Physicochemical Characterization of Airborne Particulate Matter at a Mainline Underground Railway Station

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Ⓢ Supporting Information

ABSTRACT: Underground railway stations are known to have elevated particulate matter (PM) loads compared to ambient air. As these particles are derived from metal-rich sources and transition metals may pose a risk to health by virtue of their ability to catalyze generation of reactive oxygen species (ROS), their potential enrichment in underground environments is a source of concern. Compared to coarse (PM_{10}) and fine ($PM_{2.5}$) particulate fractions of underground railway airborne PM, little is known about the chemistry of the ultrafine ($PM_{0.1}$) fraction that may contribute significantly to particulate number and surface area concentrations. This study uses inductively coupled plasma mass spectrometry and ion chromatography to compare the elemental composition of size-fractionated underground PM with woodstove, roadwear generator, and road tunnel PM. Underground PM is notably rich in Fe, accounting for greater than 40% by mass of each fraction, and several other transition metals (Cu, Cr, Mn, and Zn) compared to PM from other sources. Importantly, ultrafine underground PM shows similar metal-rich concentrations as the coarse and fine fractions. Scanning electron microscopy revealed that a component of the coarse fraction of underground PM has a morphology indicative of generation by abrasion, absent for fine and ultrafine particulates, which may be derived from high-temperature processes. Furthermore, underground PM generated ROS in a concentration- and size-dependent manner. This study suggests that the potential health effects of exposure to the ultrafine fraction of underground PM warrant further investigation as a consequence of its greater surface area/volume ratio and high metal content.
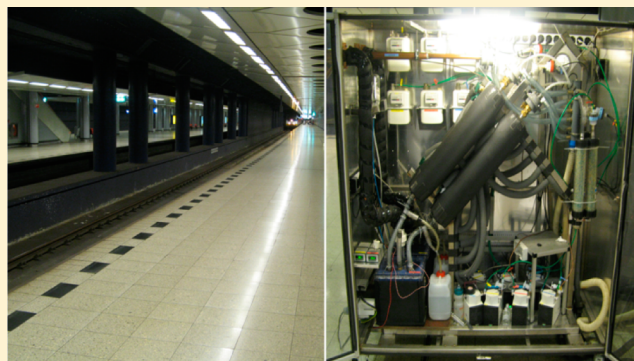
INTRODUCTION

Underground railway systems are widely used mass transit systems in many major cities, some carrying several million passengers per day.[1] High mass concentrations of respirable particulate matter (PM) with a mean aerodynamic diameter up to 10 μm (PM_{10}; coarse), 2.5 μm ($PM_{2.5}$; fine), or 0.1 μm ($PM_{0.1}$; ultrafine) have been observed in many underground railway systems.[2−4] In many cases, concentrations far exceed World Health Organization (WHO) recommended limits for 24 h average particle exposure of 50 and 25 μg/m^3 for PM_{10} and $PM_{2.5}$, respectively, presenting a potential risk for regular passengers and employees.[5] Notably, $PM_{0.1}$ levels are currently unregulated. Importantly, exposure to PM has been noted to be greater for underground journeys than for equivalent journeys

made by a variety of overground modes of transport,[6] and time spent in underground railways has been suggested to be a better predictor of metal exposure than duration of exposure to traffic-derived metal pollutants.[7]

There is evidence to suggest that underground railway PM has high concentrations of Fe and other transition metals compared to ambient PM.[8−10] Transition metals are of interest as potential airborne toxicants because of their ability to generate the reactive oxygen species (ROS) superoxide ($^\bullet O_2{}^-$),

hydrogen peroxide (H_2O_2) and, via the Fenton reaction, hydroxyl radical ($\bullet OH$) via successive single-electron reductions of molecular oxygen.[11] It is thought that many of the toxic effects of transition metals arise from oxidative stress due to ROS generation. Defined as an excess of oxidative species that outweighs the antioxidant capacity of a system, oxidative stress can result in oxidation and functional modification of biomolecules such as lipids, proteins, and nucleic acids and can result in inflammation and tissue injury.[12] However, transition metals, and also a variety of other metals and metalloids such as lead and arsenic, can exert toxic effects via mechanisms other than direct generation of ROS; hence, study of concentrations of non-transition metals in airborne PM is also warranted.

