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Time-resolved mass concentration, composition and sources of aerosol particles in a metropolitan underground railway station

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Abstract

Aerosol samples were collected using a stacked filter unit (SFU) for PM10-2.0 and PM2.0 size fractions on the platform of a metropolitan underground railway station in downtown Budapest. Temporal variations in the PM10 mass concentration and wind speed and direction were determined with time resolutions of 30 and 4 s using a tapered-element oscillating microbalance (TEOM) and a wind monitor, respectively. Sample analysis involved gravimetry for particulate mass, and particle-induced X-ray emission spectrometry (PIXE) for elemental composition. Diurnal variation of the PM10 mass concentration exhibited two peaks, one at approximately 07:00 h and the other at approximately 17:00 h. The mean $\pm$ SD PM10 mass concentration for working hours was $155 \pm 55\,\mu g\,m^{-3}$. Iron, Mn, Ni, Cu, and Cr concentrations were higher than in outdoor air by factors between 5 and 20, showing substantial enrichment compared to both the average crustal rock composition and the average outdoor aerosol composition. Iron accounted for 40% and 46% of the PM10-2.0 and PM2.0 masses, respectively, and 72% of the PM10 mass was associated with the PM10-2.0 size fraction. The aerosol composition in the metro station (in particular the abundance of the metals mentioned above) is quite different from the average outdoor downtown composition. Mechanical wear and friction of electric conducting rails and bow sliding collectors, ordinary rails and wheels, as well as resuspension, were identified as the primary sources. Possible health implications based on comparison to various limit values and to data available for other underground railways are discussed.

Keywords: Rail wear; Steel dust; Diurnal variation; Indoor aerosol; Transition metals; Metro; Subway

1. Introduction

It is estimated that people living in urban areas in developed countries spend approximately 8% of their daily time commuting (Jenkins et al., 1992; Eurostat, 2004). Concentrations of air pollutants are usually much higher in traffic microenvironments than in other (urban and urban background) environments, which can considerably increase commuters' daily aerosol exposures (Fenger, 1999). Underground railway transport systems represent a unique microenvironment because of their closed character and restricted ventilation, specific emission sources, and meteorological conditions. Underground railways transport millions of

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passengers per day in a number of cities around the world, with elevated exposure for most of these passengers repeated on a daily basis. Several studies have considered aerosols or air quality in underground railway systems (Berlin, Fromme et al., 1998; London, Pfeifer et al., 1999; Sitzmann et al., 1999; Adams et al., 2001; Hurley et al., 2003; Seaton et al., 2005; Tokyo, Furuya et al., 2001; Washington, DC, Birenzvige et al., 2003; Stockholm, Johansson and Johansson, 2003; New York city, Chillrud et al., 2004, 2005; Helsinki, Aarnio et al., 2005; Prague, Braniš, 2006; Rome, Ripanucci et al., 2006). These studies consistently show elevated pollution levels in terms of particulate mass (dust), especially for certain transition metals in comparison to the corresponding external outdoor areas. Underground railways seem to be the dominant microenvironment responsible for exposure to Fe, Cr, Mn, and possibly Ni for persons who are not subject to occupational exposure (Chillrud et al., 2004). Health effects of these metals have been identified in toxicological, occupational, or epidemiological studies at concentration levels that exceed ambient health limits (HEI Review Committee, 2002). The health effects of excess exposure to Fe (with other transition metals) are thought to be linked to its ability to generate free radicals in the body, resulting in oxidative stress, inflammatory reactions, neurodegenerative diseases, and multiple sclerosis (Donaldson et al., 1997). Chromium and Ni are known to be carcinogenic, especially in the respiratory organs, and Cr can lead to gene mutations. Manganese is classified as a neurotoxic and can cause respiratory dysfunctions such as pneumonia (WHO, 2000; ATSDR, 2000).

The metropolitan underground railway in Budapest, the capital of Hungary (Budapest metro), is one of the oldest underground transport systems in the world. Its yellow (M1) line started operating in 1896 (after London, UK, and Chicago, USA), and it is included on the World Heritage List. The red (M2) line started operating in 1970 and the blue (M3) line in 1976. Reconstruction and total refurbishment of the red line has been going on since 2003, and a new M4 line is under construction. The total length of the system is 33 km, of which 84% is in tunnels; it has 39 stations and one joint intersection, as indicated in Fig. 1. Electric trains run from 04:30 until 23:40 h (timetable at http://www.bkv.hu/angol/metro/index.html) with a frequency between 2 and 15 min, depending on the time of day. The vehicles are equipped with an electric-braking system that utilizes pneumatic braking after deceleration to a velocity of 5–7 km h^{-1}, using asbestos-free brake linings (Cosid 804). The underground railway is an important part of urban traffic, representing 22% of the city's public transport, or more than 1 million passengers per workday. The most frequent average time spent on one journey is 8–10 min (BKV, 2006). The levels of microorganisms were previously studied, and a correlation between the concentration of biocontaminants (pathogenic and anthropogenic bacteria) and the number of passengers and space size was observed (Szam et al., 1980). To the best of our knowledge, no study has been conducted on aerosols in the underground railway in Budapest so far.

To examine the aerosol air quality and its temporal variation in the Budapest metro, a central station was selected for *in situ* aerosol measurements and sample collection. The main objectives of the present paper are: to present and interpret the time variation of the PM10 mass concentration (MC); to report elemental compositions and other basic aerosol properties for PM10-2.0 and PM2.0 size fractions; to compare these to the corresponding results for external downtown areas just above the station; and to relate the information obtained to the main emission sources of indoor aerosol particles. Our aim was also to compare the data obtained to information available for other underground railways, and to discuss the health implications and conclusions for underground railway transport systems in terms of different health limits.

