Trace Metal Concentrations and Water Solubility in Size-Fractionated Atmospheric Particles and Influence of Road Traffic

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The abundance and the behavior of metals (Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Se, Ag, Cd, Sn, Ba, Pt, Hg, and Pb) and ions (Na^+ K^+ Mg^{2+} Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and oxalate) in size-fractionated atmospheric particulate matter (PM) were studied in the U. K. and Ireland at four observation sites simulating extreme degrees of vehicular-traffic influence in the environment. Trace metals in urban PM showed distinct types of size-fractionated behavior depending on the particle sources from which they originate. In coarse PM ($1.5 < D_p < 3.0$ μm) the concentrations of copper, barium, and iron correlated closely across over 2 orders of magnitude in urban air, which is seen as evidence that major portions of transition metals (Cu, Ba, Fe, and Mn) are released through abrasive vehicular emissions, particularly the wear of brake linings. Further results are strongly indicative of a decoupling of coarse iron and calcium, the former arising predominantly from vehicles, the latter from soil resuspension. In fine PM ($D_p < 0.5$ μm), several combustion and secondary sources of particulates were identified, but these were much less unique in terms of elemental fingerprints. An analysis of the water solubility of trace metals yielded that solubility varies considerably with element and, to a lesser extent, with particle size. Notable differences were found to the elemental water solubilities determined in previous work, partially explained by differences in extraction procedures.

1. Introduction

Although epidemiological studies worldwide have associated chronic and acute adverse health effects with airborne particulate matter (PM) (*1*), our understanding of the exact causes and mechanisms of these effects remains limited (*2*). It is not obvious in which particular PM size range toxic substances are concentrated, owing to the variety of atmospheric aerosol aging and mixing processes on the pathway between the sources of harmful PM and their inhalation by humans (*3*). A particular PM fraction that is known to exert toxic effects is transition metals, such as Fe, Zn, and Cu, which may release free radicals in lung fluid via the Fenton reaction, and are hypothesized to cause cellular inflammation (*4*). Since particle-bound metals need to dissolve and become free ions in the lung fluid, particle solubility in lung fluid is considered a major criterion for the bioavailability and therefore toxicity of environmental PM (*5*, *6*). Due to their uniqueness to anthropogenic sources of PM, metals have also been exploited as tracers to identify such individual sources (*7*−*9*). It has been recognized that the search for reliable tracers of specific sources may be crucial for developing cost-effective air pollution control strategies (*10*−*11*). Due to significant improvements in analytical techniques as well as an increasing awareness of ultraclean preparation techniques, information on the atmospheric abundances of trace metal species has become increasingly available for marine, rural, urban, and near-source locations (*3*, *12*−*18*). A novel direction is also the application of single-particle mass spectrometry, which allows determination of elemental concentrations over very short sampling intervals (*19*). In this project, efforts were made to compare trace metal concentrations at four measurement sites that represent different degrees of anthropogenic, particularly vehicular, traffic influence. PM size fractionation allowed identification of the PM size ranges into which individual metals partition and association with specific sources. In addition, the water solubility of particle-bound metals, a surrogate for bioavailability, was studied by employing two different PM extraction procedures. The situation under which PM sampling in Birmingham, U. K., took place can be regarded as representative of western industrialized cities, where industrial pollution has largely been regulated and where increasing volumes of traffic are contributing substantial proportions of several components emitted into the atmosphere.

2. Experimental Section

2.1. Size-Fractionated PM Sampling. Size-fractionated ambient PM samples were collected using a Sierra-Andersen high-volume cascade impactor (model 235, Andersen Instruments, Inc., Atlanta, GA). This impactor fractionates PM at the aerodynamic cutoff sizes 0.5, 0.95, 1.5, 3.0, and 7.2 μm. Sheets of polytetrafluoroethylene (PTFE) filters (Zefluor, pore size 3 μm; Pall Gelman) were used both as impaction substrates and as 8 in. × 10 in. back-up filters to collect all fine particles <0.5 μm. PTFE material was selected because it avoids some artifacts associated with other filter material in in vitro toxicological tests (*20*), since the future use of such tests is envisaged using the samples obtained during this study. No preparations were made in this study to reduce the blank levels of the PTFE filters. Owing to the design of the "slotted" cascade impactor, 10 slots needed to be cut manually into each impaction substrate using hardened steel blades. For the gravimetric determination of PM mass concentrations, the PTFE substrates and back-up filters were weighed before and after each sampling event using a precision balance (±0.0001 g) in an environment of controlled temperature and relative humidity (40 ± 5%). The PTFE sheets were allowed to condition in this environment for at least 24 h before weighing. To overcome the considerable flow resistance represented by the PTFE back-up filters, industrial blowers (models MS8 and MS11/020; Air Control Industries Ltd, Silver Street, U. K.) were employed, thus achieving sampling flow rates of 1 m^3/min. Since no humidity regulation was applied to the air inlet, particles were sized close to their

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ambient state, which corresponded to typically 73% (quartile range 70–78%) ambient relative humidity in Birmingham. As the Sierra-Andersen cascade impactor has no ideal sharpness of cut, especially for impaction substrates of finite depth (21), the size fractions given in this paper need to be taken as an indication rather than exact limits of the particle sizes collected.

2.2. Field Experiment. To collect a set of atmospheric PM samples with variations in anthropogenic source contributions as wide as possible, measurements were conducted at four different measurement sites as follows.

2.2.1. Mace Head (Remote Background). Ambient PM samples were taken between August 8, 2002, and August 28, 2002, at the atmospheric research station Mace Head in Connemara, on the west coast of Ireland (22). The sampling site is located on a beach facing the open Atlantic to the west. In this study we sampled clean marine air masses that had spent the preceding days almost exclusively over the sea. These aerosols are expected to have lost most of their continental and anthropogenic signature by in-cloud and below-cloud scavenging in the oceanic environment. Owing to the low metal concentrations expected, the sampling duration was set to 5 days for each of the four samples collected in this study.

2.2.2. Birmingham University (Urban Background). Two locations on the campus of the University of Birmingham (U. K.), "Elms Road" and "Winterbourne", were used to sample urban background PM. Measurements were made at 1.5 m above ground level over grassland, with road traffic and other anthropogenic PM sources being at least 100 m distant behind large trees in both cases. The sampling events were carefully triggered after an examination of meteorological forecast and analysis maps to identify any possible influence of large-scale air masses on the urban background concentrations as clearly as possible. The sampling durations were between 18 and 130 h, and a total of 23 samples were collected between April 23, 2002, and October 7, 2002. Due to the spatial proximity and similarity of the two sites as well as the similarity found in terms of metal concentrations, their data were combined and subsequently denoted as "urban background" in the following discussion. Comparisons between the temporal variation of total PM mass concentrations in this study and concurrent PM_{10} measurements at four permanent monitoring sites of the U. K. national air quality network (Birmingham Centre, Birmingham East, Leamington Spa, and Wolverhampton Centre) suggested that the urban background measurement sites on the University campus were representative of the regional distribution of urban background PM on a scale of a few tens of kilometers.