The composition of metal-rich PM from a wide variety of sources has previously been studied, including steel mills, smelting plants, and welding fume.[13−15] However, underground PM studies generally focus on coarse and fine fractions, without parallel analysis of ultrafine PM composition.[16] Although individual ultrafine particles have a lower surface area than fine or coarse particles (0.03 vs 19.6 and 314 μm^2, respectively, for particles of 0.1, 2.5, and 10 μm diameter, assuming perfect sphericity), ultrafine PM is often present in a much greater number concentration than coarse or fine PM, and thus, their contribution to overall PM surface area has the potential to be very important, possibly being a key determinant of toxicity.[17] Furthermore, coarse and fine particles tend to accumulate in the ciliated airways by impaction and are rapidly cleared by the mucociliary escalator, whereas ultrafine particles predominantly settle by diffusion in the alveoli, from where clearance is much slower.[18] Ultrafine particles, unlike fine particles, are also able to translocate from the airway lumen to the pulmonary interstitium and potentially the systemic circulation, being detected in the liver, heart, kidneys, and brain.[19,20]

Because there is evidence that underground PM is an important potential toxicant, the aim of this study is to determine the concentration of transition and nontransition metals in respirable, size-fractionated PM collected at an underground railway station and to compare this to PM collected from other process-specific sources, namely, a woodstove, a roadwear generator, a road tunnel, and diesel exhaust.

■ METHODS

Acquisition of PM. Airborne PM was collected using a versatile aerosol concentration and enrichment system (VACES), with aerodynamic diameter cutpoints of 10−2.5 μm (coarse; $PM_{10−2.5}$), 2.5 μm (fine/ultrafine with no lower cutpoint, hereafter referred to as "fine"; $PM_{2.5}$), and 0.18 μm (ultrafine; $PM_{0.18}$).[21,22] Air flow was 0.9 m^3/min. PM was collected as a suspension in ultrapure water from the following:

(1) A woodstove, a portion of the exhaust smoke being diluted with filtered air, fed into a sealed chamber containing the VACES unit that sampled airborne PM at a concentration of ≈250 $\mu g/m^3$.

(2) A roadwear simulator, consisting of a circular road surface on which four wheels with studded tires rotate. Prior to operation, the chamber was flushed with filtered air, and the PM concentration was allowed to build up to a steady state of ≈5000 $\mu g/m^3$.

(3) A busy railway station located under the main departures and arrivals terminal of a major European airport, near the middle of a 5.1 km long tunnel, with further details published previously.[23] The station is used by 60 000−150 000 people per day, with three platform islands, each housing two platforms ≈400 m long. 25−30 trains per hour pass through the station during operating hours, all powered by overhead catenary. During the night, there are occasional diesel-powered freight trains passing through the station. The station is cleaned regularly during daytime hours, principally using electrically powered ride-on machines to clean the floor of dirt and dust. There is no active air ventilation/conditioning system in operation, with air exchange driven solely by "piston action" of train movement. The VACES equipment was located halfway along the central island platform, ≈3 m away from the platform edge and ≈6 m from the centers of each pair of surrounding tracks, with air intakes ≈3 m above the track level and ≈4 m below the overhead catenaries. Sampling was performed for ≈9 h between 08:30 and 17:30 on each of the three sampling days, all of which were working weekdays in July 2010.

(4) A heavily trafficked road tunnel in The Netherlands. Sampling was performed in a parking area immediately adjacent to the tunnel exit, with sampling performed in midsummer.

In addition, diesel exhaust particulate (DEP) samples from a diesel generator and exposure chamber were analyzed to provide comparison as an expected metal-poor PM.

Particulate Metal Analysis. All analysis steps were performed in a clean laboratory (class 100) environment to minimize possible contamination. PM suspensions were vortexed and bath sonicated for 30 s each. A 100 μL aliquot of suspension was reserved for anion analysis, and the remaining volume was recorded and transferred to a Teflon pot. Suspensions were evaporated to dryness at 130 °C. Three overnight digestion steps were performed: respectively, 900 μL of concentrated nitric acid (15 M, Primar Plus grade; Fisher Scientific, Loughborough, UK) with 100 μL of concentrated hydrofluoric acid (27 M, UpA grade; Romil, Cambridge, UK) pressurized at 180 °C, 1 mL of 6 M hydrochloric acid (12 M, Primar Plus grade; Fisher) at 130 °C, and 1 mL of 2% nitric acid spiked with Be, In, and Re to monitor instrument drift. Evaporation at 130 °C was performed after each of the first two steps. Hydrochloric and nitric acids were sub-boiled prior to use. Immediately prior to analysis, additional 2% nitric acid was added to produce a final mass of ≈3 g per digest. Standards were prepared using a variety of commercially available standard solutions to assess a range of metals (Table S1, Supporting Information). Blanks were prepared by performing acid digests in the absence of the PM suspension, to monitor the contribution of any contamination during the digestion process. Samples, standards, and blanks were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermofisher XSeries2 inductively coupled plasma mass spectrometer (Thermofisher Scientific, Bremen, Germany) located in the Isotope Geochemistry Instrument Suite at NOCS, Southampton.

