Total and water-soluble trace metal content of urban background PM_{10}, $PM_{2.5}$ and Black Smoke in Edinburgh, U.K.

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Abstract

Toxicological studies have implicated trace metals in airborne particles as possible contributors to respiratory and/or cardiovascular inflammation. As part of an epidemiological study, co-located 24 h samples of PM_{10}, $PM_{2.5}$ and black smoke (BS) were collected for one year at an urban background site in Edinburgh, and each sample sequentially extracted with ultra-pure water, then concentrated HNO_3/HCl, and analysed for Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb. This yields a comprehensive dataset for UK urban airborne trace metal. The median (n >349) daily water-soluble metal concentration in $PM_{2.5}$ ranged from 0.05 ng m^{-3} for Ti to 5.1 ng m^{-3} for Pb; and in PM_{10} from 0.18 ng m^{-3} for Ti to 11.7 ng m^{-3} for Fe. Median daily total (i.e. water + acid-extractable) metal concentration in $PM_{2.5}$ ranged from 0.3 ng m^{-3} for As to 27.6 ng m^{-3} for Fe; and in PM_{10} from 0.37 ng m^{-3} for As to 183 ng m^{-3} for Fe. The $PM_{2.5}:PM_{10}$ ratio varied considerably with metal, from <17 %, on average, for Ti and Fe, to >70 % for V, As, Cd and Pb. The $PM_{10-2.5}$ fraction contained proportionally more of the 11 trace metals (3.2 %) than the $PM_{2.5}$ fraction (0.9 %). The proportion of water-soluble metal in each size-fraction varied considerably, from <10 % water-soluble Fe and Ti in $PM_{10-2.5}$, to >50 % water-soluble V, Zn, As and Cd in $PM_{2.5}$. Although Fe generally dominated the trace metal, water-soluble metal also contained significant Zn, Pb and Cu, and for all size and solubility fractions, >90 % of trace metal was comprised of Fe, Zn, Pb and Cu. Statistical analyses indicated three main sources: traffic; static combustion; and crustal. The association of metals with traffic (Cu, Fe, Mn, Pb, Zn) was consistent with traffic-induced non-exhaust "resuspension" rather than direct exhaust emission. Meteorology contributed to the wide variation in daily trace metal concentration. The proportion of trace metal in particles varied significantly with the air-mass source and was highest on days for trajectories traversing over land. For Mn, Fe, Cu, Zn, As and Pb there was greater correlation of metal concentration with BS mass than with either PM_{10} or $PM_{2.5}$ mass, suggesting that BS reflectance monitoring could be a cost-effective surrogate measure of particle metal concentration in urban background air.

1. Introduction

The existence of significant statistical associations between airborne particulate matter, PM, (measured as PM_{10}, $PM_{2.5}$ or Black Smoke) and adverse effects on human health is generally agreed as causal (Pope, 2000b). However, PM is diverse in chemical and physical character and there is currently little or no consensus on the relevant detrimental component(s) of PM other than to total mass inhaled (Dreher, 2000). Further insight requires detailed measurements of the constituent components of PM to enable both more specific epidemiological analyses, and biologically plausible *in-vitro* and *in-vivo* models capable of explaining observed toxicological effects.

Toxicological studies have frequently implicated the metal content (particularly water-soluble metal) as a possible harmful component of PM. Metals have been shown to generate reactive oxygen species (ROS) which switch on cellular pro-inflammatory response pathways *in vitro* and *in vivo*. For example, Costa and Dreher (1997) concluded that the dose of bioavailable (which these authors defined as water-extractable) transition metal, rather than PM mass, was the primary determinant of the acute inflammatory response for both ambient PM and oil and coal fly ash instilled into rats. These workers implicated a role for Fe, V and Ni. Using samples of PM_{10} from the Utah valley, Frampton *et al*. (1999) showed the importance of soluble metal content for toxicity and pro-inflammatory potential in a range of human, animal and *in vitro* studies. Jimenez *et al*. (2000) showed that Fe and Cu from PM_{10} samples could stimulate translocation of the oxidative stress responsive transcription nuclear factor NF-κB in lung epithelial cell lines, while soluble concentration of Zn has been reported as the toxic factor in the mouse lung response to an atmospheric dust sample (Adamson *et al.*, 2000). The generation of OH radicals by soluble metal from PM_{10} samples has recently been corroborated by EPR (Shi *et al.*, 2003).

Despite the plethora of toxicological studies, there is a gap in linking identified potential *hazards* of soluble metal, and putative *risks* from actual human exposure to trace metals (i.e. its airborne concentration). Although other studies have reported total metal concentration of urban airborne PM, including a few for the UK (Chester *et al.*, 2000; Harrison *et al.*, 2003; DEFRA, 2003), there have been almost no measurements of soluble fractions. There is particular paucity of information for the fine particle fraction ($PM_{2.5}$), which has often (but not

universally) been shown to have a stronger association with adverse health outcomes than PM_{10} (Pope, 2000a), and which may form the basis of a future air quality standard for PM in Europe. In addition, the persistent strong association between adverse health outcomes and the black smoke (BS) optical reflectance measure of PM (Hoek *et al.*, 2000) has recently prompted the World Health Organisation to recommend re-evaluation of BS (or a modern-day equivalent) as an air quality standard (WHO, 2003).

The objective of this work was to provide a comprehensive time-series of the concentrations of "total" and "soluble" metal in the PM_{10}, $PM_{2.5}$ and BS fractions of a typical UK urban background aerosol for input to an epidemiological study of the association between particle-bound metal and selected health end-points. The deliberate use of quote marks reflects the difficulty in defining these terms. In practice, total and soluble metal are operationally-defined quantities because the concentration of metal measured can depend on the exact method of analysis. Only very few studies have attempted any form of speciation of total metal in PM. The aqueous solubility of trace metals in aerosols as a source of environmentally-mobile metal to the sea has been examined by Chester *et al.* (1993). Janssen *et al.* (1997), in their analysis of PM in the Netherlands, defined a "leachable" fraction using a 100-fold dilution of their 4.5 M HF/1M HCl total extractant, while Espinosa *et al.* (2002) used a four stage extraction protocol, ranging from water through to hot concentrated HNO_3:HCl:$HClO_4$, to speciate PM in Spain into soluble and exchangeable metal; carbonate, oxide and reducible metal; oxidisable and sulphidic metal; and residual metal.

In this work, the daily filter samples were sequentially extracted using ultrapure water at room temperature, followed by hot concentrated HNO_3/HCl. The choice of water as the first extractant represented considered judgement of best-practicable. The high chloride content of extractants such as phosphate-buffered saline or Hanks solution introduces interference in ICP-MS detection of some elements under study, whilst preliminary extraction experiments with other buffers such as potassium citrate and tris(ma) introduced unacceptable additional blank variability. It is also not obvious that a fairly arbitrarily chosen buffer solution provides any more realistic simulation of "lung bioavailable" than water. (The lung fluid contains a multitude of other components such as surfactants and chelators). Therefore water was chosen as the simplest and most universal extraction procedure that would not introduce additional uncontrollable variability in metal determination through additional chemical solutions and handling steps. As mentioned above, some workers including those from the USEPA, routinely

use extraction of samples with water only in toxicity testing (Costa and Dreher, 1997; Frampton *et al.*, 1999). Throughout the rest of the paper the terminology water-soluble rather than bioavailable is used in order to emphasise the operational definition of the former and to avoid implying a direct correspondence between the two.