2.2.3. Birmingham A38 Bristol Road (Roadside). Sampling of roadside PM was conducted beside the A38 Bristol Road, one of the major arteries of radial traffic in Birmingham, on workdays between July 8, 2002, and July 12, 2002. During our campaign, the traffic volume was counted in real time and amounted to 22 000 vehicles per day. Manual categorization led to the conclusion that 7% of vehicles were heavy-duty trucks and buses, both overwhelmingly powered by diesel engines. The high-volume PM sampler was situated on an elevated balustrade, ca. 4 m above street level, and ca. 4 m horizontally distant from the city-center-bound traffic lane. During peak hours, vehicles queued immediately in front of the measurement location because of traffic lights nearby. Tall trees on both sides along the road prevent effective ventilation, so that pollution from the street may accumulate in this canyon. The sampling strategy involved taking four daytime samples, each between 0800 and 1800 h local time, to expose the sampler to a maximum of vehicular emissions. A fifth sample was accumulated over four consecutive nights, between 2100 and 0500 h each, as a contrast for the nighttime with reduced traffic intensity.

2.2.4. Queensway Underpass (Road Tunnel). Road tunnel PM measurements were carried out in the Queensway underpass, part of the A38 national road that passes underneath the city center of Birmingham in two separate tubes. The PM sampler stood in a service bay of the eastern tube (southbound traffic), approximately 30 m from the tunnel exit. The tunnel was ventilated only naturally. Three consecutive samples were taken on July 2, 2002, each over approximately 4 h. Traffic was free-flowing most of the time, at speeds between 50 and 80 km/h.

2.3. Particle Extraction. Besides obtaining a concentration for the total particulate metal content, differentiating between the water-soluble (bioavailable) and insoluble metal fraction was a prime goal of this study. Sophisticated speciation schemes have been developed to characterize up to four different degrees of metal solubility by utilizing solvents of varying acid strengths (9). In this work, leaching procedures concentrated on a strong (acid) extraction procedure approximating the total metal content and a weak (aqueous) extraction procedure simulating particle dissolution close to neutral pH, such as in the human lung.

2.3.1. Strong Extraction Procedure (Acid). As a strong extraction, we applied the procedure of Harper et al. (25), which is optimized in leaching a maximum of PM sample material. Importantly, the method extracts all metals except those bound within silicates (25). Practically, exposed filter sections of 10 cm² in area were digested for 60 min in 2 mL inverse aqua regia (18.9% v/v analytical reagent grade HCl, 6.6% v/v analytical reagent grade HNO_3, 74.5% v/v distilled and deionized (DD) water) at 100 °C using sonication. High-density polypropylene vials with tight closures were used to prevent the loss of volatile species such as Hg. The vials were mechanically agitated for at least 2 h, allowed to stand overnight, and subsequently diluted with DD water to produce a solution of ca. 2% acid content.

2.3.2. Weak Extraction Procedure (Water). Sections of filter material equalling those used for the strong extraction were humidified inside polyethylene vials with propan-2-ol. Slightly different quantities were used for the back-up filter sections (0.5 mL) and impaction substrate sections (0.3 mL) corresponding to different areas of filter material. We found the prehumidification essential because propan-2-ol thoroughly soaks all filter layers and enables water to access all leachable PM material. Afterward, the vials were filled with 10 mL of DD water, mechanically agitated for 20 min, and allowed to settle overnight. Any insoluble PM fragments were then removed from the solution by filtering through Acrodisc membrane filters (Millipore). The solutions were finally acidified to 0.5% v/v with HNO_3 to prevent losses of metal ions during storage prior to inductively coupled plasma mass spectrometry (ICP-MS) analysis. DD water was our solvent of choice, because it corresponds to the solvent to be used in a toxicological study employing sample material from this work and because of the considerable difficulty in defining an alternative solvent that might correspond more closely to human lung fluid (25, 26).

2.4. Analytical Techniques.

2.4.1. Inductively Coupled Plasma Mass Spectrometry. The concentrations of Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Se, Ag, Cd, Sn, Ba, Pt, Hg, and Pb in solution were determined by inductively coupled plasma mass spectrometry (PlasmaQuad 2+ STE) in scanning mode, with ion lenses tuned for maximum sensitivity at [115]In. Calibration standards were prepared by dilution of certified multielement standards (Spex). Analytical drifts of the instrument were monitored using a 10 ppb standard solution at regular intervals. ICP-MS analysis was performed for both the strong acid and the aqueous PM extracts. The analysis of further elements including Cr, Mg, and Ca was attempted but yielded unsatisfactory results due to spectral interference from Ar,

TABLE 1. Concentrations of Metals, Cations, and Anions (ng m^{-3}) in Birmingham Background Air (Average of Nine Samples), in Order of Elemental Abundance in PM (<7.2 μm)

	PM (< 0.5 µm)		PM (0.5-0.95 µm)		PM (0.95-1.5 µm)		PM (1.5-3.0 µm)		PM (3.0-7.2 µm)		Total (PM7.2)	LLD (ICP-MS) (acid extract)	LLD (ICP-MS) (aq. extract)	LLD (IC) (aq. extract)
	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ			
Fe	11.	10.	6.2	4.2	13.	4.8	28.	13.	28.	16.	85.	0.91	0.10	-
Al	7.3	7.0	15.	35.	8.1	11.	8.7	4.7	13.	6.4	53.	0.27	0.067	-
Zn	14.	9.8	6.3	7.1	5.2	5.6	4.2	4.0	3.6	3.6	33.	0.091	0.23	-
Cu	5.8	11.	0.60	0.63	0.82	0.56	1.6	0.84	1.3	0.74	10.	0.024	0.024	-
Pb	5.4	5.7	1.8	1.6	0.82	0.67	0.82	0.86	0.75	0.65	9.6	0.47	0.053	-
Ba	0.32	0.15	0.32	0.16	0.75	0.29	1.4	0.72	1.3	0.74	4.1	0.028	0.013	-
Mn	1.4	1.1	0.63	0.61	0.44	0.21	0.77	0.41	0.85	0.46	4.0	0.017	0.023	-
Sn	1.3	1.1	0.20	0.14	0.17	0.14	0.13	0.12	0.16	0.14	1.9	0.45	0.011	-
Ti	0.23	0.24	0.18	0.14	0.16	0.14	0.31	0.24	0.43	0.28	1.3	0.13	0.074	-
Hg	1.0	2.3	0.008	0.005	0.006	0.006	0.007	0.006	0.007	0.005	1.1	0.013	0.010	-
Ni	0.63	1.0	0.051	0.038	0.059	0.048	0.10	0.26	0.083	0.100	0.93	0.0074	0.030	-
Se	0.44	0.33	0.012	0.011	0.013	0.017	0.22	0.21	0.017	0.027	0.70	0.62	0.28	-
Cd	0.15	0.15	0.025	0.028	0.015	0.010	0.011	0.008	0.013	0.010	0.21	0.005	0.0068	-
Co	0.036	0.022	0.005	0.004	0.006	0.004	0.017	0.009	0.020	0.012	0.084	0.0008	0.0015	-
Ag	0.029	0.041	0.011	0.015	0.006	0.007	0.010	0.008	0.010	0.012	0.066	0.0017	0.0005	-
Pt	0.018	0.018	0.002	0.002	0.002	0.003	0.003	0.003	0.002	0.004	0.027	0.0019	0.0019	-
NH_4^+	670.	450.	280.	260.	190.	200.	92.	87.	58.	82.	2400.	-	-	0.84
Na^+	34.	29.	36.	25.	94.	60.	150.	71.	150.	86.	470.	-	-	1.7
Ca^{2+}	17.	18.	9.0	6.6	19.	11.	42.	23.	71.	36.	160.	-	-	4.3
K^+	33.	10.	10.	6.4	7.1	3.0	9.8	2.0	11.	4.3	71.	-	-	0.8
Mg^{2+}	3.2	2.1	5.1	2.6	12.	6.3	20.	8.0	21.	11.	61.	-	-	0.17
NO_3^-	980.	1300.	660.	680.	500.	420.	380.	240.	310.	260.	5700.	-	-	18.
SO_4^{2-}	1100.	570.	500.	340.	210.	200.	110.	54.	95.	47.	2100.	-	-	0.068
Cl^-	26.	34.	29.	31.	88.	86.	150.	110.	7.1	8.4	300.	-	-	0.23
Oxalate	37.	22.	15.	6.8	11.	3.3	9.0	3.5	2.9	2.3	75.	-	-	0.097
HPO_4^{2-}	15.	9.1	4.0	3.0	3.1	2.0	4.3	3.5	29.	17.	55.	-	-	0.30