Anion Analysis by Ion Chromatography. Concentrations of the anions NO_3^-, SO_4^{2-}, and Cl^- in the particulate samples were determined by ion chromatography. A 100 μL aliquot of each particulate suspension was vortexed for 60 s and bath-sonicated for 60 min followed by centrifugation at 20 000g for 10 min, and the supernatant was retained. Supernatants
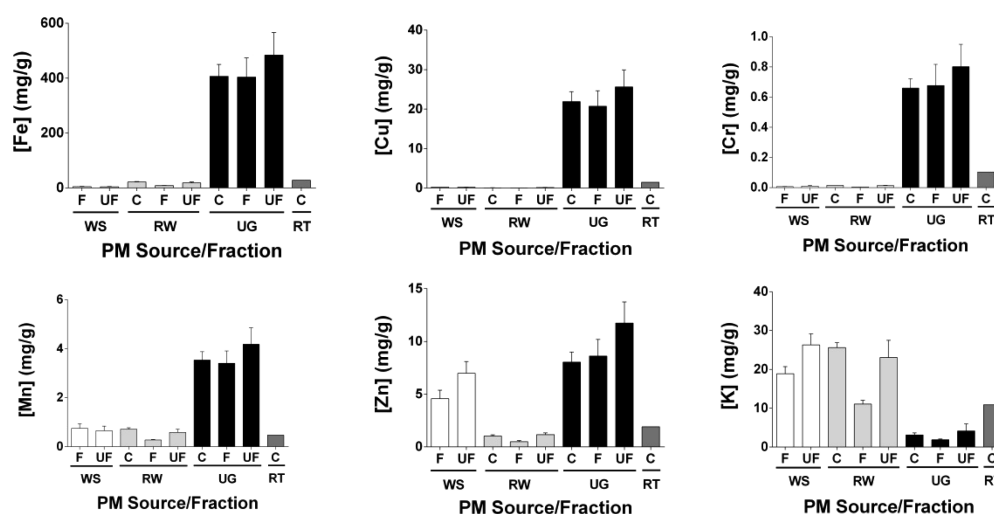
Figure 1. Concentrations of Fe, Cu, Cr, Mn, Zn, and K in PM of coarse (C), fine (F), and ultrafine (UF) fractions collected from a woodstove (WS), a roadwear generator (RW), an underground station (UG), and a road tunnel (RT). Values expressed as single values (RT) or mean ± 1 SE of two (WS, RW) or three (UG) individual samples.

were diluted in ultrapure water to a volume of ≈5 mL, before being analyzed on a Dionex ICS2500 ion chromatograph with Dionex Chromeleon software (Dionex, Sunnyvale, CA, USA). Standard solutions for NO_3^-, SO_4^{2-}, and Cl^- were prepared from serial dilutions of commercially available stock standards (Inorganic Ventures, Christiansburg, VA, USA), which were also used to monitor instrument drift.

Scanning Electron Microscopy. Underground particle suspensions were prepared for scanning electron microscopy (SEM) analysis by evaporating to dryness 100 μL of PM suspension on an aluminum stub at 50 °C overnight, followed by gold sputter coating (Hummer VI A sputter coater, Anatech, Alexandria, VA, USA) to a thickness of ≈20 nm. SEM was performed using a LEO 1450VP scanning electron microscope (Carl Zeiss Nano Technology Systems, Welwyn Garden City, UK) at 20 kV.

Measurement of ROS Generation. Primary bronchial epithelial cells (PBEC) were obtained from healthy donors by fibreoptic bronchoscopy as previously described.[24] Cells were seeded in collagen-coated 96-well plates at a density of 6000 cells per well and cultured until 80−90% confluent. Cells were then serum starved (1.5 μg/mL bovine serum albumin and 1X insulin/transferrin/sodium selenite solution (ITS) both from Sigma−Aldrich, Gillingham, UK) in bronchial epithelial basal medium (BEBM; Clonetics, San Diego, CA, USA) overnight. Cells were washed once with HBSS supplemented with Ca and Mg (HBSS$_{CaMg}$; Invitrogen, Carlsbad, CA, USA) before being loaded with 75 μL of 10 μM 2′7′-dichlorofluorescein diacetate (H_2DCF-DA; Sigma−Aldrich) at 37 °C, light excluded, for 30 min. Cells were then washed twice with HBSS$_{CaMg}$ before application of 75 μL of coarse, fine, or ultrafine underground PM in supplement-free BEBM at 6.3 or 12.5 μg/cm² (equivalent to 25 and 50 μg/mL, respectively). Controls comprised medium supplemented with phosphate-buffered saline to maintain osmolarity. DCF fluorescence was measured at 485 nm excitation and 530 nm emission 3 h postchallenge and calculated as the fold-change in fluorescence compared to the control.