2. Experimental and evaluation methods

The fieldwork was performed on the platform of the Astoria station on the red line of the Budapest metro (Fig. 1). The station is located downtown and was recently renovated. The closest metro stations undergoing renovation of the filtration system during the experimental period were Kossuth tér and Deák tér stations (Fig. 1). The Astoria metro station consists of an entrance corridor with three escalators, a vestibule, and two tunnel bores. The fieldwork took place on the platform of the tunnel bore leading from Déli pu. Station to Örs vezér tere Station. The station is ventilated without filtration by drawing air from the opposite platform to the roof level of a 12-story building next to the station. Trains usually arrive at and depart from the station within 30–40 s, and spend approximately 30 s at the platform. The air-monitoring equipment

Fig. 1. Map of the metropolitan underground railway system (metro) and the main roads in Budapest, Hungary. The research was performed at the Astoria metro station on the red (M2) line.

was located at the far end of the platform ~2 m in front of the control cabinet and ~1.5 m from the wall of the platform. The aerosol inlets and the meteorological sensors were placed at a height of ~2.5 m. This location was chosen as a compromise between meeting conditions for undisturbed measurement and obstructing pedestrian traffic as little as possible (pedestrians enter and leave the platform at the near end, where trains arrive at the station). It was assumed that the concentration gradient close to the instruments was small, since the air is presumably mixed by trains moving along the platform.

Air monitoring equipment consisted of a tapered-element oscillating microbalance (TEOM, model 1400a, Rupprecht and Patashnick, USA), a wind monitor (Campbell, model 05103, USA), and a laboratory-made Gent-type stacked filter unit (SFU) aerosol sampler. The TEOM was equipped with a PM10 inlet (Rupprecht and Patashnick, USA) facing upwards and was operated with the filter heated to 40 °C to prevent moistening. Measuring aerosol mass in this way is known to underestimate the true mass primarily due to the loss of semi-volatile aerosol constituents (e.g., nitrates and some organic compounds) caused by the increased temperature (Ayers et al., 1999). The dependence of the standard deviation (σ) of the MC baseline obtained using an absolute filter (Balston DFU filter, grade BQ, USA) on the TEOM integration time was investigated in a laboratory experiment. The results shown in Fig. 2 demonstrate that the uncertainty of the MC baseline increases with decreasing integration time, with a sharp increase as the integration time decreases to less than 1 min. Nevertheless, an integration time of 30 s allows measurement of changes in PM10 MC comparable to one-tenth of the daily ambient outdoor EU limit value (LV) of 50 $\mu g\,m^{-3}$ (Council Directive, 1999) using the conservative approximation of $3\sigma < LV/10$. For this reason, an integration time of 30 s was chosen as the time resolution for

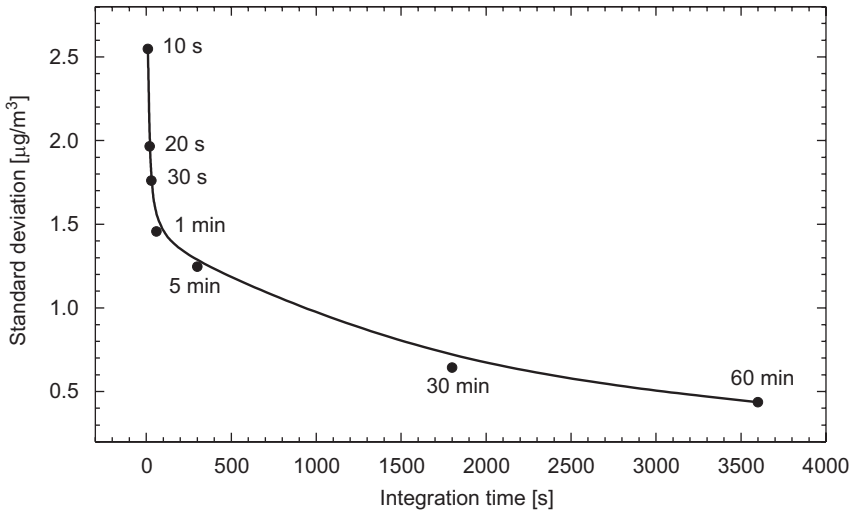

Fig. 2. Dependence of the standard deviation of the mass concentration baseline on the integration time for the TEOM (model 1400a).

regular measurements. The indoor air temperature was also recorded by the TEOM thermometer. The orientation of the wind monitor was adjusted as follows: 0° was the direction perpendicular to the wall, 90° was the direction of the departing trains, and 270° was the direction of the arriving trains. Temperature, wind direction (WD) and horizontal wind speed (WS) data were acquired using the same integration time as for the MC value. *In situ* measurements were made continuously from approximately 12:00 h local daylight saving time (UTC + 2 h) on 20 April 2006 (Thursday) until approximately 15:00 h on 21 April (Friday).

The SFU sampler contains two 47 mm diameter Nuclepore polycarbonate filters with pore sizes of 8 μm (Apiezon coated) and 0.4 μm in series in a NILU-type open-face stacked filter cassette (Maenhaut et al., 1994; Hopke et al., 1997). Upstream of the filter cassette, there is a pre-impaction stage with its inlet facing down. The sampler is designed to operate at an airflow rate of 16–17 l min^{-1}, at which the pre-impaction stage intercepts particles larger than an aerodynamic diameter (AD) of approximately 10 μm, and at which the first filter has a 50% collection efficiency at ~2 μm AD. Consequently, aerosol particles are separated into PM10-2.0 and PM2.0 size fractions. Two aerosol samples were collected on the platform, one from 12:30 h on 20 April through to 05:45 h the next day, and the other from 06:00 to 15:00 h on 21 April. A field blank was also taken. The samples were placed in polycarbonate Petri dishes and were stored in a refrigerator until analysis.

The aerosol mass was obtained by weighing each filter before and after sampling on a microbalance with a sensitivity of 1 μg. Samples were pre-equilibrated before weighing at 20 °C and 50% relative humidity for at least 24 h. A quarter section of each filter was analyzed by particle-induced X-ray emission spectrometry (PIXE) for 30 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba, and Pb) (Maenhaut et al., 1981). Particle size correction factors of 1.7 and 1.4 were applied for Mg and Al for the PM10-2.0 fraction, and 1.4 and 1.2, respectively, for the PM2.0 fraction. The correction factors were deduced on the basis of a previous comparison between PIXE and instrumental neutron activation results for SFU samples collected at urban and rural sites (Salma et al., 1997, 2001). Crustal enrichment factors (EFs) were calculated relative to the average crustal rock composition (Mason and Moore, 1982) with Al as the reference element (Zoller et al., 1974).