[a] Metal concentrations refer to ICP-MS analysis of acid extracts; ion concentrations refer to ion chromatography analysis of aqueous extracts. Lower limits of detection (LLDs) are added for illustration, each being representative for a volume of 2800 m³ of sampled air, which corresponds to the average sample duration of 61 h for the nine samples summarized in this table

the plasma gas, and probably Cl, which is part of the strong extraction solvent. Because of the large number of samples available, ICP-MS analysis had to concentrate on a representative subset. Out of a total of 33 samples from all sites that were analyzed in the PM (<0.5 μm) and PM (1.5−3.0 μm) fractions, nine samples from urban background air and one from each of the other sites were selected for a complete analysis in all five size fractions. The lower limit of detection (LLD) of the ICP-MS analysis was calculated as 3σ of the elemental concentrations measured in the leachates of six procedural blanks. As the mass of ambient PM sampled on a filter depends on the sampled volume of air, the LLDs in units of ambient concentration vary with sampling duration. LLDs are displayed for each element and extraction procedure in Table 1, representative for a 61 h sampling period, which is the average sampling duration of the nine urban background samples analyzed in detail. Longer or shorter sampling times improve or decrease these LLDs proportionally.

2.4.2. Ion Chromatography. The concentrations of sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), ammonium (NH_4^+), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), oxalate (($C_2O_4)^{2-}$), and phosphate (PO_4^{3-}) ions in aqueous solution were determined by ion chromatography. We used a Dionex model DX100 ion chromatograph fitted with CS12A and CG12A analytical and guard columns and a self-regenerating suppressor system. The size of the sampling loop was approximately 15 μL. Isocratic elution was achieved using 30 mN sulfuric acid eluent at a flow rate of 1.0 mL min^{-1}. Stock calibration standards (1000 ppm) were prepared on a monthly basis in DD water and diluted to working concentrations (0.01−10 ppm) on the day of use. Any drift in the response of the instrument was monitored by analyzing a 1 ppm standard at regular intervals throughout the analytical run. The LLDs for this procedure are shown in Table 1, representative of a 61 h sampling period.
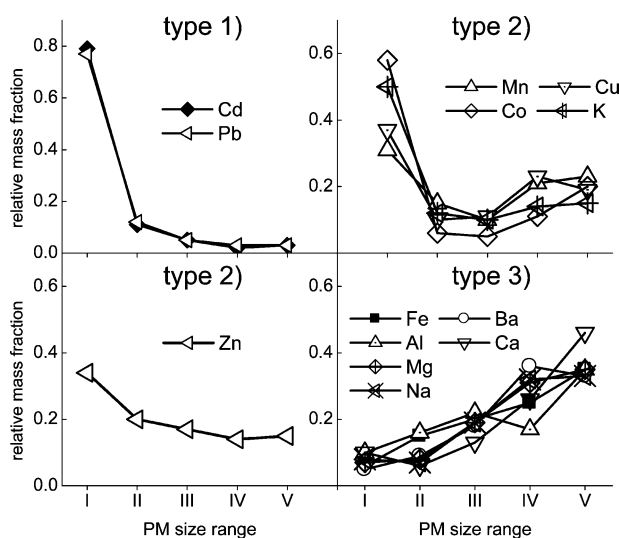
3. Results

3.1. Mass Size Distributions. The levels of $PM_{7.2}$ mass concentrations, determined here as the sum of the masses

in all stages, varied greatly between the four measurement sites, between 8 μg m^{-3} at the Irish west coast (remote background) and 72 μg m^{-3} in the Queensway road tunnel (Figure 1a). The increments in urban background and roadside PM concentrations compared to remote background conditions derive overwhelmingly from additional fine PM in the smallest size fraction (<0.5 μm). The concentrations of coarse particles, however, were higher at the Irish west coast by 80% (size fraction 1.5−3.0 μm) compared to the urban environment; this is overwhelmingly the contribution of sea spray particles in maritime air, as shown by the enrichments of Na^+, Mg^{2+}, and K^+ described below. In the road tunnel, fine PM concentrations (<0.5 μm) were enhanced by a factor of 7.5, PM (1.5−3.0 μm) by a factor of 5.3, and PM (3.0−7.2 μm) by a factor of 2.6 compared to average urban background levels. This additional material is expected to originate from direct vehicular emissions as well as traffic-induced resuspension.

From a climatological point of view, PM concentrations in England are lower than those in continental regions owing to the prevalence of clean Atlantic air masses. Nevertheless, PM concentrations were observed to peak during certain meteorological periods, as can be seen in Figure 1b. A meteorological analysis involving synoptic charts and back-trajectories showed that the highest fine PM (<0.5 μm) concentration occurred during stable, anticyclonic atmospheric conditions related to high-pressure influence. Apart from two significant events of long-range transport from continental Europe (May 7 and September 30), peak concentrations of fine PM were generated mostly in slowly moving, stable air masses over Britain itself (April 23 and 24 and September 21). As shown further below, these peak concentrations in fine PM (<0.5 μm) were associated with Ca^{2+}, Fe, and Ba. In coarse PM (1.5−3.0 μm) a single peak value at the remote background station could be explained by a lengthy wet and foggy weather period, consistent with the liquid-phase production of PM in fog droplets. At the urban background site, a peak in coarse PM occurred after a dry period of several days and high wind speeds from the north. Interestingly, observed enrichments of Na^+ and Mg^{2+}
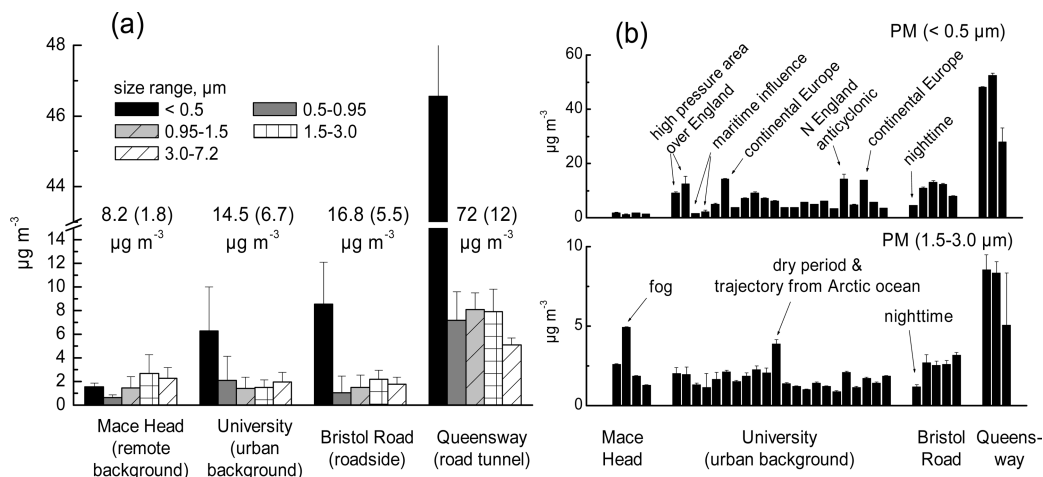
FIGURE 1. (a) Average atmospheric PM concentrations at the four measurement stations. Numbers above the bar plots indicate PM$_{7.2}$ concentrations. Whiskers refer to the standard deviations of all observations. (b) Variations of PM concentration with marked meteorological incidents. Whiskers refer to the combined uncertainties of the gravimetric and impactor flow measurements.

