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CHEMICAL FINGERPRINTS OF THE MAJOR SOURCES OF $PM_{2.5}$ IN DUBLIN, IRELAND: A FOCUS ON DIESEL VEHICLE EMISSIONS

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ABSTRACT

Particulate matter (PM) is one of the most problematic air pollutants in Ireland, and recently the associations between exposure to ambient PM and adverse health outcomes have been more firmly established. Diesel vehicles in particular are known for their significant contribution to overall emissions of PM ($PM_{2.5}$) in the atmosphere, and therefore constitute a significant threat to public health and the environment. A recent investigation of national emissions in the road transport sector in Ireland has highlighted that private diesel passenger vehicles contribute the largest proportion of total emissions in both CO_2 and PM of all vehicle categories. Owing to the recent growth in private diesel vehicles since 2008, this vehicle category represents a significant pressure on the quality of the urban environment in Ireland.

Determination of the proportion of total PM concentration in urban areas, which has originated from diesel vehicle emissions using source apportionment techniques, is invaluable in assessing the impact of diesel emissions on population exposure. We are generating evidence on the impact of diesel vehicles in Ireland on the exposure of the population to $PM_{2.5}$, through field measurement of ambient $PM_{2.5}$ and direct sampling of $PM_{2.5}$ sources. Here we present a data set of chemical fingerprints of the major sources of $PM_{2.5}$ in Dublin. These include a wide variety of vehicular exhaust emissions and solid fuels including wood, peat and coal, sea spray, mineral dust and road dust, with a particular focus on diesel vehicle emissions. A single analytical technique was employed for the chemical analysis that was carried out here; laser ablation inductively coupled mass spectrometry (LA-ICP-MS), while other $PM_{2.5}$, source apportionment studies commonly use a variety of analytical techniques for chemical analysis.

Keywords: Diesel Vehicles, Particulate Matter, $PM_{2.5}$*, Source Apportionment.*

1 INTRODUCTION

Particulate matter (PM) as $PM_{2.5}$ shows a strong association with adverse health effects including respiratory and cardiovascular illness [1]. Both short- and long-term exposures to $PM_{2.5}$ have been noted to result in negative health impacts [2]. PM is not a specific chemical entity; rather, it is a complex mixture of particles from many different sources and has diverse chemical and physical properties [3]. Sources of PM are highly variable. Nevertheless, PM in urban environments largely originates from sources such as sea salt, petrol and diesel vehicles, biomass burning, soil, secondary nitrate and sulphate and industrial sources [4]. Most of the finer particles (i.e. $PM_{2.5}$) are released from the incomplete combustion of fossil fuels, especially from diesel motor vehicles, electricity power stations and industrial operations.

Road traffic emissions of $PM_{2.5}$ are significant in terms of total pollutant loading in outdoor air, and are usually the main pollutant source in European urban environments [5–7]. Diesel vehicles in particular are known for their significant contribution to overall emissions of $PM_{2.5}$ [4, 8], emitting significantly higher levels than their petrol-driven equivalents. Diesel engines can emit 25–400 times more mass of PM per kilometre than petrol engines,

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depending on Euro class, engine size and other on-road factors [9]. However, most efficient modern diesel engines produce less CO_2 emissions than the equivalent petrol engine [10]. Thus, the automobile sector has been identified in Europe as the sector in which a technology shift from gasoline to diesel engines may ensure significant GHG savings, and Europe's new car sales have been persistently transformed from being petrol-driven to diesel-driven [11].

The growth in the number of diesel passenger vehicles in the Irish fleet since 2008 has led to this vehicle category being the largest contributor to both CO_2 and $PM_{2.5}$ emissions, five years later [8, 12]. In 2013, 73% of all new private cars were diesel fuelled [8], resulting in 36% of all car stock and over 99% of buses being fuelled by diesel in Ireland [13]. This increase in diesel passenger vehicles is very much a European-wide phenomenon; just over 50% of new vehicle sales in 2015 and 2016 were diesel in the EU-15 countries, on average [14]. However, Ireland had the highest percentage of new vehicle diesel sales in the EU in 2015 and 2016, significantly ahead of the EU average (70%) [14].

An assessment of the extent of the impact of these emissions on the population is required. Here we present a data set of chemical fingerprints of the major sources of $PM_{2.5}$ in Dublin. These include a wide variety of vehicular exhaust emissions, solid fuels including wood, peat and coal and sea spray.