This paper presents a general analysis of this resource of size- and solubility-resolved airborne metal concentration data. The dataset is of general applicability to UK urban background air. The application of these data to epidemiology will be reported elsewhere.

2 Methodology

2.1 Sampling

Daily (midnight to midnight) samples were collected on the roof of the University Old College, in central Edinburgh (3° 12′ W, 55° 57′ N) from 16th September 1999 to 15th September 2000, inclusive. Edinburgh has a population of about 450,000, does not contain major heavy industry, and is bounded by coastal estuary to the north and comparatively rural environs elsewhere. At 18 m elevation above neighbouring streets, the site is representative of urban background air in the city. The PM_{10} and $PM_{2.5}$ samples were collected in parallel using two R&P Partisol 2025 sequential samplers (flow rate 16.7 L min^{-1}) , both with PM_{10} heads and one containing a sharp cut cyclone to select further for $PM_{2.5}$. The site was also equipped with a standard 8-port UK Black Smoke (BS) sampler (flow rate ~1.5 L min^{-1} precisely measured), and an RM Young wind vane logging hourly wind speed and direction.

The Partisols, and BS sampler, were operated in accordance with guidance specified by the USEPA (1998), and the UK national smoke network (DETR, 1999), respectively. PM_{10} and $PM_{2.5}$ sampling heads were cleaned every 4 weeks and the volumetric flow rate calibrated against a NIST traceable critical orifice flow meter (Chinook Engineering). Prior to the sampling campaign, both samplers were operated as PM_{10} samplers for 14 days, and both as $PM_{2.5}$ samplers for a further 14 days. The correlation coefficients between sample masses were 0.991 and 0.985, respectively. The median relative difference in mass (sign ignored) was 3 % or 4.9 % for operation as PM_{10} or $PM_{2.5}$ samplers, respectively, well within the USEPA (1998) guideline of <10 %.

Following initial trials, Gelman Zefluor filters (PTFE, 2 μm pore) were used for the PM_{10} and $PM_{2.5}$ gravimetric and chemical analyses since they had low metal content, did not char or otherwise perish at the high temperatures used in the acid extraction and had low susceptibility to mass variability. Whatman no. 1 cellulose filters were used in the BS sampler for consistency with the national network (DETR, 1999).

2.2 Gravimetric analysis

The Zefluor filters were double-weighed before and after exposure on a Sartorius MC5 6-place balance equipped with anti-static ionising blower. Following the methodology of Vaughan *et al.* (1989), the 95 % confidence interval for a single filter weighing was calculated as 2.4 μg, equivalent to a concentration of 0.1 μg m^{-3} for a 24 h sample volume. A set of six "weigh blank" filters was interspersed within the pre- and post-weighing sessions of each batch of sample filters and the mean change in weigh blank filter mass between weighing sessions used to correct the sample filter mass changes. All blank and sample filters were conditioned for 24 h before weighing at $T = 17 \pm 3$ °C and RH = 53 ± 7 %. The mean weigh-blank filter correction was 1.1 % and 2.1 % of the mean PM_{10} and $PM_{2.5}$ sample masses, respectively.

The reflectance of the BS filters was measured using an EEL Model 43D reflectometer and converted to a notional mass concentration using the UK BS calibration curve (DETR, 1999).

2.3 Metal analysis

To determine water-soluble metal, filters were ultrasonicated at room temperature for 1 h in 7 ml ultrapure 18 MΩ water, after which 5 ml of extract was removed and acidified to 2 % HNO_3 to prevent metal adsorption. Concentrated HCl and HNO_3 acids were then added to the filters to give 7.7 ml total volume of 2.8:1 v/v acid mixture, respectively, boiled to dryness over ~20 h and re-suspended in 10 ml 2 % HNO_3 acid for analysis. The digest followed the optimisation of Harper *et al.* (1983).

The pH of the solution in the water extraction step was measured on 28 occasions and was always in the range 5.1-5.4. The lack of variation is expected because the UK atmospheric aerosol is well-neutralised (Clarke *et al.*, 1999).

Quantification of As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, Ti, V and Zn in the two sets of extracts was performed using a VG Elemental PasmaQuad 3 ICP-MS. Where possible, two or more isotopes

were monitored as a cross-check against potential interferences by other species of the same, or closely overlapping, *m/z* value. Each ICP-MS run contained two series of 11 point calibration standards diluted from a multi-element reference standard solution. The final corrected sample concentration for each element was obtained by subtracting from each sample the median concentration of that element in the 6 weigh-blank filters taken through the same analytical protocol with each batch of sample filters. The limit of detection value for each element on each run was expressed as 3 times the sd of the blank filter analysis values for that element on that run. A summary of the blank filter and LOD concentrations obtained in this work is given in Table 1.

The sum of the mass of metal from both extractions gave the total metal content. Metal data were expressed as both ng m^{-3} airborne concentration and ng µg^{-1} particle concentration.

The precision and accuracy of the extraction protocol was evaluated using the NIST airborne particulate matter Standard Reference Material SRM 1648. Six SRM samples, with masses between 400 and 1000 µg (representative of 24 h sample masses) were precisely weighed out onto Zefluor filters and analysed as for sample filters. RSDs of water-soluble metal concentration in the *n* = 6 SRM samples were <4.7 % for 10 of the 11 metals (7.0 % for Ti). The corresponding RSD values for precision in acid extraction of the SRM were <7.6 % for 10 of the 11 elements (18.2 % for Ni). Recovery of total metal ranged between 98 and 122 % (mean, 108 %) for the 6 elements analysed that had certified SRM values (V, Mn, Cu, Zn, Cd, Pb). A second acid digest of Zefluor filters previously digested did not yield concentrations of metal significantly higher than blank filter concentrations, indicating that the acid extraction yielded all metal digestible by this extraction at the first attempt. Of the elements analysed that did not have certified SRM values, it is expected that only Ti would be significantly under-extracted by the hot aqua-regia digest as compared with a digest including HF.

2.4 Air-mass back-trajectory calculation

Air-mass back-trajectories for each day were calculated using the 3-D model available at the British Atmospheric Data Centre (www.badc.rl.ac.uk). Trajectories were calculated backwards for 5 days from a mid-day arrival at the 930 hPa pressure level.

3. Results and Discussion

3.1 Particle mass concentrations

Only a summary of gravimetric data is presented since the focus of this paper is trends in metal concentration. Annual mean PM_{10}, $PM_{2.5}$ and BS at this site was 15.5, 8.5 and 6.6 µg m^{-3}, respectively (Heal *et al.* submitted). Daily PM_{10} and $PM_{2.5}$ were highly correlated ($r = 0.87$, $n = 349$), as noted before for the UK (EPAQS, 2001). On average, $PM_{2.5}$ constituted 0.54 of PM_{10}, with a range in daily ratio of 0.32 to 0.95. The BS:$PM_{2.5}$ ratio was significantly lower in spring/summer (0.75), than in autumn/winter (0.96), reflecting the different measures of PM that these measure represent, with decreased contribution from primary combustion carbonaceous fine particles and increased contribution from photochemical (non-black) secondary fine particles in spring and summer.

3.2 Total metal concentrations

A summary of the total metal concentration in PM_{10}, $PM_{2.5}$ and BS is given in Table 2, along with corresponding data for other air pollutants. It is important to note that, although mass concentrations derived from reflectance of BS filters are indicative, extraction of the filters yields absolute ng m^{-3} concentrations of metal in a particle fraction that corresponds very approximately to PM_4 (McFarland *et al.*, 1982). The BS metal data are limited, first, because the brass filter holders in the sampler caused contamination for several elements and, secondly, because the factor of ten lower daily sample volume yielded many metal concentrations below l.o.d. Concentrations of trace metal in the particle fraction sampled by a BS sampler have not been previously reported, but Table 2 shows that the concentrations for which there is analytical confidence are consistent with a size fraction between $PM_{2.5}$ and PM_{10}.