RESULTS

Particulate Composition. Over the three sampling days at the station, the mean (±1 standard mean error (SE)) underground PM_{10} mass concentration was 287 ± 8 μg/m³, with coarse PM at 169 ± 6 μg/m³, fine at 75.3 ± 5.9 μg/m³, and ultrafine at 37.7 ± 4.5 μg/m³. Chemical analysis was carried out on underground PM as well as from the other three distinct sources and DEP. For woodstove, roadwear, and underground PM sampling, individual daily samples were analyzed separately. Road tunnel PM and DEP were analyzed in the coarse fraction only, as well-characterized references for comparison (Figure 1 and Figure S1, Supporting Information). Underground PM was the most transition-metal-rich PM, with Fe the most abundant element, comprising (mean ± 1 SE) 407 ± 43, 404 ± 70, and 484 ± 82 mg/g for coarse, fine, and ultrafine fractions, respectively. Thus, Fe comprises greater than 40% of the total mass of the PM (Figure 1). Conversely, while all other PM samples contained detectable levels of Fe, only coarse and ultrafine roadwear PM (21.5 ± 0.1 and 18.1 ± 3.5 mg/g) and road tunnel PM (27.7 mg/g) contained Fe levels greater than 1% of the total mass of the PM. Cu was also elevated in underground PM compared to PM from other sites, although the Cu concentration (21.9 ± 2.5, 20.7 ± 3.9, and 25.6 ± 4.3 mg/g for coarse, fine, and ultrafine fractions, respectively) was lower than that of Fe. As with Fe, these Cu levels were considerably higher than those seen in any other sampling locations, across all size fractions analyzed. Other transition metals that were present at high concentration in underground PM included Mn, Zr, Mo, and Sn. In addition, levels of V, Cr, Ni, Nb, and Hf were higher in underground PM than other sources, although they were found at lower absolute concentrations. Additionally, Ca was high in underground PM, particularly in the ultrafine fraction (54 ± 31 mg/g), and Mg, Ca, Zn, Ba, and Sb were also found to be elevated in underground PM, with relatively high levels of Ga and As also noted.

Woodstove PM showed a marked enrichment for K, while levels of B and Zn were similar to underground PM and in excess of levels in other PM types. Furthermore, Rb (144 ± 3.2 μg/g F, 192 ± 1.8 μg/g UF), Cd (40.4 ± 7.1 μg/g F, 58.0 ± 5.4 μg/g UF), and Pb (185 ± 43 μg/g F, 266 ± 37 μg/g UF) were

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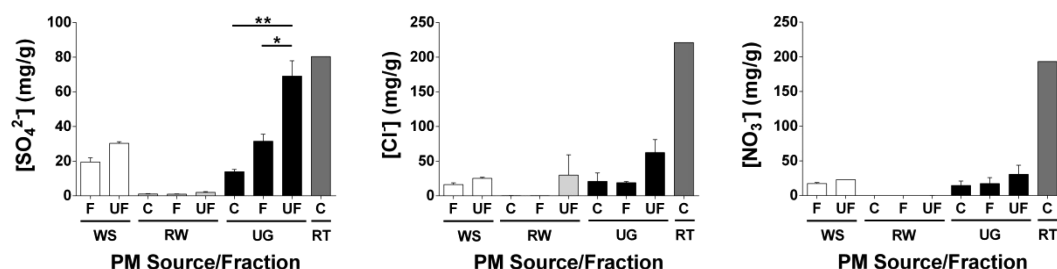dx.doi.org/10.1021/es304481m | Environ. Sci. Technol. 2013, 47, 3614−3622

Figure 2. Concentrations of SO_4^{2-} (left panel), Cl^- (center panel), and NO_3^- (right panel) in coarse (C), fine (F), and ultrafine (UF) fractions of PM collected from a woodstove (WS), a roadwear generator (RW), an underground station (UG), and a road tunnel (RT). Values expressed as single values (RT) or mean ± 1 SE of two (WS, RW) or three (UG) individual samples. (*) $p < 0.05$ and (**) $p < 0.01$, analyzed by one-way repeated measures ANOVA.
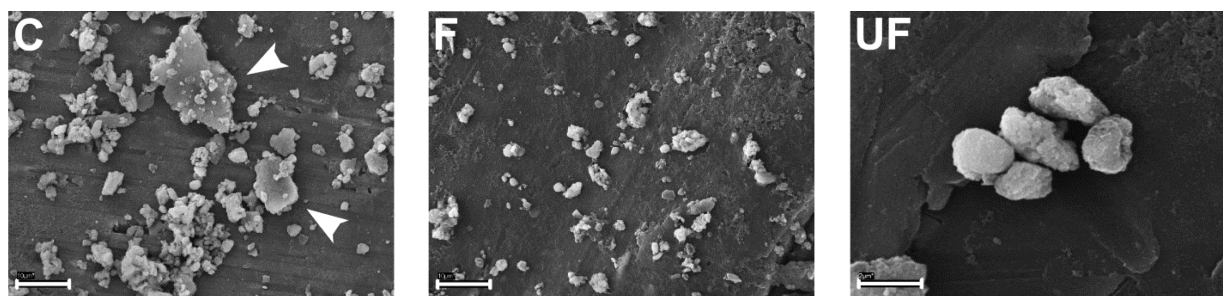

