., 2010. Pro-inflammatory responses of human lung epithelial cells to particles generated from combustion of wood, peat and coal. Presented at *All Island Environmental Health Forum (12th National Graduate/Post Graduate Research Colloquium on Environmental Health, Protection and Safety)*. Athlone, Ireland. May 2010.

Bell, J.M., Kourtchev, I., O'Connor, I.P., Hellebust, S., Allanic, A., Healy, R.M., Healy, D., Sodeau, J.R. and Wenger, J.C., 2010. Quantification of quinones and their associated health effects from PM_{2.5} collected at Tivoli Docks, Cork, Ireland. Presented at *International Aerosol Conference*. Helsinki, Finland.

O'Connor, I.P., Hellebust, S., Kourtchev, I., Allanic, A., Healy, R.M., Bell, J.M., Sodeau, J.R. and Wenger, J.C. 2009. *Air Quality of Cork Harbour and Effects on Health*. Presented at Environmental Research Institute Research Open Day, UCC, Cork, Ireland. 29 April 2009.

O'Connor, I., Hellebust, S., Kourtchev, I., Allanic, A., Healy, R., Bell, J., Sodeau, J. and Wenger, J., 2009. Chemical composition of PM_{2.5} in Cork Harbour, Ireland. Presented at *Irish Environmental and Health Research Day*. UCD, Dublin, Ireland. 25 August 2009.

O'Connor, I., Hellebust, S., Kourtchev, I., Allanic, A., Healy, R.M., Bell, J.M., Sodeau, J. and Wenger, J., 2010. Chemical composition of PM_{2.5} in Cork Harbour, Ireland. Presented at *The 62nd Irish Universities Chemistry Research Colloquium*. Queens University, Belfast, Northern Ireland. 1–2 July 2010.

Sodeau, J., Hellebust, S., Allanic, A., O'Connor, I., Healy, D., Healy, R. and Wenger, J., 2009. Airborne emissions in the harbour and port of Cork 2008. Presented at the *Institute for Science and Health Conference (Aerosol Dynamics and Health) Strategies to Reduced Exposures and Harm*. Cardiff University, UK. 22–26 June 2008.

Poster Presentations

Kourtchev, I., O'Connor, I.P., Allanic, A., Hellebust, S., Healy, D.A., Wenger, J.C., and Sodeau, J.R., 2009.

Organic composition of PM_{2.5} aerosols in Cork Harbour, Ireland. *European Aerosol Conference*. Karlsruhe, Germany. September 2009.

O'Connor, I.P., Allanic, A., Hellebust, S., Healy, D. A., Jourdan, C. and Sodeau, J.R., 2008. Environmental Linkage between in-port emissions of particulate matter, their chemical analysis and health effects in Cork Harbour, Ireland. *Harbours, Air Quality and*

Climate Change Conference. Rotterdam, Netherlands. 29–30 May 2008.

O'Connor, I.P., Allanic, A., Hellebust, S., Healy, D. A., Wenger, J.C. and Sodeau, J.R., 2007. Environmental linkage of in-port emissions of PM, their chemical analysis and health effects in Cork, Ireland. *Aerosol Conference*. Salzburg, Austria. 9–14 September 2007.

Acronyms

Al	Aluminium
AMS	Aerosol mass spectrometer
As	Arsenic
ATOFMS	Atmospheric time-of-flight mass spectrometer
Ba	Barium
Br⁻	Bromide ion
C₆H₆	Benzene
Ca	Calcium
CAFÉ	Clean Air for Europe Directive (2008/50/EC)
Cd	Cadmium
Cl⁻	Chloride ion
CO	Carbon monoxide
CO₂	Carbon dioxide
Cr	Chromium
Cu	Copper
DSF	Domestic solid-fuel
EC	Elemental carbon
EDS	Energy-dispersive X-ray spectroscopy
ELIPSE	Environmental Linkages of In-Port Ship Emissions of Particulate Matter, their Chemical Analysis and Effects on Health
EPA	Environmental Protection Agency
EU	European Union
F⁻	Fluoride ion
Fe	Iron
H₂O	Water
HF	Hydrofluoric acid
Hg	Mercury
HNO₃	Nitric acid
HVCI	High-volume cascade impactor
IC	Ion chromatography
ICP-OES	Inductively coupled plasma – optical emission spectroscopy
IDL	Instrumental detection limit

K⁺	Potassium ion
L2MS	Two-step laser mass spectrometry
MDL	Method detection limit
Mg²⁺	Magnesium ion
Mn	Manganese
MXP	Methyl- β -D-xylanopyranoside
Na⁺	Sodium ion
NH₄⁺	Ammonium ion
(NH₄)₂SO₄	Ammonium sulfate
(NH₄)HSO₄	Ammonium bisulfate
Ni	Nickel
NO	Nitric oxide
NO₂	Nitrogen dioxide
NO₃⁻	Nitrate ion
NO_x	Nitrogen oxides
O₃	Ozone
OC	Organic carbon
PAH	Polycyclic aromatic hydrocarbon
Pb	Lead
PCA	Principal component analysis
PM₁₀	Particulate matter with diameter less than 10 μ m
PM_{2.5}	Particulate matter with diameter less than 2.5 μ m
PMF	Positive matrix factorisation
PO₄	Phosphate
ppb	Parts per billion
PUF	Polyurethane foam
Sb	Antimony
SMPS	Scanning mobility particle sizer
SO₂	Sulfur dioxide
SO₄²⁻	Sulfate ion
SOA	Secondary organic aerosol
TEOM	Tapered element oscillating microbalance
V	Vanadium
Zn	Zinc

An Gníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomh-nithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil agus Rialtais Áitiúil a dhéanann urraíocht uirthi.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreal.
- Scardadh dramhuisce

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce.
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí chomhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOIL

- Monatóireacht ar chaighdeán aer agus caighdeán aibhneacha, locha, uisce taoide agus uisce talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntiú a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdeán aer agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Gníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstíúrthóir agus ceithre Stíúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.