3. Results and discussion

3.1. Temporal variation

Fig. 3 shows temporal variation of the PM10 MC and horizontal WS for 24 h as measured (30 s mean values) and as 1 h smoothed curves. The data exhibit large variability, particularly for the WS data. During working hours, WS varied from 0.04 to 2.7 m s^{-1}, with a mean ± SD of 0.81 ± 0.51 m s^{-1}. Each curve shows two maxima, one between 07:30 h

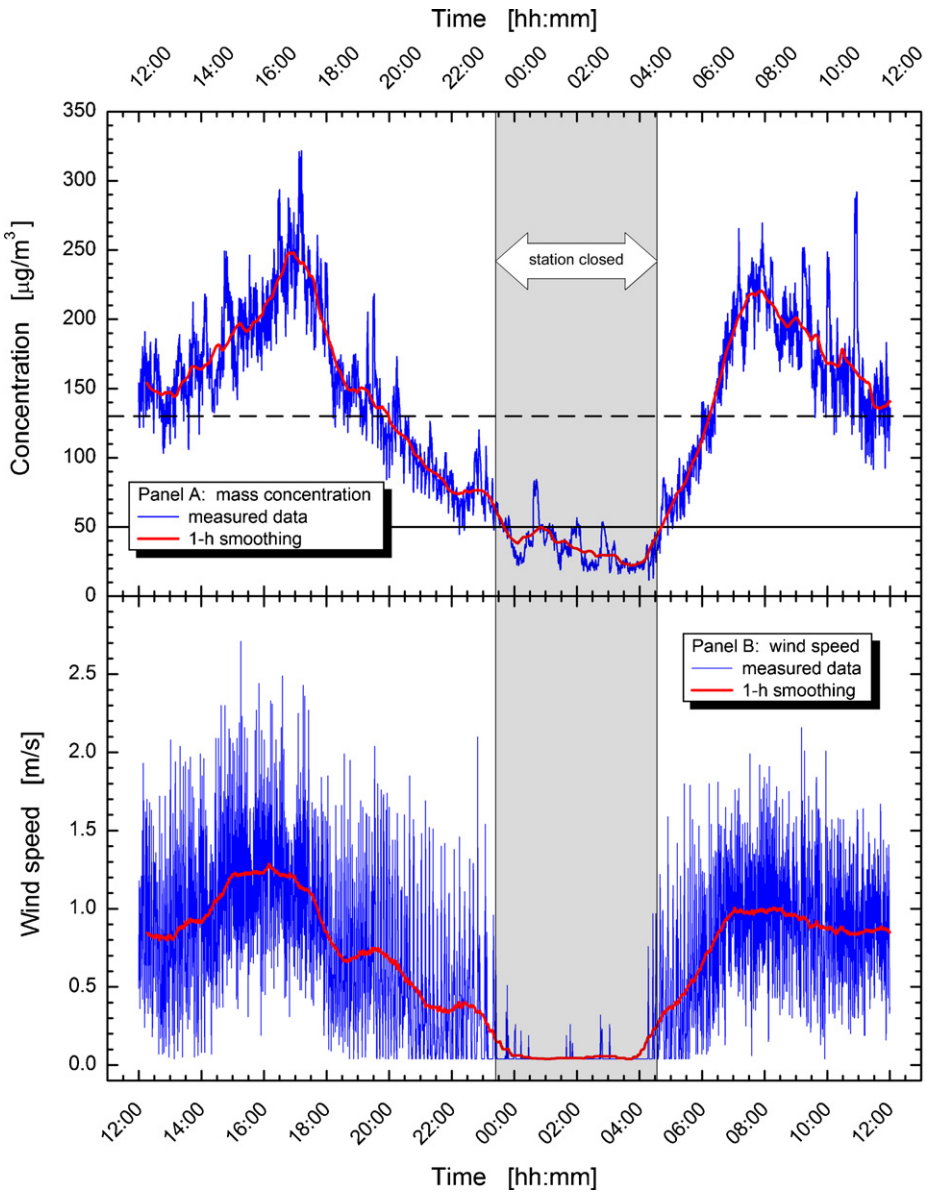

Fig. 3. Temporal variation of (A) PM10 mass concentration and (B) horizontal wind speed as measured (30 s averages) and 1 h smoothed curves for 20 and 21 April 2006 in the Astoria metro station. The ambient outdoor daily EU health limit of 50 $\mu g\,m^{-3}$ for PM10 mass concentration, and the 24 h mean mass concentration of 130 $\mu g\,m^{-3}$ are also shown in A by solid and dashed lines, respectively.

and 08:00 h and the other around 17:00 h, corresponding to the morning and afternoon rush hours in the time–activity pattern of travelers, when the train frequency is greatest (2–4 min). MC levels were high at these times, with a maximum of approximately 220 $\mu g\,m^{-3}$ in the morning and ~250 $\mu g\,m^{-3}$ in the afternoon. The data measured even reached 300 $\mu g\,m^{-3}$. Between the rush hours, the curve showed a local minimum of ~150 $\mu g\,m^{-3}$ at approximately 12:00 h. The mean ± SD MC for the morning (04:30–12:00 h) and afternoon/evening (12:00–23:20 h) working hours were 158 ± 55 and 153 ± 55 $\mu g\,m^{-3}$, respectively. After the departure of the last train at approximately 23:20, MC decreased very rapidly below the ambient outdoor EU PM10 limit within 40 min, which indicates a rather short residence time for aerosol particles in the air, since the air ventilation rate at the station remained constant. This also means that coarse particles dominated the mass size distribution. Some abrupt

changes in MC and WS also occurred while the station was closed. The MC peak at approximately 00:30 h was not accompanied by a significant increase in WS, and was thus attributed to cleaning of the station (the platforms and vestibule). The other two MC peaks at approximately 02:00 h and just before 03:00 h were associated with increased WS and fluctuations in WD, and therefore can be explained by the motion of diesel-driven trains (work cars) involved in overnight freight shipment, maintenance, and service activities. The mean MC while the station was closed was $36 \pm 14\,\mu g\,m^{-3}$. The concentration increased rapidly with the arrival of the first vehicle in the early morning, and continued monotonically until the morning maximum value (from ~30 to $220\,\mu g\,m^{-3}$). The mean ± SD and median MC during working hours were 155 ± 55 and $157\,\mu g\,m^{-3}$, respectively. The shape of the diurnal MC variation presented is comparable to that for downtown surface areas since the time–activity patterns are common. MC in the metro closely follows the vehicle intensity, as demonstrated by a scatter plot of the 30 min mean MC and the number of trains passing the platform over 30 min intervals (Fig. 4).