2 METHODOLOGY

2.1 Sample collection

A conical inhalable sampler (CIS) was used in conjunction with a Casella VORTEX Ultra Flow sampling pump to carry out the direct sampling of the major sources of $PM_{2.5}$ in the greater Dublin area. For this study, we used CIS $PM_{2.5}$ cassettes containing either Quartz (Whatman® QM-A quartz filters) or Teflon filters with a 2 μm pore size (Teflo, Pall Gelman Sciences, Chicago, IL) following the procedure described by [15]. The VORTEX Ultra Flow sampling pump was set to continuously collect 16.7 litres of free air per minute for up to 15 minutes per sample (see Fig. 1 for details of the sampling site set up). The samples were then prepared for analysis by cutting ca. 1 × 1 cm strips of the loaded filters, with a ceramic scissors in order to avoid any metal cross-contamination, and mounting them on a glass slide with double-sided sticky tape. All filter handling was carried out in a clean environment while wearing gloves and using plastic tweezers.

Figure 1: Photographs of the sampling set up of the (yellow) Casella sampling pump and the (red) CIS for collecting PM samples from vehicular exhaust emissions (i), smoke emitted from the burning of solid fuels (ii), and a sea-spray PM source (iii).

2.2 Chemical analysis and data reduction

The trace element concentrations of these samples were obtained with laser ablation inductively coupled mass spectrometry (LA-ICP-MS). Th LA-ICP-MS method has a number of advantages over other analysis techniques. A full suite of trace metals can be analysed very rapidly and the method has very low detection limits, yielding precise and accurate data for elements present at ppm concentrations [16]. Thirty seven isotopes (^{13}C, ^{23}Na, ^{24}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{34}S, ^{35}Cl, ^{39}K, ^{43}Ca, ^{44}Ca, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{73}Ge, ^{75}As, ^{77}Se, ^{79}Br, ^{85}Rb, ^{88}Sr, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{137}Ba, ^{202}Hg, ^{205}Tl, ^{208}Pb, ^{209}Bi) were acquired as described in detail in [16].

Previous investigations examining the chemical fingerprint of emissions in relation to PM have used multiple chemical analysis techniques resulting in significantly longer processing time and cost, as well as a significantly lower number of resulting isotopes than the 37 recorded here.

3 RESULTS

3.1 Direct source sampling – solid fuels used for residential heating in Ireland

Samples of chimney smoke emitted from burning of a variety of solid fuels were collected on both quartz and Teflon filters for a duration of 7 mins each, as described in Section 2.1. The solid fuels that were tested included the most commonly used for residential heating in Dublin; oil, smokeless coal, peat briquettes, wood and mixed fuel fires. Photographs of these chimney smoke samples are shown in Fig. 2. An initial visual inspection of these filter photos clearly shows that a wood fire emits the largest amount of black carbon. This was confirmed by LA-ICP-MS analysis of these filters, which shows that the smoke emitted from a wood fire contained ca. 1,000,000 CPS (counts per second) more carbon than a peat briquette fire, and ca. 2,000,000 CPS more carbon than a smokeless coal fire (Fig. 3a(i)). The results from

Figure 2: Photographs of chimney smoke samples, collected on both quartz and Teflon filters, of the most commonly used solid fuels for residential heating in Dublin; oil, smokeless coal, peat briquettes, wood and mixed fuel fires.