FIGURE 2. Normalized mass distributions of particle-bound metals in Birmingham background air ($n = 9$). PM size ranges are (μm): I ($<$0.5), II (0.5−0.95), III (0.95−1.5), IV (1.5−3.0), V (3.0−7.2).

suggest this peak concentration to be the result of a conservative transport of sea spray over long distances in a nonprecipitating air mass. Another visible effect was the ratio of approximately 1:2 in roadside PM concentrations between night and day, suggesting that the local contribution of traffic near the busy road was of the same magnitude as the prevailing urban background.

3.2. Metal Concentrations.

3.2.1. Metal Size Distributions in Urban Background Air. Table 1 shows averages of the size-fractionated metal and ion concentrations in urban background PM ($n = 9$), sorted groupwise and according to their abundance in PM$_{7.2}$, which was calculated as the sum of all impactor stages. ICP-MS results of the strong acid extracts are shown, except for ions, which were determined by ion chromatography. If a concentration was below the LLD, then half of that value was used in the calculation of averages. The most abundant transition metals in the fine PM fraction ($<$0.5 μm) were Zn, Al, Fe, and Cu. Conversely, the concentrations of Ti, Se, and Sn were near the LLD in most of these samples. Figure 2 displays normalized mass size distributions, thereby illustrating the PM size ranges into which individual metals tended to partition. Essentially three types of behavior were recognized: (1) metals that had their greatest mass portion

in the fine PM range ($<$0.5 μm), Cd and Pb, (2) metals that showed significant concentrations in both the fine and the coarse PM size range, K$^+$, Co, Cu, Zn, and Mn, (3) metals that occurred predominantly in the coarse mode, Na$^+$, Mg^{2+}, Ca^{2+}, Al, Ba, and Fe. This observation reflects the dominating sources of particulate metals in the Birmingham area, namely, combustion in the case of fine PM and mechanical generation in the case of coarse PM. Cd and Pb show the characteristic size distribution of PM emitted from high-temperature combustion sources such as waste incinerators (3) and metallurgical industries, both present in the Birmingham area. A number of species, including Zn, Co, Cu, K$^+$, and Mn, were observed to be spread over all size ranges and therefore need to originate from several source mechanisms. The structure of the metal size distributions determined in this work is consistent with previous observations at rural sites in the Birmingham area (16) and urban aerosol in Helsinki, Finland (28).

Hg was the species that appeared the be the most difficult to measure in this work. The reasons for this are probably both its volatility, and therefore uneven distribution in the environment, and an increased risk of contamination during sample handling. Due to the short sampling durations of only 4 h, our procedure appeared insufficient to quantify Hg in the road tunnel, so these samples were removed from the data set.

3.2.2. Comparison of Na$^+$, K$^+$, Mg^{2+}, and Ca^{2+} between All Measurement Sites. Figure 3 shows the normalized mass size distributions of Na$^+$, K$^+$, Mg^{2+}, and Ca^{2+} obtained from ion chromatography at the four different measurement sites. At the remote background station Mace Head, the size distributions of all four elements agree extremely well, suggesting oceanic sea spray as the single dominating source. The relative mass fraction of submicrometer PM amounts to less than 10%, illustrating that this source generates overwhelmingly coarse PM. In urban air, the size distribution structure is very different; increasing anthropogenic (i.e., traffic) input generally correlates with fine PM ($<$0.5 μm), whereas the relative fraction of the coarsest PM (3.0−7.2 μm) decreases. The latter aspect is consistent with a deposition of a major proportion of the coarsest sea spray particles during transport across the U. K. to Birmingham (on the order of 100−200 km). Smaller sea spray particles ($<$3.0 μm) are subject to deposition by sedimentation to a lesser extent and can contribute to Na$^+$ and Mg^{2+} (and, to a lesser extent, Ca^{2+}) in Birmingham background PM. For potassium, a dominating mode appears in the fine PM fraction, except at Mace Head. The absence of enrichment at the roadside or
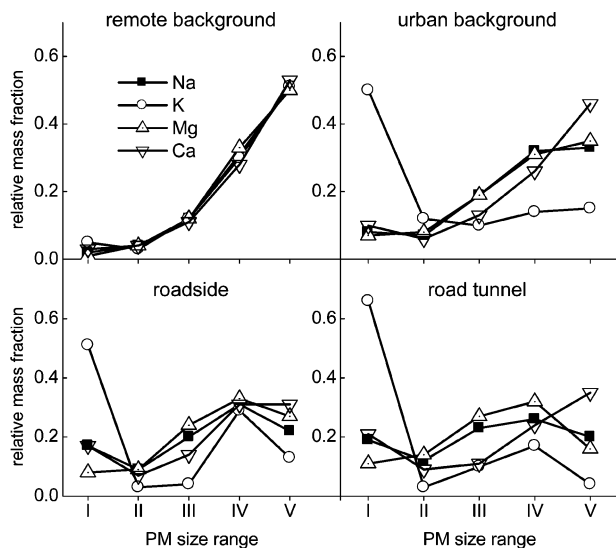
FIGURE 3. Comparison of the normalized mass distributions of Na^+, K^+, Mg^{2+}, and Ca^{2+} between four measurement sites. PM size ranges are (μm): **I** (<0.5), **II** (0.5–0.95), **III** (0.95–1.5), **IV** (1.5–3.0), **V** (3.0–7.2).

in the road tunnel suggest that this is not traffic-related. Another feature in urban PM is the calcium peak concentration in the coarsest PM fraction (3.0–7.2 μm). Our conclusion is that this coarse PM Ca^{2+}, together with Al, is the best indicator of resuspended mineral dust in the Birmingham atmosphere.