Figure 3. SEM micrographs showing morphology of coarse (C; ×5000), fine (F; ×5000), and ultrafine (UF; ×30 000) underground PM. Flakelike particulates in the coarse fraction are indicated by arrowheads. Scale bars represent 10 μm (C and F) or 2 μm (UF).

also relatively high in woodstove PM compared to other PM sources, although they were low in terms of absolute concentration. Roadwear PM possessed especially high concentrations of Al, with the three fractions showing concentrations of 71.0 ± 3.1, 27.3 ± 1.8, and 53.9 ± 7.2 mg/g, respectively. These concentrations were second only to underground PM Fe concentrations in terms of the most prevalent metals found at any site. Roadwear PM also contained notably high levels of Ti and to a lesser extent Sr, whereas levels of Sc, La, and Hg were found to be greater than other PM types, albeit at trace levels. Interestingly, roadwear PM showed generally lower metal concentrations in the fine fraction compared to the coarse and ultrafine fractions.

Road tunnel coarse PM showed relatively high levels of Li, B, and Na. Road tunnel PM also contained elevated levels of Pb relative to other PM samples at 516 μg/g. DEP was also analyzed, as a source of PM expected to be low in transition metals. As expected, the majority of elements analyzed were present in lower concentrations in DEP compared to PM from the other sources tested, and many were not detected (Table S2, Supporting Information).

Statistical analysis was performed to determine whether there was any significant difference in the concentration of any element assayed across each of the size fractions. Only B showed any pairwise difference, the ultrafine fraction being high versus coarse ($p < 0.05$) and fine ($p < 0.01$) fractions. The data were further analyzed to test for correlations between Fe and other elements across the underground PM samples, testing with Spearman's rank correlation coefficient. Sr was the element most strongly correlated with Fe ($r = 1.00$; $p < 0.0001$). However, this may be of limited importance due to the low overall concentration of Sr, generally below 100 μg/g. Indeed, 32 of the 40 elements showed concentrations correlated with those of Fe ($p < 0.05$). The strongest correlations among the abundant metals were observed for

Mn, Ni, and Cu, while V was also strongly correlated with Fe (Figure S2, Supporting Information). Although no negative correlations were found, the crustal elements Na ($r = 0.517$) and K ($r = 0.433$) along with B ($r = 0.467$) showed the weakest correlation with Fe.

Particulate Anion Analysis. Ion chromatography analyses show that road tunnel PM possessed the highest concentrations of SO_4^{2-}, Cl^-, and NO_3^- (Figure 2). Roadwear PM generally showed the lowest SO_4^{2-}, Cl^-, and NO_3^- concentrations of any of the PM tested, suggesting that these anions are derived from fuel combustion rather than road and mechanical sources in the road tunnel PM. When the concentrations of each species were compared between the three size fractions of underground PM, coarse and fine fractions showed similar levels of the three anions, but ultrafine underground PM showed enrichments of SO_4^{2-}, Cl^-, and NO_3^-, and for SO_4^{2-}, this difference was of statistical significance versus coarse and fine fractions. Each anion showed only weak positive correlation with Fe concentration ($r = 0.583$, 0.483, and 0.367 for SO_4^{2-}, Cl^-, and NO_3^-, respectively).

Particulate Morphology. Examination of the coarse fraction of underground PM revealed that most particles were well below the 10 μm diameter used as a cutpoint for this fraction, with a smallest dimension of 2−3 μm or less. However, there was a clear population of particles with sizes close to the 10 μm cutpoint. The smaller particles had a nonuniform, irregular granular morphology, while the larger particles had a flakelike appearance with jagged edges (Figure 3). When examined at a greater magnification, the flat surfaces of these larger, flakelike particles were often marked by ridges or indentations. The fine fraction of underground PM contained a similar set of small particles with a largest dimension of ≈2 μm. Significantly, there was a paucity of flakelike particles compared to the coarse fraction. The ultrafine fraction of underground PM contained particles of a nonuni-

form granular shape. All fractions contained some particles of a larger size than should theoretically have been permitted by the cutpoint of the virtual impactor. These larger particles were commonly composed of 1−2 μm particles agglomerated to form a single mass, suggesting agglomeration post-collection.