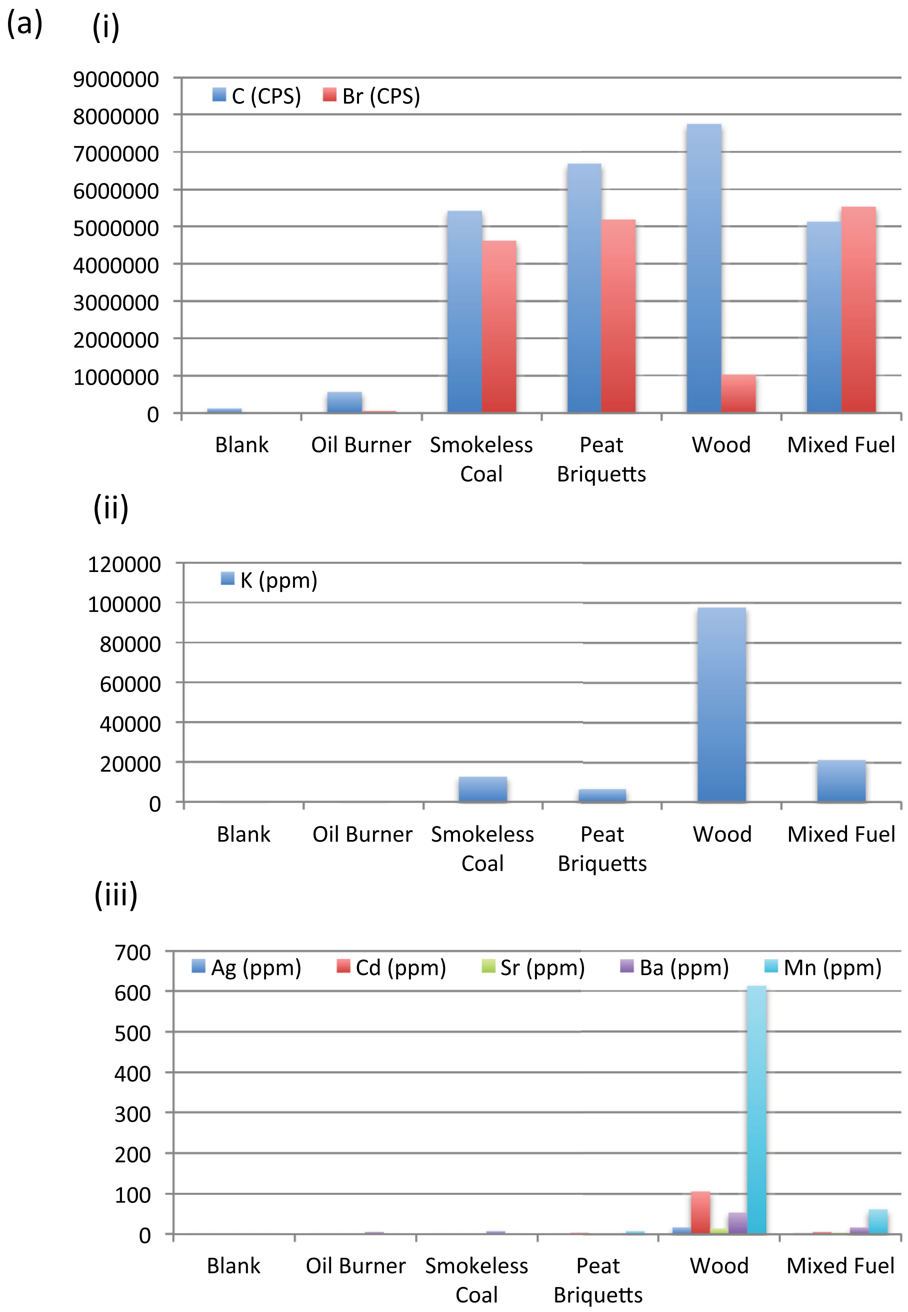

Figure 3: Elemental composition of chimney smoke samples collected on Teflon filters, of the most commonly used solid fuels for residential heating in Dublin; oil, smokeless coal, peat briquettes, wood and mixed fuel fires. Figure 3(a) shows the relative concentrations of C, Br, K, Ag, Cd, Sr, Ba and Mn and Figure 3(b): shows the relative concentrations of Se, Te, Na, Hg, V, Bi, Sn, In and Mo in the $PM_{2.5}$ emitted from the solid fuels that were tested.