Correlation between measured MC and WS data for the time periods when WS was not $< 0.3\,m\,s^{-1}$ was not significant, implying that the relationship between them is not simple. There seems to be a delay in MC in relation to WS changes. Correlation coefficients between the smoothed MC trend and WS values $> 0.1\,m\,s^{-1}$ were large ($R > 0.95$) for time periods between 17:00 h and 23:20 h, and between 04:30 h and 07:30 h, implying a common main source. This was undoubtedly the train traffic.

During actual measurements on the platform, both the MC levels ($> 150\,\mu g\,m^{-3}$) and changes (several tens of $\mu g\,m^{-3}$) caused by the motion of the trains were much greater than anticipated (see Section 2). Therefore, we decided to further decrease the integration time to 4 s for complementary high-resolution measurement for approximately 1 h at the end of the 24 h campaign. Fig. 5 shows WD, WS, and MC data for a selected time interval during which the coincident effect of trains running in the opposite direction in the other tunnel

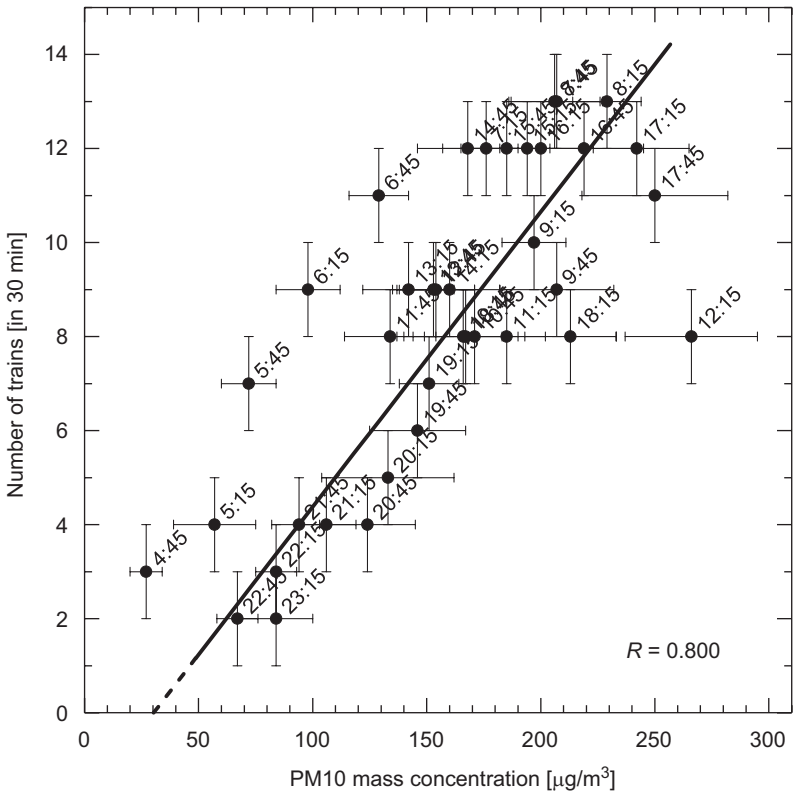

Fig. 4. Scatter plot of the PM10 mass concentration versus the number of trains that passed Astoria metro station in the direction examined for 30 min periods. The first five data in the morning (04:45–06:45 h) were disregarded in deriving the regression line to reduce the effect of the finite residence time of particles in the air.