ROS Generation by Underground PM. In order to measure the ROS-generating capacity of underground PM, PBEC monolayers were loaded with the oxidant sensitive dye H_2DCF-DA, which is fluorescent only after oxidation. Following 3 h exposure to underground PM, fluorescence was seen to increase in a concentration- and size-fraction-dependent manner (Figure 4), with ultrafine and fine fractions
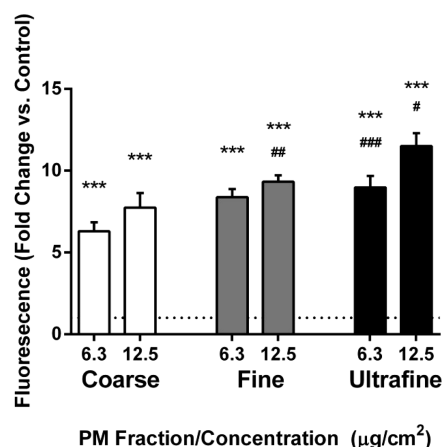

Figure 4. DCF fluorescence induced by 3 h incubation of PBECs with coarse, fine, or ultrafine underground PM. Values expressed as mean ± 1 SE, $n = 3-5$. (***) $p < 0.001$ vs control; (#) $p < 0.05$ for fine or ultrafine vs respective concentration of coarse PM. (##) $p < 0.01$ and (###) $p < 0.001$, analyzed by one-way repeated measures ANOVA.

generally inducing greater fluorescence than the coarse fraction (11.5 ± 0.8, 9.3 ± 0.4, and 7.7 ± 0.9 mean fold increase ± 1 SE, respectively).

DISCUSSION

This study examined the levels of transition and nontransition metals and selected metalloids in size-fractionated underground railway PM, with woodstove, roadwear, and road tunnel PM used as comparators. ICP-MS analyses of a large range of metals, especially in the rarely studied ultrafine fraction, provides new information on the chemistry of underground airborne PM. The underground railway station on which this study focused forms part of a mainline international railway. This is important because (1) the studied railway draws power from an overhead catenary, as opposed to an electrified rail, and (2) trains running on this line are larger than would generally be found on urban underground railway networks. The effects of increased load on rail wear have been detailed elsewhere.[25]

The present study showed that underground PM contained a high concentration of Fe. This observation is in agreement with other studies, which have found high Fe content in underground PM (e.g., 40−59% in Stockholm underground PM_{10},[8,26] 61% and 42% from Paris RER and Metro PM_{10}, respectively[3]). Interestingly, Stockholm underground $PM_{2.5}$ was found to contain almost undetectable levels of metal.[8] Overall, the results from underground stations are in clear contrast to samples from road traffic predominant areas, which tend to be rich in elemental carbon.[2]

Unlike the vast majority of studies of underground PM, the present study also analyzed the elemental composition of ultrafine PM ($PM_{0.1}$), which is rarely studied.[16] In urban environments, ultrafine PM is generally metal-poor[27−29] and mainly composed of elemental C along with the products of secondary reactions between gaseous pollutants that condense to form PM.[29−31] In terms of their chemistry, these secondary ultrafine particles are thought to be of little toxicological significance.[32] However, some processes involving high temperatures and resultant vaporization or combustion of substrate material have the potential to generate metal-rich ultrafine PM.[33,34] Indeed, most metals analyzed in this study were found to have higher concentrations in the ultrafine fraction compared to the coarse and fine fractions, although the differences were not statistically significant for any metal. Furthermore, our study may underestimate the relatively metal-rich nature of the ultrafine fraction compared to the fine fraction as the VACES equipment includes some ultrafine PM in the $PM_{2.5}$ fraction.[22] The majority of particles in underground PM samples are thought to be derived from interaction between wheels, rails, and brakes,[2] generating airborne particles that consist mainly of Fe but also contain among others Mn, Cr, V, Zn, and As.[35] Although abrasive forces between wheels, rails, and brakes can clearly generate coarse and fine PM due to shearing, there is evidence to suggest that ultrafine PM can be generated via the high temperatures of friction at interfaces between these components, with subsequent vaporization of the substrate.[25,34] There is also likely to be a contribution from arcing of the electrical current from the source to the contact point on the train, through which electrical current is drawn to power the train.[36,37] Crucially, however, unlike most urban underground systems that draw electric current through a third rail running parallel to the other rails, the railway in the present study is powered by an overhead catenary with the current drawn through a pantograph. Contact wires, which run above the railway line, are generally composed of Cu, alloyed with 0.1−0.5% Ag, Sn, Mg, or Cd.[38,39] The precise composition of these wires depends on the speed reached by trains drawing current. Similarly Cu or Cu−Pb−Sn alloys form the contact material of the pantograph, although in this case, it is generally as a component of a metallized carbon contact strip.[40,41] This can be contrasted with the third-rail system of power, where similar materials are used on the current-collecting component (in this case a third-rail "shoe"), but the third rail itself is an Al−stainless steel composite.[42] As such, overhead contact wire-powered underground railways may be expected to show increased airborne Cu levels compared to electrified rail-powered systems. By using the previously stated underground airborne PM mass concentrations for each size fraction described above, in conjunction with the concentration of Mn in each fraction, the mean (± 1 SE) airborne Mn concentration over the three days is calculated as 1010 ± 93 ng/m^3 well in excess of the WHO recommended limit of 150 ng/m^3 annual average and would still exceed this limit after allowing for working a 35 h exposure period per week, with zero Mn exposure outside of working hours.[43] Because Mn overexposure in welders and miners has been linked to symptoms resembling those of Parkinsonism, further study is needed of the potential effects of chronic exposure to underground dust.[44]