Other data for trace metal concentration in UK urban PM_{10} and $PM_{2.5}$ are shown in Table 3. Some studies report data for TSP rather than PM_{10} (Chester *et al.*, 2000; DEFRA, 2003). The data from Harrison *et al.* (2003) for PM_{10} in Birmingham are the most relevant comparison, although samples were roadside rather than urban background, and size fractionation was by cascade impactor rather than reference PM_{10} inlet. Nevertheless, given the different sampling environment and Edinburgh's smaller size, the concentrations are broadly comparable. The only previous data for trace metal in $PM_{2.5}$ in the UK were collected 8 years before the Edinburgh samples (Harrison and Yin, 2000), during which time there has been significant decline in atmospheric emissions of PM_{10}, $PM_{2.5}$ and trace metals (NAEI, 2003). Table 3 includes comparison with the study by Lee *et al.* (2003) in Toronto, since they also collected and analysed daily $PM_{2.5}$ for one year from a rooftop location, using procedures almost

identical to those in Edinburgh. Taking into account that annual median $PM_{2.5}$ in Toronto was 12.7 µg m^{-3}, compared with 7.1 µg m^{-3} in Edinburgh, there is considerable consistency in the particle mass proportion of most of the trace metals between the two cities.

3.2.1 Size-resolved metal concentrations

The distribution of each trace metal in Edinburgh PM between $PM_{2.5}$ and $PM_{10-2.5}$ is shown in Fig. 1a, with each size fraction further divided as water-soluble or non water-soluble. The data are shown as ng µg^{-1} particle, rather than ng m^{-3} airborne concentration (as in Tables 2 and 3), in order to illustrate the typical proportion of PM_{10} constituted by each of these components. Fig. 1b shows the data normalised so that the relative distribution of each metal between each of the four fractions can be compared. The sum of the two shaded parts of the bars on Fig. 1b illustrates the proportion, on average, of the total metal that is contained within the $PM_{2.5}$ fraction. This proportion varies widely between element, ranging from only 13 % (Ti), 17 % (Fe) and 21 % (Ni), through 28 % (Cr), 30 % (Mn) and 33 % (Cu), to 63 % (Zn), 72 % (V), 82 % (As), 84 % (Pb) and 95 % (Cd). Pb and Cd were also observed to be predominantly associated with fine (submicron) particles in Birmingham (Harrison *et al.*, 2003) and Los Angeles (Singh *et al.*, 2002), as was V in the latter study. The Birmingham study also observed Fe and Cu to be mainly in the coarse fraction (PM_2/PM_{10} ratios ~30 and ~35 %, respectively), while Ni and Zn had PM_2/PM_{10} ratios of ~75 %. (N.B. Impactor cut-off in Birmingham was at 2 µm, rather than 2.5 µm). In Kofu, Japan, $PM_{2.5}/PM_{10}$ ratios were approximately 15 % (Ti), 25 % (Fe), 40 % (Mn), 60 % (V, Pb), 75 % (Cu, Zn) which again agree well with the Edinburgh values (with the exception of Cu), although these Japanese data are based on a very small number of samples (Kyotani and Iwatsuki, 2002). The observation of generally similar particle mass proportions and size distributions for trace metals in urban background air from different locations suggest a reasonable consistency in source contributions.

3.2.2 Water-soluble proportions

Fig. 2 shows the median daily ratio of water-soluble to total metal for each metal in each of the PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ size fractions. Water-soluble proportions varied considerably with metal. For PM_{10}, the water-soluble proportion was ≤10 % for Ti, Fe and Ni, but ≥50 % for V, Zn, As and Cd. A substantial proportion (~35-45 %) of Mn, Cu and Pb was also water-soluble. For all 11 trace metals, a greater proportion of metal was water-soluble in the fine fraction than in the coarse fraction, presumably a consequence, in part, of the increase in particle surface area to volume ratio with decrease in diameter. As indicated in the introduction, very few

studies have attempted to quantify an "available" proportion of trace metal in airborne particles. Janssen *et al*. (1997) reported almost all (80-100 %) of their trace metals to be "leachable", but since this extraction was a dilution of concentrated HF and HCl solution used for total extraction these data do not provide much insight. Espinosa *et al*. (2002), in a sequential extraction of <0.61 μm particles in Seville, report <8 % and <4 % water-soluble Ti and Fe, respectively, and 50 %, 40 %, 33 %, and 27 % water-soluble V, Ni, Mn and Cu, respectively, all in good agreement with the Edinburgh fine fraction data. However, these workers report much lower Pb water-solubility than observed in Edinburgh. In contrast, Kyotani and Iwatsuki (2002) observed significant water-solubility for Pb in PM_{10} and $PM_{2.5}$ in Kofu, together with agreement in the trend for low water-solubility of Ti, Fe and Cr and greater water-solubility of V, Zn and Mn.

In general, a higher proportion of water-soluble metal is indicative of anthropogenic rather than crustal sources. Metal in anthropogenic particles consists as metal-dominated abrasion or hot-vapour condensation particles or metals that have condensed onto the surface of other particles, and thus tend to be more labile than metal bound within crustal material.

3.2.3 Relative amounts of each trace metal

Fig. 3 shows the median daily relative contribution of each of the 11 trace metals to the sum of all measured trace metals within each of PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$. Although Fe is the most abundant metal, its proportion of the sum of trace metal varies widely between PM fractions. The contribution of total Fe to Σ(total metal) in PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ was 80 %, 51 % and 89 %, respectively, whereas the contribution of water-soluble Fe to Σ(water-soluble metal) was only 43 %, 19 % and 64 %, respectively. Within $PM_{2.5}$, Pb and Zn together constituted >35 % of the total metal measured and >65 % of the water-soluble metal measured. In the latter case, the amount of water-soluble Pb and Zn both exceeded that of Fe. Across all the particle size fractions, over 90 % of the water-soluble or total mass of metals analysed was always contributed by the four metals Fe, Cu, Zn and Pb. The metals Ti, V, Cr, Mn, Ni, As and Cd each only constituted <2 %, on average, of the total metal measured in each size fraction. These data show that other trace metals as well as Fe can make significant contributions to trace metal exposure in certain particle fractions.

Some significant differences were observed in the daily relative proportions of the metals in each PM fraction as a function of season, but systematic trends were not strong.

3.2.4 Contribution of trace metal to particle mass

Table 4 summarises the proportion of PM constituted by the 11 measured trace metals. For the year of study, these 11 metals constituted 1.8 % of daily PM_{10} (expressed as the median % daily proportion for the whole year dataset). The maximum proportion of daily PM_{10} constituted by the metals was 9.0 %. In contrast, these 11 metals constituted in total only 0.8 %, as a median daily value, of $PM_{2.5}$. The $PM_{10-2.5}$ fraction was therefore almost a factor of 4 more enriched with these metals (median daily value 3.1 %) than the $PM_{2.5}$ fraction. The water-soluble concentrations of these 11 metals together constituted 0.24 % of daily PM_{10} (as median daily value) and 0.26 % of daily $PM_{2.5}$, indicating that a greater proportion of the trace metal in $PM_{2.5}$ was water-soluble than in PM_{10}. About $1/3^{rd}$ to $1/4^{th}$ of $PM_{2.5}$ trace metal content was water-soluble compared with only about $1/7^{th}$ to $1/8^{th}$ of PM_{10} trace metal content.