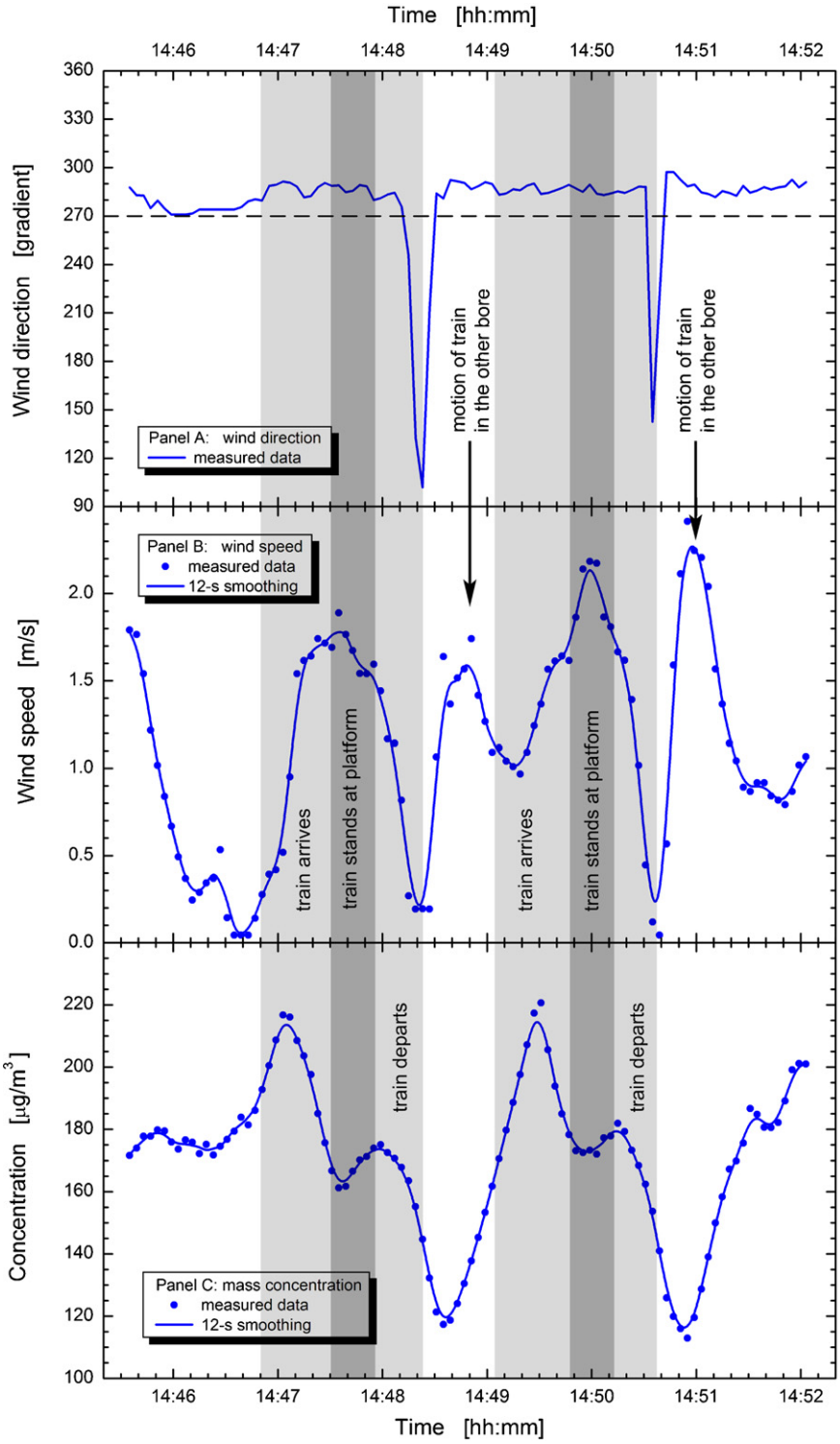

Fig. 5. Temporal variation of (A) wind direction, (B) horizontal wind speed, and (C) PM10 mass concentration as measured (4 s averages) for a selected time interval on 21 April 2006 in the Astoria metro station. The dashed line in A indicates the mean wind direction for moving trains; 12 s smoothed curves are shown in B and C. Time intervals for arriving trains, trains standing at the platform, and departing trains are also displayed.

bore was well separated so the effect of train arrival and departure on WS, and MC could be resolved. Train movements are clearly reflected in changes in WS and WD. A broad maximum for the WS curve was observed, corresponding to the arrival of trains in the station, standing at the platform, and then departing from the station. The sudden change in WD and decreasing tendency of the WS curve indicate the end of the departure of trains from the station. Two maxima were observed on the MC curve for each arrival–standing–departure cycle. The first maximum is much greater than the second and occurred during the arrival phase. The increase in MC was caused by vehicles pushing in polluted air from the tunnel bore as they entered the station, and MC decreased during deceleration. During passenger entry and exit, the airflow from the tunnel bore was maintained (as indicated by the WS curve), which resulted in another increase in MC. Train departure pulled in some polluted air from the tunnel bore, as well as cleaner air from the vestibule and corridor, and therefore MC decreased. The local maxima and minimum in the MC data followed the WS tendencies with a delay of approximately 12 s, which can be explained by turbulent mixing in the station. The magnitude and shape of the individual peaks of WS and MC were also influenced by the actual deceleration and acceleration conditions of the vehicles.

3.2. Residence time and particle diameter

The undisturbed decrease in MC levels between approximately 23:40 and 00:15 h (Fig. 3) was utilized to estimate roughly the residence time in air for large (diameter $d > 1\,\mu m$) particles. Idealized stirred settling of monodisperse aerosol was considered since ventilation was carried out at a constant airflow rate and 72% of the PM10 mass was found in the PM10-2.0 fraction (see Section 3.3). Diffusion and deposition on the walls were assumed to be negligible. When the particle Reynolds number (Re) is small, the change in the MC can be expressed as (Hinds, 1999)

$$\frac{\mathrm{d\,MC}}{\mathrm{MC}} = \frac{v_{TS}\,\mathrm{d}\,t}{H}, \tag{1}$$

where t is the time, v_{TS} is the terminal settling velocity (average net particle velocity), and H is the height of the TEOM inlet. The calculation yielded a terminal settling velocity of 0.4 and 0.2 mm s^{-1} for measured and smoothed data, respectively, implying a residence time in air of $\tau = H/v_{TS}$ (for dry deposition and a closed reservoir) between approximately 1.5 and 3 h. The results from this simplistic model are comparable to data in the literature, although the real case is likely to be much more complicated.

Using the terminal settling velocity, it is possible to estimate the equivalent diameter d of particles (for $d > 1\,\mu m$ and $Re < 1$) from the equilibrium of the drag force and the force of gravity (Hinds, 1999):

$$v_{TS} = \frac{\rho_p d^2 g}{18\eta}, \tag{2}$$

where g is acceleration due to gravity and η is the dynamic viscosity of air (1.8×10^{-5} Pa s at 20 °C and 1015 hPa). It should be noted here that the indoor ambient air temperature varied from 19 to 22 °C, with a median of 20 °C. Considering that approximately 40% of the PM10-2.0 mass in the metro consisted of Fe (see Section 3.3), and assuming that the density of the remainder was similar to that of soil dust, the particle density ρ_p was estimated to be 4600 kg m^{-3}. Typical aggregate diameters of 37 and 43 μm were obtained for the coarse mode from the settling velocity for smoothed values assuming spherical particles, and particles having a shape factor of quartz dust ($\chi = 1.36$, $v_{TS}(\chi) = v_{TS}\sqrt{\chi}$), respectively.