As the antithesis of an element found to be relatively enriched in underground PM, K was particularly high in woodstove PM. Wood combustion is a significant contributor

to airborne K,[45−47] so it is unsurprising that K was found at high levels in wood burner emissions. Interestingly, woodstove PM displayed levels of Rb, Cd, and Pb that were markedly enriched relative to other PM. Cd is a characteristic waste product of many industrial processes and is toxic to multiple organs, and it may be significant that the trees used to fuel the woodstove in this study were grown in the vicinity of a waste incinerator.[48] Waste incineration plants have been shown to release Cd as part of the incineration process,[49,50] and Pb was also enriched in woodstove PM compared to all other PM with the exception of road tunnel PM. It is well documented that the alkali metals Rb and Cs (which was also elevated in woodstove PM compared to other PM, although only at trace levels) act as analogues for K, also an alkali metal, in plant cation uptake, explaining their accumulation in plant material.[51]

Both roadwear PM and road tunnel PM have slightly raised levels of Ba but well below those seen in underground PM. Ba is also found in the brake shoes of trains; hence, brake wear is a possible source of the high Ba concentration in underground PM.[45,52] Roadwear and road tunnel PM samples also have high concentrations of Na, while roadwear PM was relatively rich in Al, K, Ti, and Sr and road tunnel PM was rich in B and Pb. These differences may reflect generation: roadwear PM is from an artificial roadwear generator while road tunnel PM is from an operational road tunnel. Ti and K are both found in brake pads,[53] while road dust contains aluminosilicates.[54] Elevated Na levels in road tunnel PM likely derive from the nearby (≈30 km) North Sea coast or from the addition of road salt. The elevated level of Pb in road tunnel PM is noteworthy as Pb is not currently used in Dutch petrol. However, Pb has been detected in road dust samples in other studies,[47,53] and probably reflects the greater volatility of Pb compared to other anthropogenically enriched toxic metals.[55]

The analyses presented here only yield the concentrations of the various elements under consideration. While this information is important, more detailed assessment of the biochemical impacts of these elevated metal levels would require information concerning their oxidation states. For example, distinction between Fe(II) and Fe(III) is important in discussing Fenton reactions and radical formation, which influences interaction with biomolecules. In addition, there is a need for study of the nature of the metal compounds in the PM. For example, environmental Fe is often found in an insoluble oxide form,[56,57] whereas metal chlorides are generally soluble. Indeed, more than one form of iron oxide has been observed in airborne PM, with urban PM Fe being mainly in the form of the hematite (Fe_2O_3), while the predominant species of underground iron has been reported for different systems as being magnetite (Fe_3O_4) or metallic iron, with minor hematite levels.[26,58] Improved identification of particular compounds could, for example, be attained by use of X-ray diffraction.[26,52]

Although metal speciation was not explicitly determined in this study, ROS generation by underground PM was investigated. Not only is ROS generation dependent upon the metal oxidation state, but it is also an intermediate step in transition-metal toxicity. In the present study, each fraction of underground PM was found to result in increased ROS generation as measured by DCF fluorescence. Furthermore, this ROS generation increased with PM concentration and was also greater for fine and ultrafine fractions compared to the coarse fraction. Considering the similarities in the metal composition of the different fractions, this effect is most likely

due to the increased surface area/volume ratio as the PM size decreases. Previous studies have suggested that transition metals in lower oxidation states are better able to exert oxidative effects than those in the higher oxidation states,[59,60] which suggests that a toxicologically significant proportion of underground PM is either in a submaximal oxidation state or is able to be reduced in vitro to a state where it can further catalyze ROS generation.

Analysis of metal concentrations in all samples showed a strong correlation between different elements. Notably, Fe was positively correlated with 32 of the elements, including several of the most abundant transition metals, such as V, Cr, Mn, Co, Ni, Cu, and Zn. It is likely that these correlations are partly due to elements coming from the same source, such as Fe being alloyed with other elements to modify the properties of steel, but also partly due to the level of general mechanical activity contributing to PM load.