For comparison, the average proportion of trace metals to roadside PM_{10} in Birmingham was 1.5 % (total excludes contribution from Ti, V, Cr and As which were not measured) (Harrison *et al.*, 2003), compared with 1.8 % in Edinburgh, whilst the average proportion of trace metal to background $PM_{2.5}$ in Toronto was 0.7 % (total excludes only Ti) (Lee *et al.*, 2003), compared with 0.8 % in Edinburgh. The consistency of these data again suggests generally similar source contributions to trace metal in urban particles.

The data summary in Table 4 obscures significant seasonal differences in the proportion of metal in the various PM size fractions, as illustrated in Fig. 4. For example, the measured total metal content of fine particles was lower, on average, in the spring/summer (0.77 %) than in the autumn/winter (0.98 %), whereas for coarse particles the metal content was considerably higher in spring/summer (3.3 %) than in autumn/winter (2.3 %).

3.3 Correlations between metal concentrations and pollutant metrics

Spearman rank correlation coefficients, r_s, were significantly positive between concentrations of most metals and the mass concentrations of different size fractions (Table 5). An interesting observation was substantially stronger correlation of Mn, Fe, Cu, Zn, As and Pb in both PM_{10} and $PM_{2.5}$ with BS gravimetric concentration than with either PM_{10} or $PM_{2.5}$ gravimetric concentration. For example, r_s values for the correlation of Cu concentration in PM_{10} with gravimetric PM_{10}, $PM_{2.5}$ and BS were 0.43, 0.51 and 0.80, respectively. This suggests that the particle concentrations of these metals are strongly influenced by sources and process related to

the fine fraction of particles, in particular to "dark" fine particles, i.e. to combustion and/or traffic related sources. It also suggests that measurement of BS may be a cost-effective surrogate for insight into the PM_{10} and $PM_{2.5}$ concentrations of a number of trace metals, including the most abundant, with putative adverse health associations. In contrast, concentrations of Ti in PM_{10} and $PM_{2.5}$ were more strongly correlated with mass concentration of PM_{10} than with $PM_{2.5}$ or BS (Table 5), as expected if the major source for this element is coarse crustal particles unrelated to combustion.

The results of factor analyses on gas and PM_{10} or $PM_{2.5}$ total metal concentrations are shown in Tables 6 and 7, respectively. Outcomes were similar in both cases, as were analyses using water-soluble metal concentrations (not shown). Three factors encompass >50 % of the variability of the 18 variables. One factor has high loadings on BS and NO_x (and inversely for O_3) and is attributed to local road traffic sources (Factor 1 in Table 6 and Factor 2 in Table 7). Cu and Pb have high loadings on this factor. A strong correlation between NO_x and Cu and Pb (and Mn) was also observed in Birmingham (Harrison *et al.*, 2003). There was an appreciable loading of Mn on this factor for the Edinburgh data also. Although Pb is no longer used as an additive in petrol, road traffic remains a major atmospheric source for Pb (NAEI, 2003) and it is still present in the road environment. Cu arises from vehicle brake wear (Weckwerth, 2001; Sternbeck *et al.*, 2002). Therefore this factor incorporates road traffic induced resuspension as well as direct exhaust emissions, which it is not possible to separate with the current variables. A resuspension component is consistent with the strong association with BS since the main source of road traffic derived BS is diesel-fuelled buses and lorries, and these heavy vehicles dominate resuspension of particles from the road.

A second factor (Factor 2 in Table 6 and Factor 1 in Table 7) has high loadings on V, As and $PM_{2.5}$, and also, to different extents, on BS, Zn and Cu. V is a marker for fuel-oil, and As for coal, so this factor indicates fine particles derived from static combustion sources, with some emphasis on regional transport from sources more distant than local road traffic.

Factor 3, with high loadings on Ti, Fe and Mn, corresponds to a crustal source, with significant contribution to the coarse fraction shown by the high loading on $PM_{10-2.5}$ (Table 6). Concentrations of these metals are also strongly associated within $PM_{2.5}$ (Table 7). This factor may include contributions from local suspension of road dust, as well as transported crustal

material. As noted above, Mn, and to a lesser extent, Fe, are also associated with a road traffic factor.

The two remaining factors that include trace metals have high loadings on Ni and Cr, or Pb and Cd, only, and correspond to specific metaliferous industrial sources (including, for Pb and Cd in particular, non-ferrous combustion sources (NAEI, 2003)). A non-exhaust vehicle-related emission of Cd has been identified from tunnel studies in Sweden (Sternbeck *et al.*, 2002), but this is not apparent in the Edinburgh data.

3.4 Seasonal and meteorological influences on metal concentrations

Some time-series epidemiological studies have suggested a stronger association between particle mass and adverse health in summer than in winter (Hoek *et al.*, 2000; Anderson *et al.*, 2001), so particle metal concentrations measured in this work were likewise analysed by season. Fig. 5 shows summer (Apr-Sept) and winter (Oct-Mar) concentrations of water-soluble metal in PM_{10} and $PM_{2.5}$. Trends were similar for total metal concentration data. Kruskal-Wallis tests showed that concentrations of Ti, V, Mn, Fe, Cu and Zn were significantly higher, on average, in summer than in winter in both PM_{10} and $PM_{2.5}$ (except for Zn in $PM_{2.5}$). The last three of these metals (along with Pb) also deliver the highest absolute concentrations of trace metal from PM exposure (Section 3.2) and all have also been implicated as mediators of inflammation in toxicological studies (Section 1). For all other metals there was no significant difference in concentration with season. The elevated metal concentrations in summer, while intriguingly consistent with observations from epidemiology, do not contribute any causal evidence.

Previous work using the Jenkinson classification of regional-scale synoptic weather maps has shown PM_{10} in Edinburgh to be significantly enhanced on days indicating air flow from continental Europe (Buchanan *et al.*, 2002). To investigate the influence of air-mass source region on particle metal concentration the daily back-trajectories were grouped using statistical hierarchical clustering (via mean distance squared and average linkage) on the vectors of the following 30 variables: distance north of Edinburgh, distance south of Edinburgh, and pressure level, each at 12, 24, 36,…120 h prior to arrival at Edinburgh. There was no *a priori* expectation for the "best" number of clusters into which to classify the trajectories. Instead, plots of root mean square value and r^2 as a function of number of clusters were examined for major discontinuities in slope, which indicate major step-changes in dissimilarity, i.e. of

distinct groupings (Cape *et al.*, 2000). Six main clusters emerged (Table 8), together accounting for 94 % of the total number of trajectories (366) and none containing less than 1.5 % of the total.

The influence of back-trajectory cluster on both airborne particle metal concentration (ng m^{-3}) and particle mass metal proportion (ng μg^{-1}) was investigated. The former measures absolute exposure to trace metal whilst the latter may yield insight into different source contributions from different geographic sectors. The particle mass metal proportions varied significantly with air-mass source cluster (Table 9). For example, PM_{10} with source corresponding to Cluster 3 (European) were relatively more enriched with trace metal than particles arriving along other trajectories (Fig. 6). Although particles with sources corresponding to Cluster 1 (British Isles) were not enriched with metal compared with particles from long-range Atlantic or Arctic trajectories, absolute particle metal concentrations were significantly elevated on days corresponding to both Cluster 1 and Cluster 3 trajectories. This was due to significantly higher PM_{10} mass on Cluster 1 (and Cluster 3) days (data not shown) and the general correlation between individual metal concentration and total particle mass concentration. Results were similar for metal content of $PM_{2.5}$.