3.2.3. Comparison of All Metals between All Measurement Sites. The concentrations of all species are now compared for all four measurement sites. Since not all size fractions could be analyzed by ICP-MS, the following discussion concentrates on the size fractions PM (<0.5 μm) and PM (1.5–3.0 μm) as representative of fine and coarse PM fractions, respectively. Only the major findings are presented in the following discussion; the full table including all elemental concentrations can be found in the Supporting Information (Table S1).

3.2.4. Fine PM (<0.5 μm). None of the 26 species except Ni occurs at Mace Head at higher concentrations in fine PM than in Birmingham urban background air, demonstrating the relative absence of trace metals but also inorganic ions in fine PM in the marine environment. This trend even holds for the seawater-specific species (Na^+, Mg^{2+}, and Cl^-) The species least abundant were Cd, Pb, Mn, Zn, Ba, K^+, and Cu, whose concentration ratios (remote background/urban background) were between 1% and 12%. When comparing roadside PM (daytime samples) to urban background PM, we found Ba, Fe, Na^+, Ca^{2+}, Cu, Al, Mg^{2+}, Mn, and phosphate (PO_4^{3-}) to be significantly increased, by factors between 14 and 1.5. For most of these species (Ba, Fe, Ca^{2+}, Cu, Al, Mg^{2+}, and PO_4^{3-}), this trend continues when road tunnel and urban background levels are compared, yielding ratios between 30 and 14. Especially, the latter figures suggest that the corresponding species are contained in fine PM vehicular emissions. If the contributions of resuspension and abrasive processes are regarded as negligible to the fine PM fraction, then the prime source would be vehicle exhaust. This hypothesis has been confirmed by the X-ray electron microscopic detection of Ba, Fe, Na, Ca, Al, Mg, and Mn in diesel exhaust particles (29).

In the search for source fingerprints and correlations between different elements, linear correlations between the concentrations of pairs of metals were examined. As the observations spanned the entire range between urban background, roadside, and road tunnel environments, all

concentrations were transformed into their logarithms before correlation analysis; this was considered appropriate for this combined data set where elemental concentrations varied by more than 1 order of magnitude. Table 2 displays the measure of determination (R^2) for these correlations, with values <0.2 being ignored and values >0.5 being highlighted by color coding. It can be seen that the best associations (0.67 < R^2 < 0.80) exist between Ba, Al, and Ca^{2+}, and weaker individual associations (R^2 > 0.5) between these elements, Fe, Mg^{2+}, and Na^+. This is the best fingerprint available in the data set for PM (<0.5 μm), and we hypothesize that it is representative of diesel exhaust emissions. Our earlier work showed increasing correlations of calcium with methylphenanthrenes with decreasing particle size (23), which was interpreted as due to a common source in diesel engine exhaust emissions. Other correlations associate Zn and Mn (R^2 = 0.74), another fuel combustion term, and $NH_4^+/NO_3^-/SO_4^{2-}$/oxalate (0.30 < R^2 < 0.66), which clearly represents PM formed through secondary formation. The potassium ion, which clearly has its peak concentration in fine mode PM (<0.5 μm), shows only weak correlations to other elements, suggesting that it originates from a wider range of anthropogenic sources in the Birmingham area, such as high-temperature combustion sources. Similar considerations apply to Cl^- and the heavy metals (Cd, Hg, and Pb).

3.2.5. Coarse PM (1.5–3.0 μm). For coarse PM, the situation is remarkably different: The sea-spray-derived Mg^{2+}, Na^+, K^+, and Cl^- occurred at higher concentrations in the marine environment than in the urban background atmosphere (cf. also Figure 2b), at ratios of 3.9, 2.6, 2.5, and 5.5, respectively. Significantly less abundant in marine coarse PM were Ba, Fe, Pb, Ag, Zn, Mn, Ti, Pt, and Co, showing only 1–16% of comparable urban background concentrations. Since these species are associated mainly with the soil as well as anthropogenic sources, our data demonstrate their rapid depletion in a marine environment within a matter of days. A comparison of roadside and urban background PM showed Ba, Cu, Fe, Mn, Co, Zn, and PO_4^{3-} to be increased by factors between 10 and 2 in the roadside environment. The enhancement of Al at the roadside was negligible (<10%), suggesting that Al may be a good representative for soil-derived dusts, which influence all open urban sites. This leads to a first conclusion that the excess Ba, Cu, Mn, Co, Zn, and PO_4^{3-} in roadside coarse PM does not originate from soil-derived road dust but rather from direct vehicular emissions. For Ba, Cu, Fe, Mn, Co, Pb, and PO_4^{3-}, this trend of increased concentration continues to the road tunnel site, with road tunnel/urban background ratios varying between 60 (Cu) and 12.

Table 3 shows the measure of determination (R^2) for pairwise linear correlations between the logarithms of elemental concentrations. Notably, several major clusters of correlating elements are evident in coarse PM. Large co-variations exist between Na^+, Mg^{2+}, and Cl^- (R^2 = 0.80–0.93), which represent the sea spray source. The simplistic assumption of zero sources of coarse PM Na^+ and Mg^{2+} over land suggests that a survival of 20% of the sea spray particles originally present in the marine planetary boundary layer would explain the Birmingham observations 100–200 km farther inland. Further associations include NH_4^+/NO_3^- (R^2 = 0.78), which represents secondary coarse PM, and a number of geogenic elements, including Ca^{2+}, Mn, Ba, Fe, Cu, Al, and Co (0.41 < R^2 < 0.98), which evidently represent several fractions of resuspended dust. The strongest association was found between the elements Fe, Cu, Ba, and Mn (0.89 < R^2 < 0.98), which represent vehicular metal emissions; the interpretation of this emission source is expanded further below.

3.2.6. Crustal Enrichment Factors. To assess geogenic contributions, crustal enrichment factors (CEFs) were cal-

TABLE 2. Correlation Matrix of Elemental Concentrations in 29 Samples of Urban Fine PM ($<0.5\ \mu$m)[a]

	Ba	Al	Ca^{2+}	Zn	Fe	PO$_4^{3-}$	Cu	Mn	Ox	NH$_4^+$	Mg^{2+}	Na$^+$	SO$_4^{2-}$	NO$_3^-$	Cl$^-$	Cd	Ag	Hg	Co	Sn	K$^+$
mass	0.64	0.52	0.51	0.49	0.45	0.43	0.43	0.34	0.26	0.24	0.20	0.20									
Ba		0.70	0.67	0.22	0.50	0.43	0.41	0.21		0.06	0.28	0.44				0.23					
Al			0.80	0.21	0.29	0.26	0.40	0.25		0.18	0.36	0.59		0.23							
Ca^{2+}					0.22	0.34	0.37		0.22	0.35	0.54	0.65		0.21		0.21					
Zn					0.38	0.34	0.52	0.74											0.24		
Fe						0.61	0.31	0.41													
PO$_4^{3-}$							0.54	0.32				0.21									
Cu								0.32													
Mn																			0.22		
Ox										0.59			0.38	0.30	0.28						
NH$_4^+$											0.52	0.20	0.57	0.66	0.23						
Mg^{2+}												0.42		0.37		0.24					
Na$^+$														0.27		0.39					
SO$_4^{2-}$																					
NO$_3^-$															0.33						
Cl$^-$																					
Cd																	0.37				0.26
Ag																					0.21
Hg																					
Co																					
Sn																					

| $R^2 \geq 0.9$ | $R^2 \geq 0.8$ | $R^2 \geq 0.7$ | $R^2 \geq 0.5$ | $R^2 \geq 0.2$ | Ox = Oxalate (C$_2$O$_4^{2-}$) |

[a] The table indicates the measure of determination (R^2) obtained from pairwise linear correlation of the logarithm of elemental concentrations. The species were sorted after their correlation to fine PM mass.