3.3. Elemental composition

Table 1 presents volume-weighted mean atmospheric concentrations, crustal EFs, and metro/outdoor EF ratios for the PM10-2.0 and PM2.0 size fractions. The PM10 MC of 125 μg m^{-3} derived by summing and averaging the fractionated mass data was somewhat lower than the 24 h mean MC of 130 μg m^{-3} obtained by the TEOM (Fig. 3). The MCs for the separate PM10-2.0 and PM2.0 size fractions were much greater (in accordance with the TEOM data) than the mean values of 37 and 19 μg m^{-3}, respectively, obtained for the outdoor sampling site just above the Astoria metro station (4 Rákóczi Street) using the same sampling and analytical methods as in the present study (Salma and Maenhaut, 2006). In terms of elemental composition, PM10 concentrations of Fe, Mn, Ni, Cu, and Cr (obtained by summing the two separate size fractions) were most enhanced. These were greater by factors of 20, 12, 10, 8, and 5, respectively, for the metro than for the outdoor

Table 1
Mean atmospheric concentrations and crustal enrichment factors (crustal EF) for the Astoria underground railway station, and mean indoor/outdoor EF ratio (indoor EF) for the PM10-2.0 and PM2.0 fractions

Aerosol constituent	PM10-2.0 size fraction			PM2.0 size fraction		
	Conc. (ng m^{-3})	Crustal EF	Indoor EF	Conc. (ng m^{-3})	Crustal EF	Indoor EF
Mg	296	2.3	1.2	130	6	–
Al	531	–	–	93	–	–
Si	2.09[a]	1.2	1.5	442	1.4	2
S	978	597	3	828	3027	1.1
Cl	305	352	2	104	722	
K	318	1.9	1.7	127	4	1.3
Ca	2.57[a]	11	1.8	413	10	2
Ti	47	1.6	1.3	25	5	3
Cr	35	53	8	15	136	
Mn	310	49	20	148	143	27
Fe	33.5[a]	101	32	15.5[a]	285	43
Ni	29	59	20	8	101	11
Cu	496	1343	15	190	3096	11
Zn	118	245	2	50	661	2
Br	13	797	4	DL		
Ba	145	51	5	DL		
Pb	47	612	6	21	1975	2
PM	83.6[a]	13	4	33.0[a]	30	1.5

The indoor/outdoor EF ratio represents the enrichment factor relative to the average outdoor downtown atmospheric aerosol (and is denoted indoor EF). DL, detection limit.
[a]Expressed in μg m^{-3}.

downtown air. On average, 40% of the PM10-2.0 mass in the metro was made up of Fe, and the contributions of Si and Ca were approximately 3% each. In the PM2.0 size fraction, Fe and S showed the greatest contributions of 46% and 2.5%, respectively. The results agree well with most observations available for other underground railways (Sitzmann et al., 1999; Chillrud et al., 2004; Aarnio et al., 2005; Seaton et al., 2005), but differ from findings for Rome, where a different braking system is used (see Section 3.5; Ripanucci et al., 2006). Mass concentrations of Cu, Mn, Cr, and Ni in the PM10-2.0 size fraction were 0.58%, 0.37%, 0.042%, and 0.035%, respectively, and were similar in the PM2.0 size fraction. The abundance of the elements mentioned was very different for the outdoor atmospheric aerosol in downtown Budapest (see Fig. 5 in Salma et al., 2001). In the metro, the Fe mass contribution was 10- and approximately 35-fold greater in PM10-2.0 and PM2.0 size fractions, respectively, while the contributions of other elements were typically two- to three-fold lower (as expected) compared to the corresponding average outdoor aerosol. Our preliminary results show the black carbon concentration in air in the PM2.0 size fraction for the underground railway station (measured by a commercial smoke-stain light reflectometer and corrected for Fe interference) was lower than but comparable to that for the average outdoor downtown aerosol. Its contribution to the particulate mass was approximately 9%. The contribution is very similar to that for Berlin and Helsinki (Fromme et al., 1998; Aarnio et al., 2005), but is remarkably lower than the mean of 21% for downtown air in Budapest (Maenhaut et al., 2005).

The PM2.0/PM10-2.0 concentration ratios for each constituent and the particulate mass were lower than 1.0, implying that the particles and their constituents were mainly formed by mechanical disintegration. In comparison to the outdoor air, most PM2.0/PM10-2.0 ratios for the metro were 1.1- to 1.7-fold greater, while for S and Pb, the ratios were smaller by a factor of 0.4. The mean PM2.0/PM10-2.0 ratio and standard deviation for the particulate mass in outdoor downtown Budapest slightly increased from 0.61 ± 0.24 in 1996 to 0.68 ± 0.33 in 2002, in agreement with general trends for aerosol properties and chemical mass balance (Maenhaut et al., 2005; Salma and Maenhaut, 2006).

In contrast, a mean PM2.0/PM10-2.0 mass ratio of 0.39 was derived for the indoor underground environment, which means that 72% of the particulate mass was in the PM10-2.0 fraction. The mean ratio converted to the PM2.5/PM10 ratio [$\approx 1/(1+$PM10-2.0/PM2.0)] of 0.29 is in perfect agreement with that of 0.3 reported for London (Seaton et al., 2005). This emphasizes the importance of disintegration emission sources. A large mass fraction of these particles is deposited in the upper airways of the human respiratory tract and the lungs. The larger PM2.0/PM10-2.0 ratios for most aerosol constituents in the metro compared to the outdoor air can most likely be interpreted as broadening of the size distribution for coarse particles. This is consistent with earlier findings that coarse particles in underground railways are more evenly distributed over the size interval than coarse atmospheric particles (Sitzmann et al., 1999). This explanation needs to be confirmed by measuring mass size distributions.