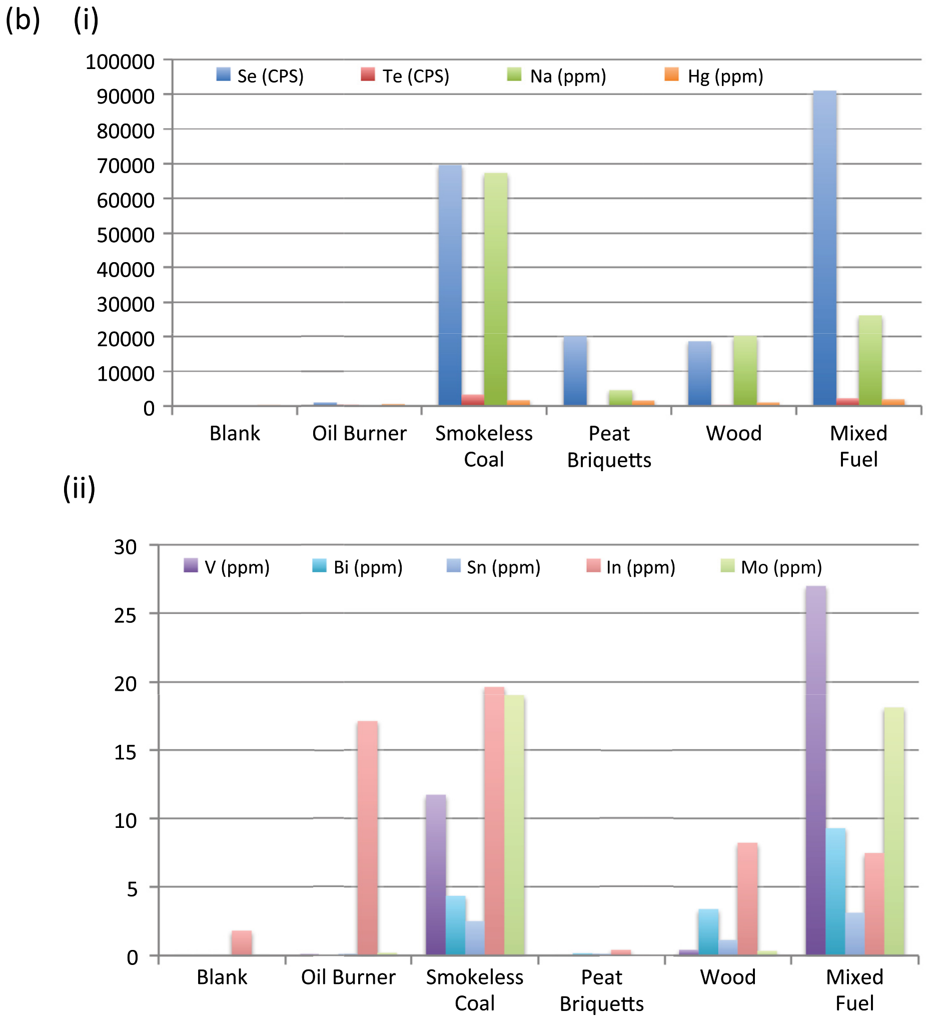

Figure 3: (*Continued*)

the LA-ICP-MS analysis of these filters also suggest that it is possible to distinguish different chemical fingerprints for each of the solid fuels that were sampled. PM emitted from a wood fire could be identified and distinguished from PM emitted from other solid fuels by high loadings of Ag, Cd, Ba, Sr, Mn and K (Fig. 3a(ii) and (iii)). PM emitted from a smokeless coal fire could be identified and distinguished from PM emitted from other solid fuels by high loadings of Se, Te, V, Bi, Hg, Sn, In, Mo and Na (Fig. 3b(i) and (ii)). PM emitted from a peat fire could be identified and distinguished from PM emitted from other solid fuels by high loadings of Br along with an absence of marine metals such as Mo, Te and Se (Figs. 3a(i) and 3b).

3.2 Direct source sampling – diesel and petrol vehicle exhausts

Successive vehicular exhaust emission samples were collected on Quartz filters after 1–5, 10 and 15 minutes, from a single Euro 3 diesel vehicle (Fig. 4(i)). A visual inspection of these filters clearly shows that the emissions of black carbon from the vehicle's exhaust increased in proportion to the sample duration. The carbon concentrations are plotted against the mass