Ion chromatography analyses showed that road tunnel PM contained the highest concentrations of SO_4^{2-}, Cl^-, and NO_3^-. This finding is unsurprising, given that much of the PM from a road tunnel is likely to be derived from fuel combustion and thus be more representative of urban PM that is known to contain high concentrations of these anions.[47,61−63] There is also likely to be a contribution from aged PM originating from outside the tunnel, which has accumulated these anions during transport to the sampling site. Nonetheless, the lack of these anions in roadwear PM compared to other particles analyzed also accords with their predominance in environments where fuel combustion is taking place and also explains their high levels in woodstove PM. However, it may be noteworthy that, of all the PM sources, with the exception of road tunnel, underground PM showed the greatest concentration of anions. Weak correlations of SO_4^{2-}, Cl^-, and NO_3^- concentrations with Fe concentration indicates that they are unlikely to be derived from mechanical wear. One source may be motor vehicles in the vicinity. The airport is one of the busiest airports in the world, by passenger number, and there is a considerable amount of motor vehicle usage in the vicinity of the airport. The railway station lies beneath a complex of car parks and passenger drop-off/pick-up points. Thus, it is likely that PM from car exhaust is drawn into the station by the "piston action" of train movement, although the extent of this input is a matter of debate.[64−66] Additionally, contributions from aircraft particulate emissions cannot be excluded.[67] Another potential source is the diesel-powered goods trains that pass occasionally through the station at night. Although no such trains passed through the station during sampling periods, particles deposited by diesel locomotives could be re-entrained by trains passing during the day or by cleaning vehicles that are in regular use. In support of this hypothesis, the reduced levels of Cl^- and NO_3^- compared to levels of SO_4^{2-} in underground PM, especially the ultrafine fraction, suggest that the contribution of secondary species from outside is minor.

As this study focused on metals in PM, there remains a proportion of the mass of underground PM that was not identified in this study (45%, 44%, and 19% by mass for coarse, fine, and ultrafine fractions, respectively). Si was not quantified in this study as the hydrofluoric acid digestion technique precludes accurate quantification. However, Si has been found in underground PM by other groups and has been ascribed to either brake blocks or the dumping of sand to improve wheel traction under braking.[2,4] Furthermore, oxygen as found in metal oxides was not measured. Because underground PM

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contains substantial levels of iron oxide, it is likely that oxygen makes up a significant proportion of the unidentified PM mass.[68] Finally, carbon, either elemental or organic, was not assayed. A wide range of organic compounds have been found in underground PM,[16] and while these may be derived from diesel train passage, it has also been noted that PM in areas located immediately below ground level, as with the station in this study, may be more influenced by above-ground sources than would be the case for deeper environments.[69] This is particularly pertinent here as the underground station lies directly beneath a large multistory car park. Indeed, underground PM is likely to contain toxicants such as polyaromatic hydrocarbons and redox-active quinones,[70] although the source of these is harder to verify. They are likely to be derived from above-ground traffic sources, and their concentrations may vary depending on the underground system (e.g., ventilation controls), above-ground urban pollution levels, and weather conditions.

This study also examined the morphology of underground PM because morphology can often serve as an indicator of the source of the particulate or at least the processes involved in its creation.[2] In terms of particle numbers, most PM of all size fractions had a granular appearance, with rough, uneven faces. No fibrous structures were observed. However, coarse PM contained a considerable number of particles of a flakelike, angular appearance, characteristic of particles created by abrasion and shearing. Such flakes may have considerably lower aerodynamic diameters than geometric diameters, resulting in an increased likelihood of deposition in the respiratory tract. Similar morphology has previously been observed in PM in other underground systems.[2,4,26] Very few flakelike particles were observed in the fine fraction, while none were seen in the ultrafine PM. Whether particulate angular shape affects uptake by cells or particle–particle interactions is not known. However, the angular nature of these particles may allow them to impinge upon the structure of the cell.[26]

Particle agglomerates were seen in all fractions, smaller structures comprising fewer than 10 individual particles, while larger structures were also observed, in excess of the respective VACES cutpoint, suggesting that the agglomerate had formed after collection. It was also observed that some particles particularly in the ultrafine ($PM_{0.18}$) fraction were larger than the stated cutpoint, although this may be reconciled by understanding that the diameter relates to the aerodynamic behavior equivalent to a sphere of unit-density of a set diameter.[71] Therefore, a particle may have an aerodynamic diameter lower than suggested by consideration of only its largest dimension.[72] Furthermore, the stated VACES cutpoint is not an absolute value but a 50% elimination value, meaning that, although 50% of particles larger than the cutpoint of 0.18 μm are eliminated, some larger particles, including up to 5% of those above 0.5 μm, may remain.[22] There also exists the possibility for smaller particles to enter larger-cutpoint fractions by adhering to larger particles.[35]

In conclusion, this study has characterized and compared size-fractionated mainline underground PM. The results show that underground PM contains a high concentration of Fe, correlated with levels of other transition metals, notably, Mn, Ni, Cu, and V, which are significantly elevated compared to PM from other sources. Crucially, ultrafine underground dust was at least as rich in metals as coarse and fine underground PM, which may have important implications for potential hazards posed by underground PM, and warrants further study of the hitherto neglected ultrafine fraction in particular.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Elements analyzed by ICP-MS with sources of standards; particulate analysis results for elements not included in the main body of the paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ABBREVIATIONS USED

DEP	diesel exhaust particulate
PM	particulate matter
ROS	reactive oxygen species
RT	road tunnel
RW	roadwear simulator
UG	underground railway
VACES	versatile concentration and enrichment system
WS	woodstove

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