3.4. Emission sources

The indoor/outdoor EF ratios shown in Table 1 as a matter of fact represent the enrichment relative to the average outdoor downtown aerosol; in the following section these are denoted as indoor EFs. The crustal EFs for Mg, Si, K, and Ti in the PM10-2.0 fraction of the metro aerosol are close to 1.0, suggesting that the emission sources for these elements were most likely disintegration, dispersal and resuspension of the crustal rock and ballast due to normal operation and construction work in the tunnels and stations. For the other elements, crustal EFs are much greater (Table 1), indicating that their main emission sources were of non-crustal origin. The PM10-2.0-fraction mass is also enriched. All indoor EFs are greater than 1.0, indicating that the aerosol constituents were substantially enriched in relation to the average outdoor downtown air. The indoor EF for the particulate mass is 4, and the greatest indoor EFs were observed for Fe, Mn, Ni, Cu, and Cr. The large crustal and indoor EFs and the association with the PM10-2.0 size fraction imply that these metals were primarily emitted into the air within the underground railway from non-crustal sources by mechanical disintegration, most likely by friction and rubbing of the electric conducting rail and bow sliding collectors, and by wear of the ordinary rails and wheels. The sliding collectors are made of alloy steel (A44), and considerable mechanical wear is routinely noted by maintenance staff (BKV, 2006). A special grease (Tramlub S5, Fuchs Lubritech, Germany) is used to lubricate the rails, switches, and wheel flanges of the railway vehicles. Wind erosion of construction materials, and of the materials covering the surfaces, including paint, may also play a role. The brakes are less likely sources of metals in the Budapest metro, since the vehicles are equipped with an electric-braking system. For the PM2.0 fraction, the crustal and indoor EFs are greater than or similar to those for the PM10-2.0 fraction in many cases. This is consistent with the interpretation of a broader size distribution for coarse particles as outlined in the previous section. The PM2.0 indoor EF for S and K are close to 1.0, suggesting that these aerosol constituents could be transported together with outdoor air through the filterless ventilation system (this may also be partly true for the particulate mass, and black carbon). The mass contribution of coarse mode to the PM2.0 fraction is greater for elements associated with indoor emission sources that were present at high concentrations (Fe, Mn, Ni, and Cu). Vaporization by sparking is thought to be a less significant source of metals relative to the overlapping contribution of coarse particles, since it is minimized by technical design. Traffic exhaust fumes on the surface cannot be excluded as a detectable contribution to the metro air, since the concentrations of some related aerosol constituents in the metro are similar to outdoor concentrations. A direct relationship between the air quality within underground railway systems and outdoor pollution levels was identified in Helsinki and Prague (Aarnio et al., 2005; Braniš, 2006). It is also worth noting here that the number concentration of ultrafine particles in underground systems is usually lower than for outdoor air; their origin is related to the introduction of outdoor air that contains pollutants from traffic on nearby streets (Chillrud et al., 2004; Aarnio et al., 2005; Seaton et al., 2005).

Mean Fe/Mn, Fe/Cr, and Fe/Ni concentration ratios of 108, 956, and 1155, respectively, were derived for the PM10-2.0 fraction in the Budapest metro. These are significantly different from the ratios of 500, 53, and 667, respectively, for the average crustal rock composition (Mason and Moore, 1982). The Fe/Mn ratio is comparable to the ratio of 107 obtained for New York (Chillrud et al., 2004) and of 92 for Helsinki (Aarnio et al., 2005). The various ratios are also remarkably

similar to the typical ratios obtained for elemental compositions of the rails and electric sliding collectors. Several types of alloy steel are in use in the underground railway (e.g., EN 13674–1:2003, Fe275B, MA1 Grade 900A; BKV, 2006), with average Fe/Mn and Fe/Cr ratios of 109, and 767, respectively. Taken together, these data indicate that emissions from the electric rail–collector and rail–wheel interfaces were the major source of Fe, Mn, and Cr. Differences in the ratios among underground railways can most likely be explained by the different types of steel and iron alloys used.

3.5. Comparison to other underground railways

Particulate mass data from the current study were compared with those from other underground railway studies. The ranges and averages for two size fractions are given in Table 2. The average MC for the PM2.0 fraction for Budapest was estimated from the PM10 MC and the PM2.0/PM10 ratio for the particulate mass. Despite the fact that friction products from the main emission sources are found in the coarse fraction, in a few studies only the PM2.5 size fraction was examined. It is evident that all underground railway systems exhibit significantly greater concentrations than the daily ambient EU PM10 limit (cf. Section 4). The pollution levels in all underground railways are also greater—usually several fold—than for outdoor areas above the stations (references in Table 2). At the same time, there are substantial differences in air quality and potential exposure among the different underground railway systems. The explanation involves differences in the engineering systems, technical, construction and operational circumstances, number of train passages, ventilation and air-conditioning systems, dimensions of the underground spaces, normal cleaning frequency, and other factors not studied so far. The braking system (either pneumatic brake blocks or electrodynamic brakes) and the emergency braking system (brake blocks with or without spraying sand on the rails) can be considered one of the major differences influencing the particulate air quality (Fromme et al., 1998; Seaton et al., 2005; Ripanucci et al., 2006). The effect of washing on indoor aerosols in the Stockholm underground railway systems was studied and found to be of limited importance, reducing the PM2.5 MC by approximately only 13% (Johansson and Johansson, 2003). Measurements in the Prague underground railways were made immediately after a complete clean up and reconstruction after severe floods in the city in August 2002, which likely explains the low PM10 concentrations found (Braniš, 2006). The conclusions of the Stockholm and Prague studies are not contradictory, because the washing in Stockholm was confined to the walls and tracks between the platforms, and thus was less thorough. Complete and frequent (at least twice a year, BKV, 2006) washing seems to affect the aerosol air quality in the Budapest metro; the relatively low aerosol levels in Budapest could be linked to or associated with this routine.

Little information on the elemental or chemical composition of aerosols in underground railways is available at present. Elevated levels of Fe, Mn, Cr, and often Cu were found in all other underground railways and are reasonably similar to the values presented in Table 1.