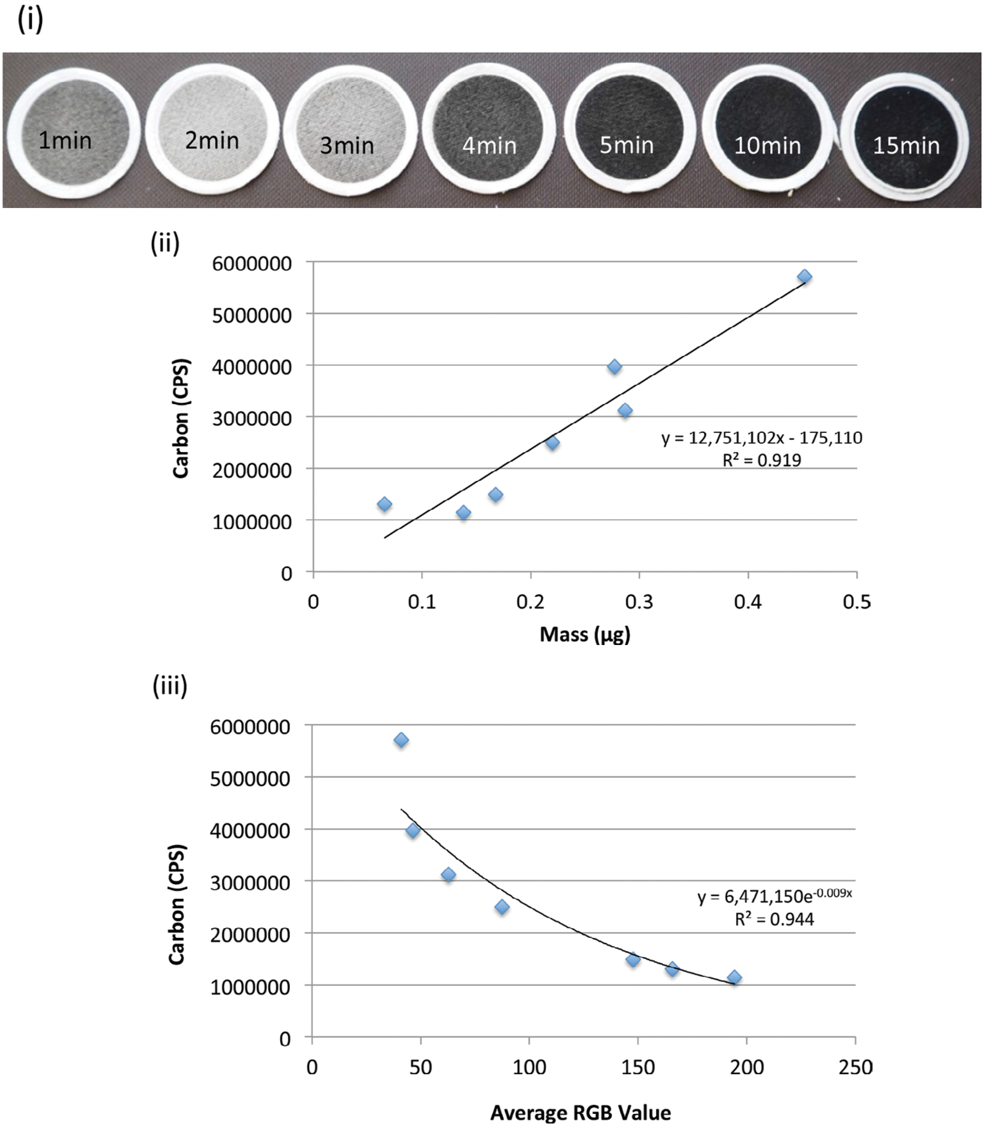

Figure 4: A photograph of successive vehicular exhaust emissions samples, collected after 1–5, 10 and 15 minutes, on quartz filters, from a single Euro 3 diesel vehicle (i). The carbon concentrations in counts per second (CPS) are plotted against the mass collected on these filters in micrograms (µg) (ii), and against the RGB value of the particulates collected on the quartz filter (iii).

collected on these filters (Fig. 4(ii)), forming a near-perfect correlation with an R^2 of 0.919. This suggests that as emissions of $PM_{2.5}$ from a vehicle's exhaust increase, so do the emissions of black carbon. The carbon concentrations were also plotted against the average red green blue (RGB) value of the particulates collected on the quartz filters (Fig. 4(iii)), and these form a near-perfect exponential relationship with an R^2 of 0.944. The RGB value quantifies the degree of blackness of the $PM_{2.5}$ collected on the filters, and these data also suggest that as emissions of $PM_{2.5}$ from a vehicle's exhaust increase, so do the emissions of black carbon. Furthermore, the 15-minute sample, which exhibits the highest carbon concentration, plots as an outlier as it has reached a saturation point for its RGB value.

Samples of vehicular exhaust emissions from a variety of Euro 3 to Euro 6 Diesel vehicles, along with a Euro 4 Petrol vehicle, were collected on Teflon filters for a duration of 15 minutes each. A total of ten different cars were sampled, and photographs of some of these vehicle exhaust samples are shown in Fig. 5. An initial visual inspection of these photos clearly shows that Euro 3 and Euro 4 diesel vehicles emit the largest amount of black carbon. More notably, these photos also show variability within a Euro class of diesel vehicle exhaust emissions; two of the Euro 4 samples are heavily loaded with black carbon, while the third is more lightly coloured, containing lesser loadings of black carbon. Chemical analysis of these filters confirms this variability, both between and within the Euro classes of diesel vehicles.

Figure 6(a) illustrates the carbon concentrations of these vehicular exhaust samples plotted against their nickel concentrations. Samples taken from the petrol vehicles, the Euro 6, Euro 5 and one of the Euro 4 diesel vehicles plot close to the origin, having low concentrations of both C and Ni. The other two exhaust samples taken from the Euro 4 diesel vehicles and the sample taken from the Euro 3 diesel vehicle exhibit higher concentrations of both C and Ni along with greater variability in these concentrations, with these data points exhibiting a weaker correlation than the data points that plotting closer to the origin. Other elements, in addition to nickel, that are strong indicators of a diesel source are chromium, copper, sulphur, zinc and phosphorous (Fig. 6b). Cr exhibits concentrations of up to 40 ppm and has