Overall, therefore, exposure to trace metals in Edinburgh was elevated when air-masses had passed predominantly over land in the preceding few days resulting in either or both higher PM mass and higher metal proportion. The results in Table 9 indicate that air-mass back-trajectory coordinates can provide a means by which (approximately) to estimate particle trace metal concentration retrospectively from PM_{10} (or $PM_{2.5}$) data.

4 Conclusions

This work has provided a large dataset of trace metal content of UK urban background PM_{10} and $PM_{2.5}$. Where other relevant data exist for comparison (in the UK or comparable cities in other developed countries), there appears to be reasonable consistency in time-averaged proportions of trace metal within PM_{10} and of its distribution between the fine and coarse size fractions. This suggests that, in the absence of major point-source influences, there is a reasonable commonality in the general source contributions of trace metals. Within this broad-brush assessment, particle-associated trace metal at particular receptor locations will depend on the relative influences of particular local sources such as road traffic, and/or the extent by

which long-range transport from different geographical sectors changes source contributions. For example, the proportion of trace metal in particles in Edinburgh varied significantly with air-mass back trajectory; concentrations were elevated when air-masses had passed predominantly over land in the preceding few days because PM mass was higher or PM metal proportion was higher. Such meteorological influences contribute to the variation in trace metal concentration in the short-term (i.e. daily). Nevertheless, the overall general correlation of trace metal composition with particle mass is consistent with the broadly similar adverse health associations derived from different epidemiological studies, should the hypothesis of a causal association be true.

Measuring the concentrations of just Fe, Cu, Zn and Pb accounted for >90% of the trace metal mass in PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$. While Fe readily dominated the contribution of trace metal to total metal mass in each particle size fraction, Zn and Pb each contributed at least as much as Fe to the water-soluble metal mass of PM_{10} and $PM_{2.5}$. The mass proportion of trace metal within $PM_{2.5}$ was less than in PM_{10}, which means coarse particles were more enriched in trace metal. The differential in proportion metal between size fractions was considerably less for water-soluble metal.

Correlation and factor analyses indicated three main source contributions for trace metals: traffic, static combustion and crustal. In common with other recent studies, it seems likely that emission of metals most associated with traffic (Cu, Fe Mn, Pb, Zn) is probably more related to suspension or resuspension of vehicle wear or crustal dust than to direct exhaust emission.

Although most trace metal concentrations correlated with PM_{10} and $PM_{2.5}$, for some metals (Mn, Fe, Cu, Zn, As, Pb) correlations were stronger with BS. This means BS measurements could be used as a crude, surrogate indicator of concentrations of the most abundant trace metals in particles. A number of epidemiological studies have shown significant associations of adverse health directly with BS concentrations. Other epidemiological studies have shown associations between adverse health and exposure to traffic and combustion-related air pollution quantified indirectly by apportionment modelling techniques. For example, daily mortality in six US cities was significantly associated with $PM_{2.5}$ apportioned by factor analysis to mobile and coal combustion sources but not to crustal sources (Laden *et al.*, 2000), while cardiopulmonary mortality in the Netherlands was significantly increased in subjects living closer to main roads (Hoek *et al.*, 2002), taken to be indicative of increased traffic-

related air pollution. These epidemiological findings, coupled with the fact that BS is still indicative of fine particles from combustion plus the correlation between trace metal and BS, indicate that BS (or some updated measure of particle "darkness") remains a relevant measure of air pollution. The World Health Organisation recently reached a similar conclusion of the importance of BS as an exposure metric in air pollution in environmental epidemiology (WHO, 2003). Consequently, it is recommended that relevant agencies carefully review retaining or instigating a network of filter reflectance measurement co-located with PM_{10}.

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Table 1: Median concentration of metal in Zefluor filter blanks, and at limit of detection, of 26 separate derivations. On each occasion 6 weigh-blank filters were analysed. Data are expressed as equivalent airborne metal concentration for a 24 h sample of PM_{10} or $PM_{2.5}$.

	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Water extraction											
Median blank concentration (n =26) / ng m^{-3}	0.04	0.00	0.04	0.01	1.57	0.09	0.04	0.90	0.00	0.30	0.82
Median LOD concentration (n =26) / ng m^{-3}	0.08	0.00	0.03	0.01	1.50	0.05	0.10	1.96	0.00	0.40	1.41
Acid extraction											
Median blank concentration (n =26) / ng m^{-3}	1.28	0.03	1.11	0.24	9.15	1.26	0.64	5.68	0.01	0.36	1.74
Median LOD concentration (n =26) / ng m^{-3}	0.93	0.02	0.75	0.15	6.40	0.97	0.41	5.00	0.01	0.65	2.40

Table 2: Summary of total metal concentration in 24 h samples of urban background PM_{10}, $PM_{2.5}$ and Black Smoke collected for one year in Edinburgh. Also included are equivalent summaries for gravimetric PM metrics and other air pollutants. PM_c is notation for the coarse component, $PM_{10-2.5}$. n = 354, 362 and 366 for PM_{10}, $PM_{2.5}$ and BS data, respectively.

Component	Urban Background (this study)					
	PM_{10}		**$PM_{2.5}$**		**Black smoke**	
	Median	**(5 - 95)%ile**	**Median**	**(5 - 95)%ile**	**Median**	**(5 - 95)%ile**
Ti / ng m^{-3}	3.66	0.64 - 13.7	0.37	0.00 - 1.83	1.68	0.00 – 22.9
V / ng m^{-3}	1.14	0.38 - 5.9	0.72	0.21 - 3.80	0.76	0.17 - 3.47
Cr / ng m^{-3}	1.60	0.57 - 7.4	0.49	0.04 - 2.07		
Mn / ng m^{-3}	2.94	0.74 - 8.2	0.69	0.21 - 3.18		
Fe / ng m^{-3}	183	50.2 - 486	27.6	8.92 - 80.6	94.2	8.50 - 433
Ni / ng m^{-3}	3.43	0.89 - 37.9	0.97	0.16 - 5.47		
Cu / ng m^{-3}	4.93	1.78 - 13.6	1.39	0.52 - 4.61		
Zn / ng m^{-3}	13.3	2.21 - 38.6	7.49	1.08 - 27.1		
As / ng m^{-3}	0.37	0.13- 1.49	0.30	0.10 - 1.24	0.30	0.08 - 1.11
Cd / ng m^{-3}	0.34	0.00 - 10.1	0.38	0.00 - 7.98		
Pb / ng m^{-3}	14.1	1.28 - 130	13.6	0.65 -103		

	Median	**(5 - 95)%ile**
PM_{10} / µg m^{-3}	14.2	7.3 - 29.1
$PM_{2.5}$ / µg m^{-3}	7.1	3.6 - 18.3
$PM_{10-2.5}$ / µg m^{-3}	6.3	2.7 - 14.1
BS / µg m^{-3}	5.7	2.1 - 14.0
CO / ppm	0.5	0.3 - 1.0
NO_x / ppb	42	23 - 108
O_3 / ppb	15	6 - 27
SO_2 / ppb	2	1 - 5

Table 3: Comparison of total metal concentrations in UK urban PM, and with directly comparable relevant data from Toronto. The year(s) denote the period during which samples were collected