4. Implications and conclusions

The health implications for passengers and workers in the metro can be approached differently. The mean particulate MC presented in this paper for the Astoria metro station, and for all underground railways in Table 2, is several folds greater than the ambient outdoor EU 24-h PM10 limit. Even though the outdoor limit for the public does not apply indoors or in tunnels, it can serve as a guideline for comparison. It should be mentioned here that: (1) the daily ambient outdoor limit is frequently exceeded in many areas in Europe, especially during winter temperature inversions and (2) the daily ambient outdoor PM10 LV recommended by the US EPA is $150\,\mu g\,m^{-3}$ (US EPA NAAQS, 1997) compared to the EU guideline of $50\,\mu g\,m^{-3}$. Thus, some PM10 levels measured in underground system (Table 2) are within the US EPA limit. It is recognized that the average commuter spends a small fraction of a day in underground railway stations and on underground trains. It was also found in several studies that concentrations in metro vehicles with or without air conditioning were lower than in underground railway stations (Chillrud et al., 2004; Aarnio et al., 2005; Seaton et al., 2005; Braniš, 2006), suggesting that time spent in stations may be a better predictor of personal exposure than total time spent underground. Nevertheless, higher health risks for sensitive groups, such as children, the elderly, and individuals with pre-existing health conditions exacerbated by air pollution (many respiratory and cardiovascular diseases;

Table 2
Range and average particulate mass concentration for different underground railways

Location	PM conc. ($\mu g\,m^{-3}$)		Note	Reference
	Range	Average		
Coarse and fine size fractions				
Prague	–	103	Mean personal exposure to PM10 mass for 11 min intervals spent in underground spaces of metro stations over ~1 year	Braniš (2006)
Berlin	–	147	Overall average PM10 mass data from 07:00 h over 9 h inside trains	Fromme et al. (1998)
Budapest	25–322	155	Average of 30 s mean PM10 mass data for working hours	Present work
	85–234	180	Average hourly mean PM10 mass data from 06:00 h over 12 h for workdays	
Rome	71–877	407	Overall average mean PM10 mass data for five different platforms on two lines	Ripanucci et al. (2006)
Stockholm	212–722	469	Average hourly mean PM10 mass data from 07:00 h over 12 h for workdays	Johansson and Johansson (2003)
	–	357	Mean PM10 mass for workdays	
London	500–1120	795	Exposure to PM9 mass for 3 h inside trains for different lines	Priest et al. (1998)
	–	801	Personal exposure to PM5 mass for time inside trains and on platforms	Sitzmann et al. (1999)
	1100–1500	–	Average hourly mean PM10 mass data from 07:00 h over 10 h at different underground stations	Seaton et al. (2005)
Cairo	794–1096	938	Average PM35 mass for 1 h between 10:00 and 18:00 h near a ticket office	Awad (2002)
Fine size fraction				
Budapest	–	51	Estimated average for PM2.0 mass data from 06:00 h over 12 h for workdays	Present work
Helsinki	23–103	60	Average hourly mean PM2.5 mass data from 06:00 h over 12 h for workdays	Aarnio et al. (2005)
New York	–	62	Exposure integrating ca. 5 h in underground railway stations and 3 h riding in trains	Chillrud et al. (2004)
London	–	246	8-h personal exposure to PM2.5 mass with time inside trains and on platforms	Pfeifer et al. (1999)
	270–480	–	Average hourly mean PM2.5 mass data from 07:00 h over 10 h at different underground stations	Hurley et al. (2003) Seaton et al. (2005)
Stockholm	105–388	258	Average hourly mean PM2.5 mass data from 07:00 h over 12 h for workdays	Johansson and Johansson (2003)
	–	199	Mean PM2.5 mass for workdays	
	220–440	288	Mean for ca. PM2.0 mass data over 3 h in the afternoon	Axelsson (1997)

HEI Review Committee, 2002) may be significant, even for the short times spent in underground railways. The exposure is repeated almost every day for most commuters, which may cause cumulative, quasi-long-term, or chronic health effects over time. It was estimated that PM exposure increased by several percent up to several tens of percent for normal travel routines in underground railways (Chillrud et al., 2004; Braniš, 2006). The present work and other studies (Chillrud et al., 2004; Aarnio et al., 2005; Seaton et al., 2005) indicate that the chemical composition and properties of indoor aerosol particles differ from those for the outdoor air (particles are larger and heavier, are mainly composed of Fe, and contain less black carbon); therefore, their impact on morbidity and mortality may also be different. It seems to be inappropriate or over-simplistic to estimate the health risk due to increased particulate mass only. Exposure to metals that are highly enriched relative to both average crustal rock and average outdoor air may represent a major proportion of daily personal exposure. The annual PM10 health LV for ambient outdoor air in Hungary (Act 14/2001) is 50 ng m^{-3} for total Cr and 25 ng m^{-3} for total Ni. Mean Cr and Ni concentrations in the metro, although determined for a substantially shorter time than 1 year, were greater than or quite similar to the limit in both cases. Train drivers and other workers, who spend several hours a day within the underground metro are subject to greater exposure to steel dust than the commuting public, and thus possibly greater health risks. Health regulations for workplace environments apply to such workers. The 8 h average maximum permissible concentration for inhalable ($\approx$PM10 fraction) inert dust in Hungary is 10,000 μg m^{-3} (Act 25/2000). In comparison, the limit for respirable quartz particles is 150 μg m^{-3}. The permissible average concentration in the respirable ($\approx$PM2.5) size fraction for work shifts is 6000 μg m^{-3} for Fe oxides, 500 μg m^{-3} for inorganic Cr compounds [except for Cr(VI)], 5000 μg m^{-3} for Mn and its inorganic salts, 100 μg m^{-3} for Ni and its oxides, and 1000 μg m^{-3} for Cu salts (Act 25/2000). The concentrations observed in the Astoria underground station were clearly lower (by several orders of magnitude) than the corresponding workplace limits.

The transition metals mentioned, however, are biologically active, and have documented negative health effects at high concentrations. To the best of our knowledge, health effects at intermediate concentrations (comparable to the ambient outdoor limit, but lower than the workplace limit) are still unknown. Information on the chemical forms and speciation, as well as the water solubility (bioavailability), of these metals is of major importance for further investigations. For instance, it is well documented that Cr(III) is a species essential for life, while Cr(VI) is toxic (WHO, 2000). The remaining open questions include the concentration levels during weekends compared to workdays, the spatial distribution of concentrations in different railway lines and locations within stations and inside vehicles, the dependence of PM2.5-fraction concentrations and the number of ultrafine particles on outdoor air quality and local meteorology, and the presence of asbestos, radon progeny and micro-organisms. The present research indicates that further coordinated studies need to be devoted to this subject.

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