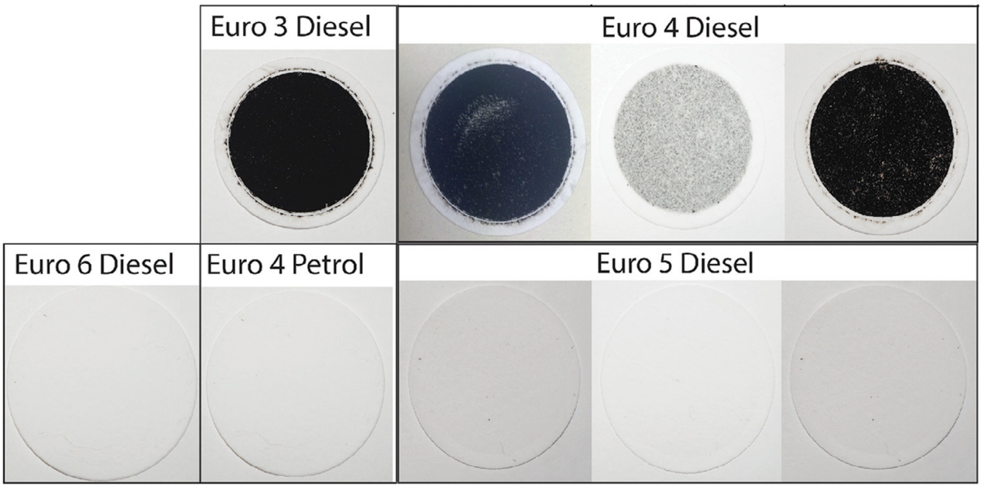

Figure 5: Images of vehicular exhaust emissions samples collected on Teflon filters, from a variety of Euro class diesel vehicles and a Euro 4 petrol vehicle.

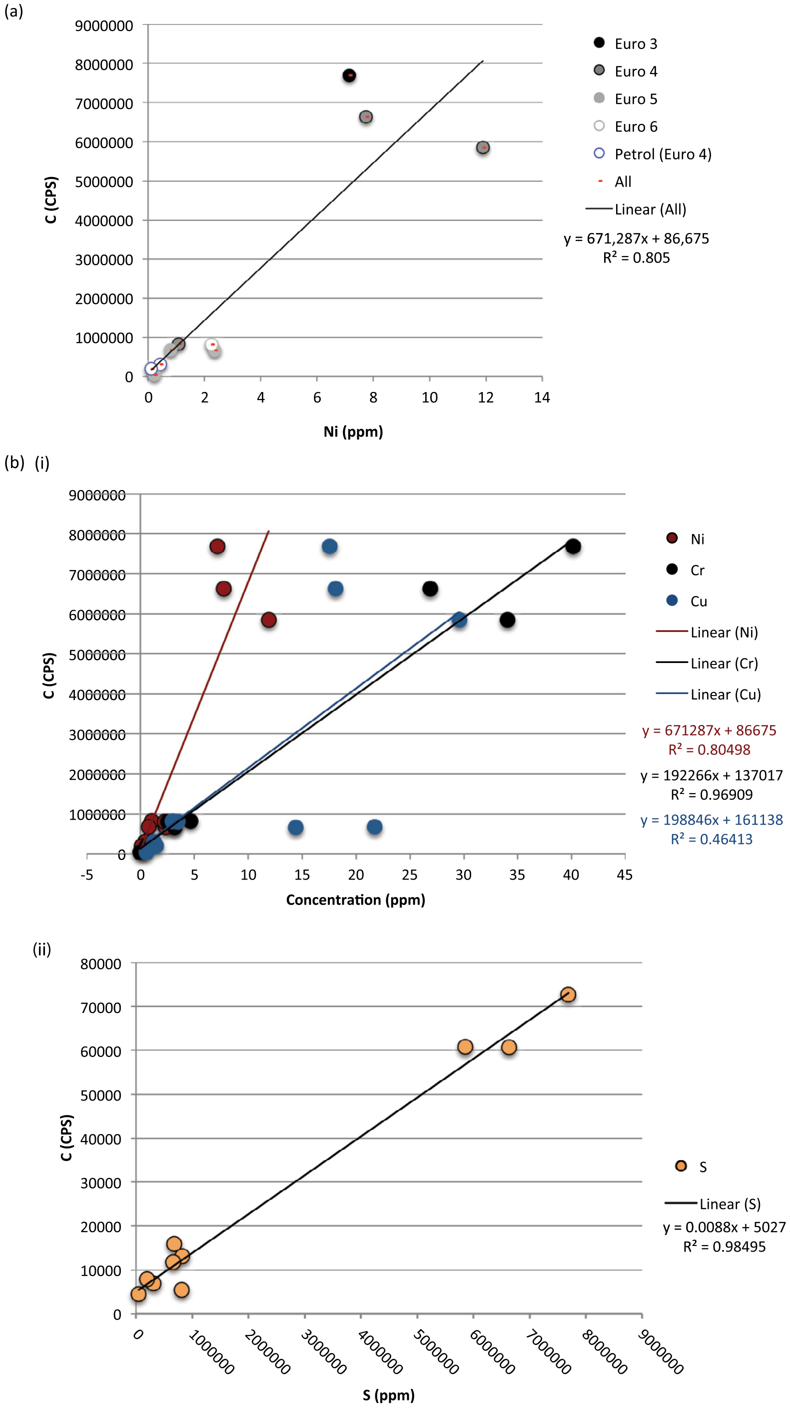

Figure 6: Elemental Fig. 6(a) illustrates the carbon concentrations plotted against the nickel concentrations of vehicular exhaust emissions samples, from a variety of Euro classes of diesel vehicles and Euro 4 petrol vehicles. Figure 6(b) illustrates the carbon concentrations plotted against the Ni, Cr, Cu, S, Zn and P concentrations for these samples.