**TABLE 3. Correlation Matrix of Elemental Concentrations in 29 Samples of Urban Coarse PM ($1.5-3.0\ \mu$m)[a]**

	Ca^{2+}	Mn	Ba	Fe	Cu	Al	NO$_3^-$	Co	Ox	Mg^{2+}	SO$_4^{2-}$	PO$_4^{3-}$	Zn	Pb	NH$_4^+$	Na$^+$	Ti	Cl$^-$	Ag	K$^+$
mass	0.73	0.68	0.60	0.59	0.57	0.52	0.48	0.47	0.43	0.35	0.34	0.32	0.25	0.24	0.22	0.21				
Ca^{2+}		0.78	0.63	0.64	0.60	0.65	0.35	0.48	0.54	0.27		0.34	0.26	0.27						
Mn			0.89	0.92	0.87	0.66		0.80	0.59			0.45	0.41		0.54		0.27			
Ba				0.98	0.98	0.45		0.77	0.50			0.57	0.42		0.57					
Fe					0.97	0.51		0.83	0.50			0.52	0.41		0.61		0.25			0.21
Cu						0.41		0.78	0.51			0.60	0.43		0.59					0.23
Al								0.51	0.36	0.20		0.20		0.28			0.40			
NO$_3^-$								0.20		0.25	0.32				0.78					
Co									0.50			0.46	0.46		0.50		0.25			0.32
Ox											0.22	0.51	0.42	0.25						
Mg^{2+}																0.93		0.83		
SO$_4^{2-}$														0.44		0.20				
PO$_4^{3-}$													0.27							
Zn														0.48						
Pb																0.38				
NH$_4^+$																				
Na$^+$																		0.90		
Ti																				
Cl$^-$																				
Ag																				

| $R^2 \geq 0.9$ | $R^2 \geq 0.8$ | $R^2 \geq 0.7$ | $R^2 \geq 0.5$ | $R^2 \geq 0.2$ | Ox = Oxalate (C$_2$O$_4^{2-}$) |

[a] The table indicates the measure of determination (R^2) obtained from pairwise linear correlation of the logarithm of elemental concentrations. The species were sorted after their correlation to coarse PM mass.

culated for all elements by dividing their abundance in a PM sample by their average abundance in the upper continental crust (UCC). In this study we refer to the composition of the UCC as described by Taylor and McLennan (30). A common practice has evolved to take CEFs >10 as indicative of PM sources different from crustal material, notably anthropogenic sources. To assess source influences in relation to crustal sources, the calculation of CEFs may involve normalization to a reference element. Aluminum was chosen as a reference element for this study because its PM mass fraction was the most insensitive to transitions across the range of urban measurement sites. Since our extraction procedure was inefficient for Al in that it did not dissolve silicate minerals, we acknowledge that this may lead to an erroneous overestimation of the absolute values of the derived elemental CEFs. Crustal enrichment factors are displayed in Figure 4 for all elements, with all elements sorted in order of their CEF in urban background PM. CEFs are typically higher by 1 order of magnitude in fine PM than those in coarse PM because the crustal material, to which concentrations were normalized through the tracer Al, is systematically less abundant in fine PM. One group of metals was outstanding in that their CEFs were far above 100. These were Hg, Cd, Ag, Pb, Sn, Zn, Cu, and Ni in fine PM and Ag, Sn, Pb, Cu, Zn, and Ni in coarse PM. Conversely, the lowest CEFs point to the species abundant in minerals or seawater
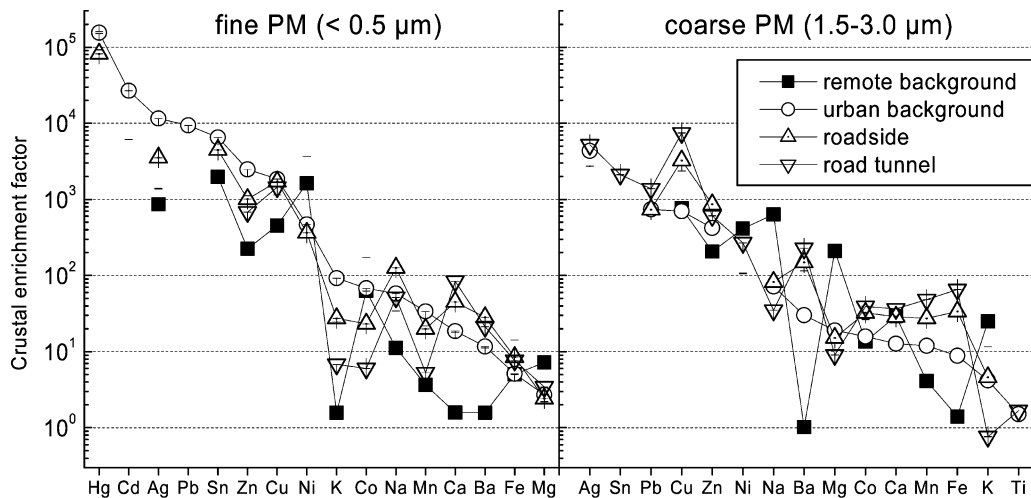
FIGURE 4. Crustal enrichment factors of individual metals in fine and coarse Birmingham background PM. Na, K, Mg, and Ca indicate the respective ion concentrations. The reference element is Al.
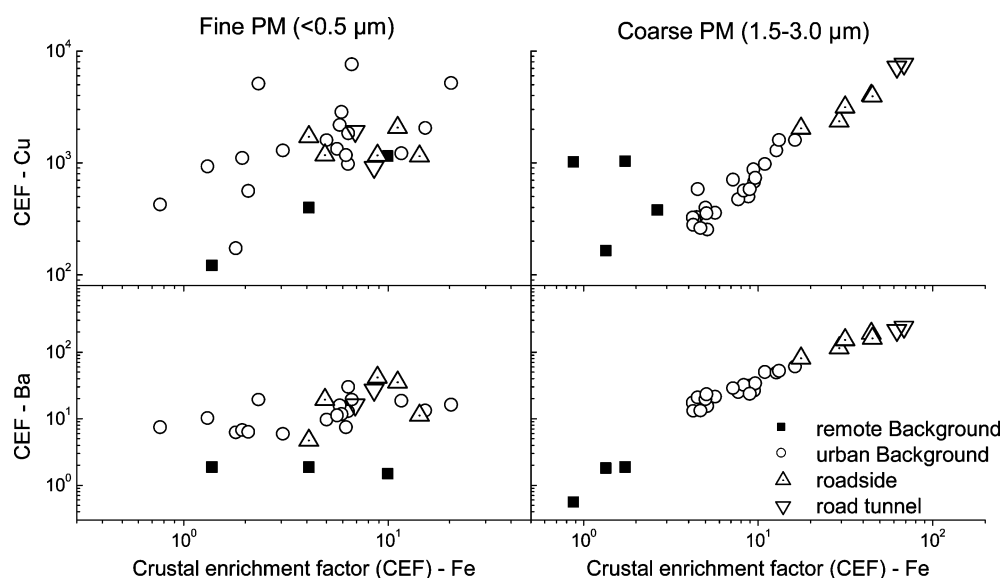
FIGURE 5. Correlation between the crustal enrichment factors of Fe, Ba, and Cu in fine and coarse PM using the reference element Al.