Component	PM$_{10}$			TSP			PM$_{2.5}$		
	Edinburgh 99-00[a]	Birmingham 00-01[b]	Birmingham 92[c]	Glasgow 00[d]	London 99[d]	Liverpool 94-96[e]	Edinburgh 99-00[a]	Birmingham 92[c]	Toronto 00[f]
Ti / ng m^{-3}	3.7		16.6				0.4	4.7	
V / ng m^{-3}	1.1		7.4	1.7	4	7.3	0.7	5.0	0.5
Cr / ng m^{-3}	1.6		12.6	8.9	2	2.1	0.5	6.4	1.2
Mn / ng m^{-3}	2.9	6.4	16.3	6.9	12	8.4	0.7	9.9	3.8
Fe / ng m^{-3}	183	204	301	399	870	340	27.6	114	55
Ni / ng m^{-3}	3.4	2.5	4.8	4.8	5	3.0	1.0	2.9	0.8
Cu / ng m^{-3}	4.9	12.0	38.7	12	21	21	1.4	30.2	2.5
Zn / ng m^{-3}	13.3	29.9	353	30	41	36	7.5	297	16
As / ng m^{-3}	0.4		5.7				0.3	4.2	0.4
Cd / ng m^{-3}	0.34	0.51			0.4		0.4		0.3
Pb / ng m^{-3}	14.1	27.4	91			43	13.6	74	3.4

[a] This study, median values ($n = 354$, PM$_{10}$; $n = 362$, PM$_{2.5}$), analysis by acid-digest and ICP-MS
[b] Harrison *et al*. (2003), mean values ($n = 30$), roadside samples, analysis by acid-digest and ICP-MS
[c] Harrison *et al*. (2000), mean values ($n = 55$), analysis by PIXE
[d] Defra (2003), mean values ($n = 12$), analysis by XRF and INAA
[e] Chester *et al*. (2000), geometric mean values ($n = 60$), analysis by acid digest and ICP-MS
[f] Lee *et al*. (2003), median values ($n = 367$), analysis by acid digest and ICP-OES/MS

Table 4: Summary of the proportion of daily PM$_{10}$, PM$_{2.5}$ and PM$_{10-2.5}$ contributed by the sum of the 11 trace metals measured.

	% proportion of PM$_{10}$		% proportion of PM$_{2.5}$		% proportion of PM$_{10-2.5}$	
	Total metal	Water-soluble metal	Total metal	Water-soluble metal	Total metal	Water-soluble metal
Median	1.8	0.24	0.84	0.26	3.1	0.18
Mean	2.0	0.31	1.1	0.36	3.4	0.29
Min	0.25	0.003	0.15	0.005	0	0
Max	9.0	4.4	6.8	3.7	25	9.3
n	349	349	362	362	349	349

Table 5: Spearman rank correlation coefficients, r_s, between total metal concentrations in PM$_{10}$ and PM$_{2.5}$ and mass concentrations of PM$_{10}$, PM$_{2.5}$ and BS. Values of r_s >0.17 and >0.11 correspond to P <0.001 and <0.05, respectively, for between $n = 349$ and 362 data.

	Total metal content of PM$_{10}$										
Mass metric	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
PM$_{10}$	0.40	0.62	0.25	0.52	0.45	0.17	0.43	0.38	0.56	0.23	0.35
PM$_{2.5}$	0.31	0.71	0.24	0.49	0.43	0.15	0.51	0.40	0.65	0.17	0.37
BS	0.32	0.56	0.27	0.58	0.59	0.20	0.80	0.48	0.78	0.20	0.58

	Total metal content of PM$_{2.5}$										
Mass metric	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
PM$_{2.5}$	0.32	0.73	0.38	0.53	0.57	0.42	0.55	0.42	0.66	0.14	0.33
BS	0.15	0.52	0.20	0.58	0.64	0.35	0.75	0.58	0.79	0.22	0.54

Table 6: Loadings of each variable in a 6-factor model using varimax rotation of principal components. Metal data used were total metal concentration in PM_{10}.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Ti	0.172	-0.059	**0.896**	0.010	-0.182	-0.004
V	0.161	**-0.757**	0.228	-0.009	-0.139	0.011
Cr	0.153	0.044	0.057	**-0.895**	-0.003	0.039
Mn	0.397	-0.251	**0.783**	-0.086	-0.090	-0.072
Fe	0.340	-0.264	**0.731**	0.022	-0.197	0.076
Ni	-0.072	-0.036	-0.062	**-0.903**	-0.074	-0.040
Cu	**0.734**	<u>-0.440</u>	0.264	0.021	-0.035	-0.028
Zn	0.261	<u>-0.440</u>	<u>0.468</u>	0.052	0.158	0.061
As	<u>0.492</u>	**-0.725**	0.120	0.022	-0.005	0.156
Cd	0.070	-0.018	0.043	0.014	-0.089	**0.946**
Pb	**0.630**	-0.311	0.157	-0.066	0.011	**0.503**
$PM_{10-2.5}$	-0.218	-0.179	**0.592**	0.017	0.101	0.109
$PM_{2.5}$	0.051	**-0.859**	0.229	-0.004	-0.017	0.018
BS	**0.751**	**-0.532**	0.136	-0.014	-0.074	-0.010
NO_x	**0.852**	-0.035	0.102	-0.128	-0.054	0.166
CO	-0.022	0.082	0.093	-0.125	**-0.796**	-0.070
SO_2	0.180	-0.248	0.056	0.070	**-0.736**	0.233
O_3	**-0.867**	0.054	-0.089	-0.032	0.069	0.028
Cum. var. %	20.7	36.5	52.0	61.3	69.2	77.0

Loadings in **bold** are > |0.500| and <u>underlined</u> are in the range |0.440| - |0.499|

Table 7: Loadings of each variable in a 6-factor model using varimax rotation of principal components. Metal data used were total metal concentration in $PM_{2.5}$.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Ti	0.049	0.079	**0.948**	-0.064	-0.038	0.008
V	**0.769**	0.013	0.133	-0.054	-0.224	0.084
Cr	0.195	-0.123	0.113	0.131	**-0.713**	-0.167
Mn	0.381	-0.386	**0.698**	0.048	0.000	-0.043
Fe	0.160	-0.178	**0.926**	-0.008	-0.072	0.005
Ni	-0.007	0.128	-0.014	-0.057	**-0.778**	0.168
Cu	**0.619**	**-0.589**	0.064	0.095	-0.057	0.047
Zn	**0.738**	-0.244	0.088	-0.019	0.124	-0.079
As	**0.737**	<u>-0.472</u>	0.050	-0.100	0.006	0.042
Cd	0.016	-0.082	0.022	**-0.922**	0.065	0.092
Pb	0.322	**-0.612**	0.041	**-0.523**	-0.026	-0.062
$PM_{10-2.5}$						
$PM_{2.5}$	**0.832**	-0.023	0.209	-0.045	-0.165	0.051
BS	**0.551**	**-0.711**	0.079	-0.082	-0.006	0.105
NO_x	0.050	**-0.875**	0.109	-0.174	-0.021	0.043
CO	-0.028	0.001	-0.054	0.071	0.106	**0.864**
SO_2	0.162	-0.203	0.073	-0.279	-0.232	**0.654**
O_3	-0.100	**0.867**	-0.104	-0.040	-0.066	-0.079
Cum. var. %	20.1	39.5	53.5	61.1	68.7	76.2

Loadings in **bold** are > |0.500| and <u>underlined</u> are in the range |0.440| - |0.499|

Table 8: Summary of assignment to clusters of one year of daily air-mass back trajectories arriving in Edinburgh.