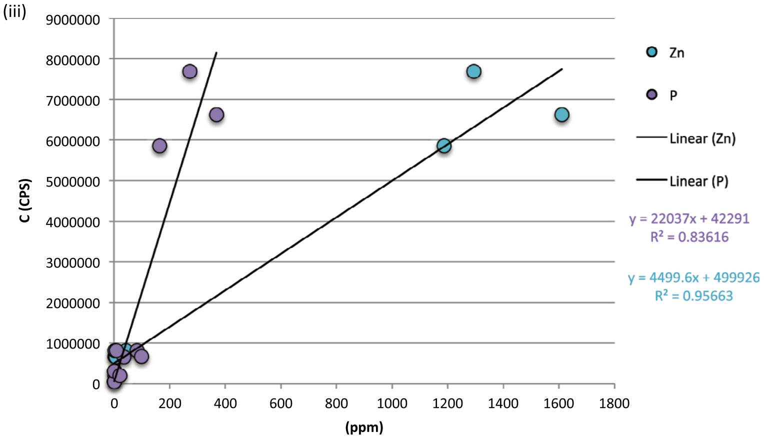

Figure 6: (*Continued*)

a better correlation when plotted against carbon than Cu, which exhibits more scatter (Fig. 6b(i)). Additional strong indicators are S and Zn; S exhibits very high concentrations of up to 8,000,000 ppm and one of the strongest correlations when plotted against carbon (Fig. 6b(ii)). Zn exhibits high concentrations of up to 1,500 ppm and has a slightly better correlation than P, which exhibits lower concentrations of up to 400 ppm and more scatter (Fig. 6b(iii)). These elements (Ni, Cr, Cu, S, Zn and P) exhibit a strong positive correlation with carbon, which suggests that with increased emissions of black carbon come increased emissions all of these elements.

In all cases samples collected from the Euro 6, Euro 5 and one of the Euro 4 diesel vehicles along with the petrol vehicles, plot close to the origin, having lower concentrations all of these elements, while the other two exhaust samples taken from the Euro 4 diesel vehicles and the sample taken from the Euro 3 diesel vehicle exhibit higher concentrations all of these elements. This variability in the concentrations of these elements that exists between the Euro classes of diesel vehicles suggests these elements are better indicators of $PM_{2.5}$ sourced from older Euro 3 and Euro 4 diesel vehicles than from $PM_{2.5}$ sourced from newer Euro 5 and Euro 6 diesel and petrol vehicles.

3.3 Direct source sampling – sea salt spray

Samples of sea spray were collected on both quartz and Teflon filters for a duration of 15 minutes each, as described in Section 2.1. Photographs of these sea-spray samples are shown in Fig. 7, and the paucity of black carbon in the sea-spray samples when compared with the chimney smoke samples (Fig. 2) and the vehicular exhaust samples (Fig. 5) is immediately obvious. The results from the LA-ICP-MS analysis of these filters also suggest that it is possible to distinguish a chemical fingerprint for a sea-spray PM source from both a solid fuel and a vehicular exhaust emission PM source. Seawater contains sulphates, chloride salts and bromide salts that are released into the air in droplets of spray. As a result, PM sourced from sea spray can be identified and distinguished from other PM sources by high loadings of both Na, Cl, S and Br (Fig. 8).

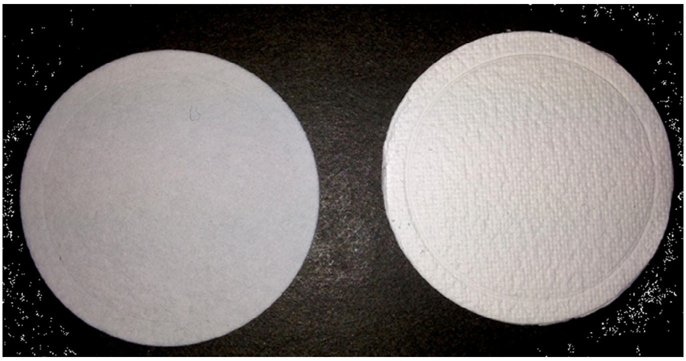

Figure 7: A sea-spray PM sample collected on both a quartz (R) and a Teflon filter (L).