(Na^+, Mg^{2+}, Ca^{2+}, Mn, and Fe). Further features of the data set including complete size distributions of CEFs can be found in the Supporting Information, Figures S1a−c.

3.2.7. Abrasive Vehicular Emissions. Figure 5 highlights the contrast between the moderate correlations of Fe, Ba, and Cu in fine urban PM (<0.5 μm) but a close linear relationship in coarse PM (1.5−3.0 μm). The three metals were also highly correlated to Mn (cf. Table 2). It is interesting to realize that the linearity in coarse PM (1.5−3.0 μm) is observed across 2 orders of magnitude in elemental concentrations without noticeable gaps (Figure 5). Since higher CEFs indicate an increasing proximity to vehicular sources, we take this as clear evidence that Fe, Ba, Cu, and Mn originate overwhelmingly from a single, relatively uniform source in the urban atmosphere of Birmingham. The coarse size of the particles suggests a vehicular source emitting mechanically abraded (pulverized) particles, which can generally stem from tires, brakes, and even the vehicular chassis. Recently, it has been demonstrated that the debris of brake wear produced under dynamometer and real driving conditions consists of significant numbers of particles mostly in the size range between 1 and 10 μm (*31*). Therefore, attention is now directed toward the generation and properties of brake wear debris.

The currently used types of brake pads (synonym "brake lining") fall into the categories "metallic" (consisting mainly of steel), "semimetallic" (consisting of similar proportions of steel and organic ingredients), "low steel" (containing even less steel), and "nonasbestos organics" (NAO, containing mainly organic ingredients) (*32, 33*). It is important to note that the share of these brake pad types differs in different countries around the globe. While the U. S. and Japanese vehicular fleets are mostly equipped with semimetallic and NAO brake pads, these are uncommon in Europe. In European countries, the prevailing type of brake linings is low steel (also dubbed "corrective liners"), which has been developed to meet the higher performance requirements for friction materials as the result of the lack of a general speed limit in most European countries. Particularly, corrective liners contain higher amounts of lubricating and stabilizing ingredients to enhance the friction values of the brake pads (*32*), simultaneously maintaining thermal and mechanical stability during the braking process at high speeds. A central ingredient to improve thermal conductivity and mechanical stability is copper. The handbook of brakes (*32*) suggests the following mass composition, being representative for a European mixture of low steel brake pad material during the past 10 years: steel (~20%), copper (~16%), Al_2O_3 (~1%),

Fe_2O_3 (~10%), ZnS (~6%), barytes ($BaSO_4$, ~10%), and more lubricating and binding materials, mostly organic. NAO brake pads, the second most important type according to the European market share, are reported to contain even higher mass fractions of copper (~22%) and barytes (~16%). Former brake pad mixtures have also included notable fractions of antimony trisulfide (Sb_2S_3) as a lubricant, but this ingredient tends to be less utilized by the industry as a result of the presumed carcinogenicity of antimony trisulfide (*34*).

As a conclusion, the list of the ingredients contained in European brake pads, notably metallic copper, steel, iron oxide, and barytes, in conjunction with the picture of the release of debris particles $>1\ \mu$m into the urban atmosphere is highly consistent with the observed correlations between Cu, Ba, and Fe in our Birmingham data set. The concentrations of a selection of metals in low steel brake pads correspond to crustal enrichment factors of of 6400 (Cu), 100 (Ba), 2 (Fe), 570 (Zn), and 0.07 (Al).

For the case of copper, we estimated the contribution of the brake debris source by assuming a two-component mixing of only the soil (accounting for the urban "baseline" level) and the vehicular component. Assuming copper to be contained to 16% in the abrasive source, a source contribution of 0.6% to ambient PM mass ($1.5-3.0\ \mu$m) would explain the observations at the urban background site. At the roadside, the calculated contributions are 1.8%, and in the road tunnel 7%. The relative uncertainty of these derived source contributions is about 20%. As a result, approximately 97% of the copper detected in Birmingham background air would be explained by this source, ca. 99.2% at the roadside, and ca. 99.8% in the road tunnel. These calculations were also performed for the upper coarse mode and yielded similar contributions of the brake wear source to PM mass ($3.0-7.2\ \mu$m) of 0.4% (urban background), 3.2% (roadside), and 7% (road tunnel). Another calculation for the intermodal size range indicated a decreasing importance of the brake wear source with decreasing particle size, yielding contributions to PM mass ($0.95-1.5\ \mu$m) of 0.3% (urban background), 2% (roadside), and 3% (road tunnel). Instead of Cu, Ba was also used in the calculations and yielded a very similar behavior, thus supporting the validity of the two-component assumption.

Our overall results are largely comparable to those of an atmospheric study in Cologne, Germany, where brake linings were estimated to account for up to 90% of the copper in urban PM (*35*). Brake wear dust is partially inhalable ($1-10\ \mu$m) and therefore represents a public health concern, especially in countries where copper is a relevant component in the brake pad material used. On one hand, some may argue that copper is a metal that is widespread in our environment (e.g., coins and building construction). On the other hand, it is known that copper may cause inflammation in the human lung through the Fenton reaction if it is soluble (*4*). As it may be important in which chemical form and through which pathway the copper enters the human body, more research is probably needed to investigate possible effects of inhaled copper-containing PM such as in the case of brake wear debris.

3.2.8. Decoupling between Coarse Mode Fe and Ca^{2+}. As already mentioned above, the correlation of enrichment factors of Fe and Ba in the coarse ($1.5-3.0\ \mu$m) fraction is remarkable (Figure 5). The gradient in concentrations of coarse fraction Fe between the remote background and the road tunnel samples (ratio = 1100) is also very large. This far exceeds the ratio for Al (22) or Ca (8.6) but is lower than that for Ba (4800). The ratios for Fe between daytime and nighttime roadside concentrations (2.5) and between daytime roadside and urban background (5.1) far exceed those for Ca^{2+} (1.1 and 1.5, respectively). The two species Fe and Ca^{2+}, often thought of as having a common source in soil, are therefore
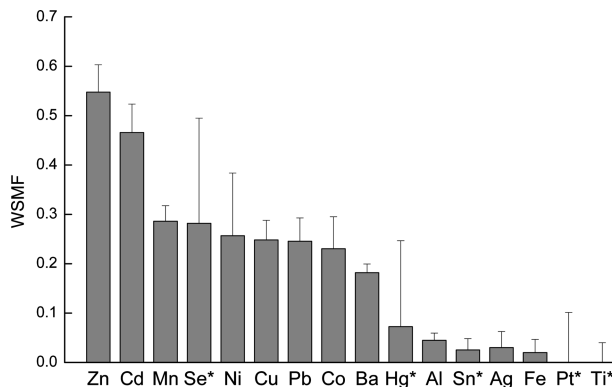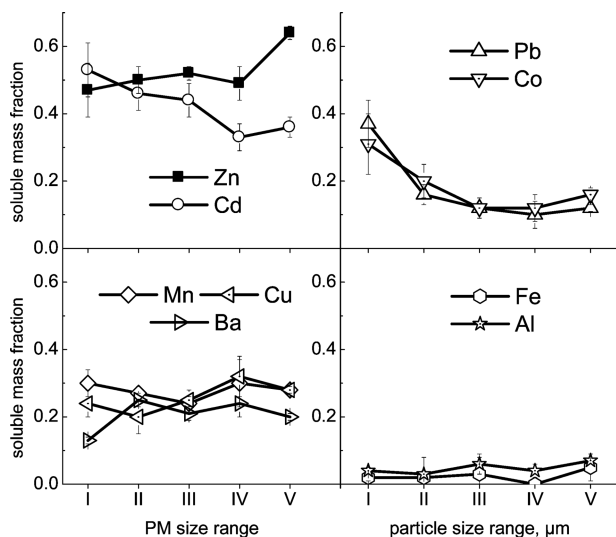