Cluster	No. of trajectories	% of total ($n = 366$)	Description
1	137	37	Local circulation around the British Isles
2	38	10	Atlantic SW, approaching over England
3	19	5	UK and central/Eastern Europe
4	46	13	Arctic, but with UK final circulation
5	96	26	Atlantic W approach, including North America land origin
6	7	2	Arctic direct from the N, not including UK circulation
	$\Sigma = 343$	94	

Table 9: *P*-values of Kruskal-Wallis tests for difference in daily PM_{10} metal enrichment factor (ng μg^{-1}) with the air-mass back-trajectory clusters defined in Table 8. Bold emphasises $P < 0.05$.

	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Water-soluble	0.07	**<0.001**	**0.017**	**<0.001**	**0.012**	**<0.001**	**0.014**	0.10	**0.003**	**0.036**	0.10
"Total"	**0.002**	**<0.001**	0.12	**<0.001**	**<0.001**	0.31	**<0.001**	0.26	**0.004**	**0.009**	0.15

Figure Captions

Fig. 1: Median concentrations of trace metals in one year of daily samples of PM_{10} in Edinburgh, sub-divided into $PM_{2.5}$ and $PM_{10-2.5}$, and further sub-divided into water-soluble, and non water-soluble metal. The upper and lower graphs are plots of the absolute and relative concentrations, respectively, for each metal.

Fig. 2: The proportion of water-soluble metal (as % of total metal) in PM_{10}, and in the fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) components separately. Data are median values of $n = 366$ daily samples.

Fig. 3: Relative contribution of each metal to the sum of all metals measured in this study in Edinburgh. Data are plotted for both the water-soluble and total metal content of each of PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$. Each bar contains median values of $n > 354$ daily samples.

Fig. 4: The proportion of PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ constituted by the 11 trace metals measured in this study (i.e. ng μg^{-1}), apportioned as water-soluble or non water-soluble metal. Data are median values of $n > 354$ daily samples, grouped by season.

Fig. 5: Winter (Oct-Mar) and summer (Apr-Sep) distributions of water-soluble metal concentrations (ng m^{-3}) in daily samples of $PM_{2.5}$ (upper graph) and PM_{10} (lower graph). Boxes correspond to upper and lower quartiles, and whiskers to 5th and 95th percentiles.

Fig. 6: Median daily particle mass concentration (ng μg^{-1}) of each metal (total) in PM_{10}, categorised by daily air-mass back-trajectory cluster.

Fig. 1: Median concentrations of trace metals in one year of daily samples of PM_{10} in Edinburgh, sub-divided into $PM_{2.5}$ and $PM_{10-2.5}$, and further sub-divided into water-soluble, and non water-soluble metal. The upper and lower graphs are plots of the absolute and relative concentrations, respectively, for each metal.
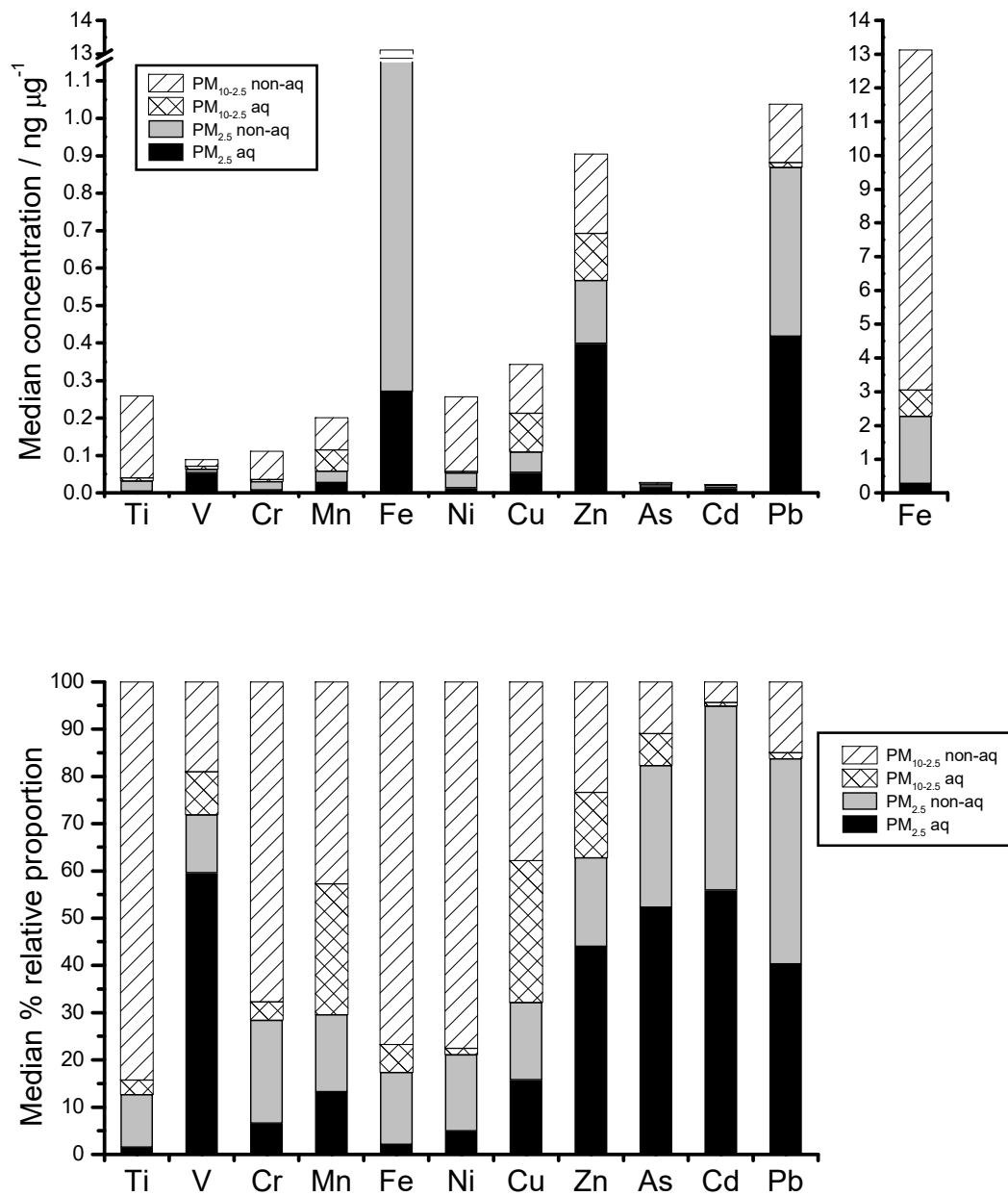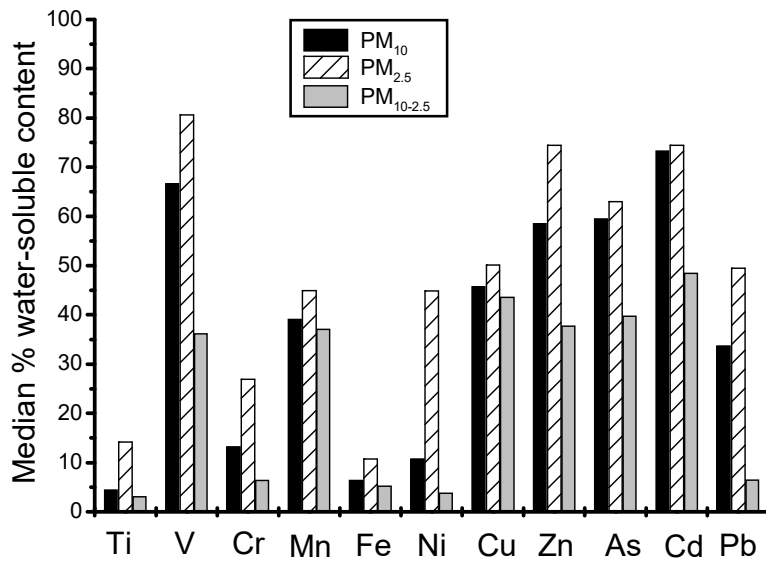
Fig. 2: The proportion of water-soluble metal (as % of total metal) in PM_{10}, and in the fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) components separately. Data are median values of $n = 366$ daily samples.