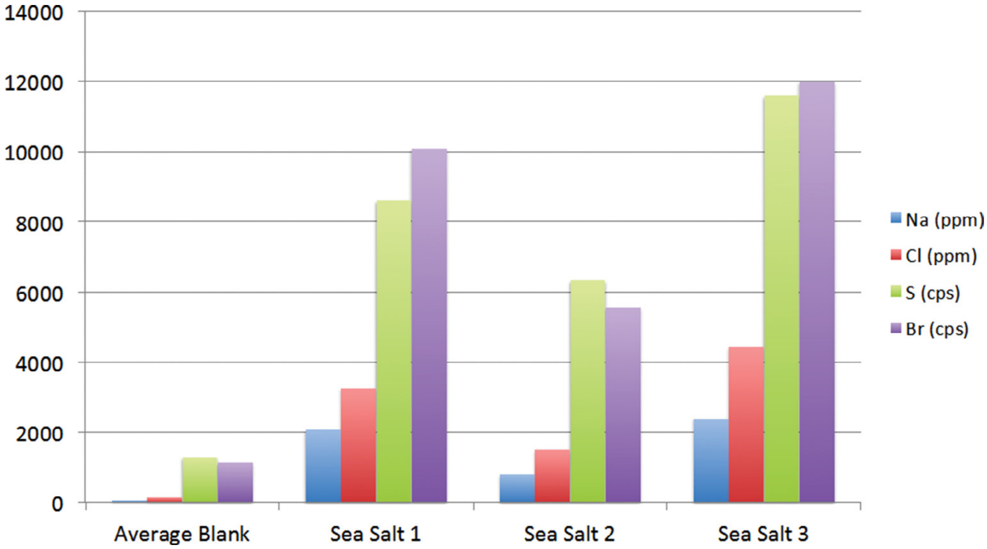

Figure 8: Sodium, chlorine, sulphur and bromine compositions of a blank Teflon filter and three sea-spray samples collected on Teflon filters.

4 DISCUSSION

4.1 $PM_{2.5}$ sourced from diesel vehicles

Chemical analysis of PM samples collected from the exhausts of a variety of diesel vehicles suggests that PM sourced from diesel vehicles can be identified by high loadings of C, Ni Cr, Cu, S, Zn and P. However, these results also show that there is large variability in the concentrations of these elements both between and within Euro classes of diesel vehicles. Samples taken from Euro 3 and the majority of Euro 4 diesel vehicles exhibit concentrations of these elements of up to an order of magnitude higher than the Euro 5 and Euro 6 diesel vehicles, while the Euro 5 and Euro 6 diesel vehicles exhibit concentrations that are comparable to the samples collected from the exhausts of petrol vehicles. This is significant in terms of $PM_{2.5}$ pollution originating from diesel vehicles in Ireland, as Euro 4 diesel vehicles dominate the

Irish diesel fleet [18]. Furthermore, these results also suggest that $PM_{2.5}$ source apportionment studies may be more successful in distinguishing $PM_{2.5}$ sourced from older Euro 3 and Euro 4 diesel vehicles than from $PM_{2.5}$ sourced from newer Euro 5 and Euro 6 diesel and petrol vehicles. Variability in the concentration of these elements within the Euro 4 class of diesel vehicles is also noteworthy, as it suggests that the vehicles servicing history and the maintenance of the vehicles particle filter has an impact on whether or not the vehicle meets its European emissions standards.

4.2 Chemical fingerprints the major sources of $PM_{2.5}$ in Dublin

Samples of PM were collected directly from the major sources of $PM_{2.5}$ in Dublin. These sampled sources included a variety of vehicular exhaust emissions, smoke emitted from the burning of solid fuels, which included wood, peat and coal, and a sea-spray PM source. A single analytical technique was employed for the chemical analysis that was carried out in this study; LA-ICP-MS.

LA-ICP-MS has not yet been utilized in other source apportionment studies, e.g. [4, 18, 19], which commonly use a variety of analytical techniques for chemical analysis. LA-ICP-MS analysis of the PM collected from each of these the major sources of $PM_{2.5}$ in Dublin suggests that it is possible to obtain a distinct chemical fingerprint for each of these sources, which can be used to distinguish PM originating from different sources from one another. Chemical fingerprinting using LA-ICP-MS has also significantly reduced the cost, labour intensity and time required to conduct analysis of a larger amount of chemical species than existing techniques. Summaries of the chemical fingerprints obtained for the major sources of $PM_{2.5}$ in Dublin are listed below:

- PM sourced from a wood fire could be identified by high loadings of Ag, Cd, Ba, Sr, Mn and K.
- PM sourced from a smokeless coal fire could be identified by high loadings of Se, Te, V, Bi, Hg, Sn, In, Mo and Na.
- PM sourced from a peat briquette fires could be identified by high loadings of Br along with an absence of marine metals such as Mo, Te and Se.
- PM with a vehicular source, in particular vehicular exhaust emissions from Euro 3 and Euro 4 diesel vehicles, could be identified by high loadings of C, Ni, Cr, Cu, S, Zn and P.
- PM sourced from sea spray could be identified by high loadings of Na, Cl, S and Br.

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