FIGURE 6. Water-soluble mass fraction (WSMF) of metals in Birmingham background PM. Values indicate the average of nine samples for PM$_{7.2}$. The asterisk indicates that data were not available for all size fractions.

strongly decoupled. This finding provides additional support for the concept suggested by Harrison et al. (*33*) of using coarse Ca^{2+}, on one hand, as a tracer of particles from soil, i.e., construction, demolition, and other resuspension processes, and coarse Fe, on the other hand, as a tracer of vehicle-generated particles. It still remains obscure, however, as to how much of the Fe-related particles arise from vehicle-induced resuspension and how much from direct emission of abrasion products. It is however clear both from these results and from those of Harrison et al. (*36*, *37*) that in the U. K. urban environment resuspension of soil particles from roads is a relatively minor contributor to coarse particle mass at the roadside.

3.3. Water Solubility of Individual Metals. Only the soluble fraction of particle-bound metals is likely to become bioavailable and therefore harmful to humans. It is a practical challenge to determine the soluble fraction of PM in a defined manner, since the solubility depends sensitively on the speciation method (*24*). In this work, the water-soluble PM fraction was determined by employing two different extraction procedures, a weak and a strong extraction (cf. section 2.3). The water-soluble fraction was subsequently defined as the quotient between the mass concentrations obtained for the weak and strong extraction procedures.

In Birmingham background PM, the water solubilities of individual metals were found to differ significantly (Figure 6). Most soluble were Zn and Cd; the least soluble were Al, Sn, Ag, Fe, Pt, and Ti. In Figure 7, these results are additionally presented as a function of particle size as long as enough concentration data above the LLD was available. Three groups of metals could be identified, showing high (~50%; Zn, Cd), medium (10−40%; Mn, Cu, Ba, Pb, and Co), or low (<10%) water solubility. For some species (Pb, Co, and Cd), a significant size-dependent trend was found, involving higher solubilities in the fine size range (<0.5 μm), whereas others (Zn and Ba) showed an opposite trend. The observed differences in water solubility with particle size are indicative of the respective elements being present in a different chemical speciation. Since Pb, Co, and Cd originate from high-temperature combustion sources, it is suggested that these sources emit a higher fraction of water-soluble PM. A comparison between the water solubilities determined for fine PM (<0.5 μm) in this work and a previous study on PM$_{0.6}$ at various urban locations in Sevilla, Spain, by Fernandez-Espinosa et al. (*24*) is shown in Figure 8. It can be seen that particularly for the elements Fe, Ti, Cu, Mn, Co, and Ni both studies are in agreement within a mass fraction range of ±0.1. Deviations between the two studies, however, occurred for the elements Pb and Cd, which were found to be significantly more soluble in Birmingham PM compared to

FIGURE 7. Variation of the water solubility of metals with particle size and element in Birmingham background air. PM size ranges are (μm): I (<0.5), II (0.5−0.95), III (0.95−1.5), IV (1.5−3.0), V (3.0−7.2).
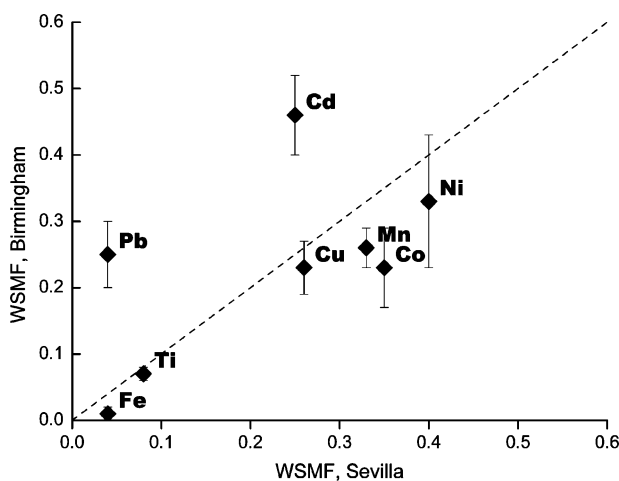
FIGURE 8. Comparison of the water-soluble mass fractions (WSMFs) determined for PM$_{0.6}$ at Sevilla (Fernández-Espinosa et al., ref *24*) and for PM$_{0.5}$ at Birmingham (this work).

Sevilla PM. The analytical methods used in our work and in ref *24* are equivalent, so we anticipate this to be a real difference in the chemical state of the metals found in Birmingham and Sevilla. As this relates to two elements overwhelmingly derived from high-temperature combustion and metallurgy (Pb and Cd), we speculate that process-related technological differences between the emission sources in the two regions could be an explanation. In any case, the results imply that the inhalation of equal masses of Pb and Cd would lead to a higher bioavailable dose in Birmingham than that in Sevilla. Comparisons were also made to the recent works of Janssen et al. (*38*) and Graney et al. (*27*), who studied the water solubility of metals in urban background PM$_{2.5}$ in Arnhem, The Netherlands, and in indoor PM$_{2.5}$ in Cincinnati, OH, respectively. Interestingly, both studies found considerably higher fractions of soluble metals. Jannsen determined soluble fractions of Mn (91%), Fe (68%), Cu (80%), and Zn (83%). Given the aforementioned qualitative agreement in solubilities between the Birmingham and Sevilla studies, we suspect that the differences with the data of to Janssen et al. result from their approach in using a weak acid solution (0.045 N HF + 0.01 N HCl) for the weak extraction. Since weak acids may liberate metals in a range of chemical states,

such as carbonates, oxides, and metals bound to organic matter (*24*), it is explicable that the Birmingham and Arnhem extraction methods do not generate comparable results. Since relatively low solvent acidities, such as present in the lung fluid, appear to liberate a range of particle-bound metals, it will be a challenge to establish analytical procedures simulating size-selective extraction of PM constituents by the lung fluid.

Acknowledgments

Supporting Information Available

Overview of metal and ion concentrations in fine and coarse PM at the four different measurement sites and enrichment factors of individual metals versus UCC for nine urban background samples, a roadside sample, and a road tunnel sample. This material is available free of charge via the Internet at http://pubs.acs.org.

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