Fig. 3: Relative contribution of each metal to the sum of all metals measured in this study in Edinburgh. Data are plotted for both the water-soluble and total metal content of each of PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$. Each bar contains median values of $n = 366$ daily samples.

Fig. 4: The proportion of PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ constituted by the 11 trace metals measured in this study (i.e. ng μg^{-1}), apportioned as water-soluble or non water-soluble metal. Data are median values of $n > 354$ daily samples, grouped by season.
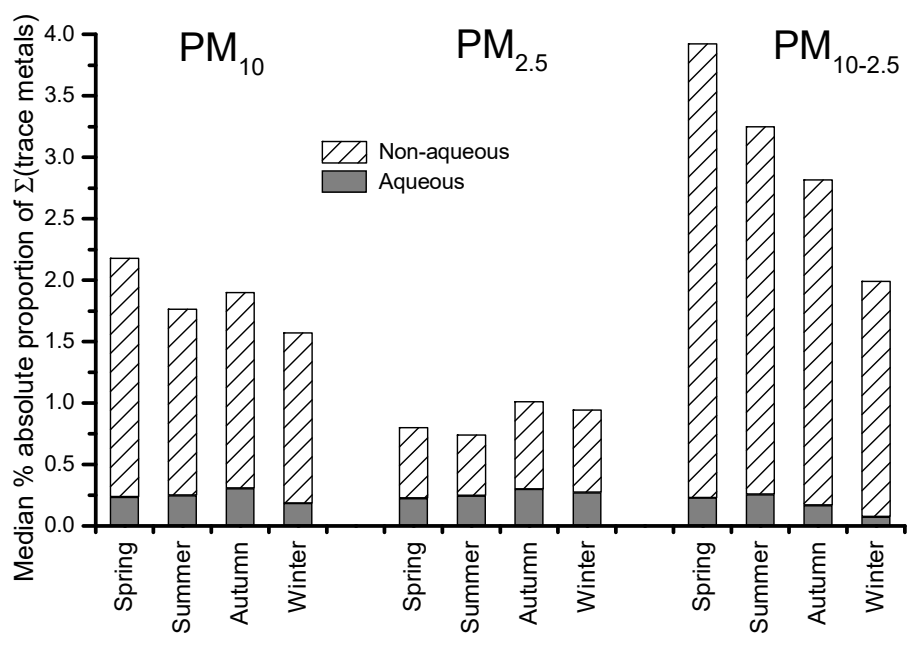
Fig. 5: Winter (Oct-Mar) and summer (Apr-Sep) distributions of water-soluble metal concentrations (ng m^{-3}) in daily samples of PM$_{2.5}$ (upper graph) and PM$_{10}$ (lower graph). Boxes correspond to upper and lower quartiles, and whiskers to 5th and 95th percentiles.
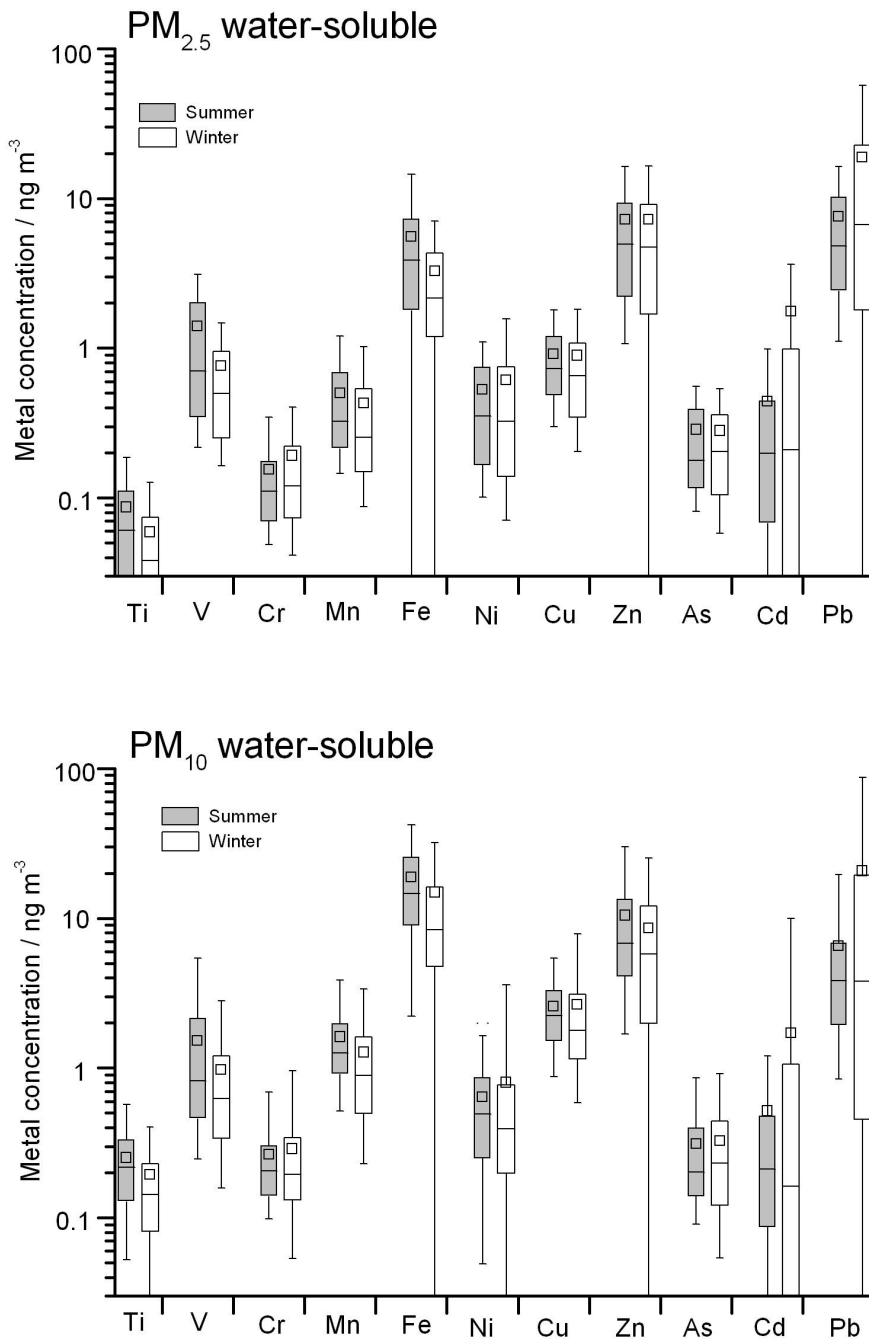
Fig. 6: Median daily particle mass concentration (ng μg^{-1}) of each metal (total) in PM_{10}, categorised by daily air-mass back-trajectory cluster.