Review on air pollutants sources and parameters to test

Deliverable Action A1
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When aiming to recommend abatement strategies to control and reduce PM exposure inside the underground metro system, information on the main sources in the area of study should be considered. A list of studies in recent published literature that include a discussion on the possible sources emitting airborne particles within the subway environment is shown in Table 1. Most of these publications involve chemical characterization and all agree on the high contribution of friction and abrasion processes between wheel and rail, brakes, or power cable (e.g. Aarnio et al., 2005; Abbasi et al., 2012; Colombi et al., 2013; Gómez-Perales et al., 2004; Loxham et al., 2013; Ma et al., 2012; Moreno et al., 2015; Murruni et al., 2009; Park et al., 2012; Park et al., 2014; Querol et al., 2012; Şahin et al., 2012; Salma et al., 2007; Salma et al., 2009; Sioutas, 2011). The effect of outdoor contamination, including secondary inorganic compounds and traffic emissions, has been identified in a number of metro systems, as for example in Shanghai (Zhang et al., 2012), Barcelona (Querol et al., 2012), and Stockholm (Midander et al., 2012). The impacts of other minor sources, such as ballast erosion (Ma et al., 2012), oil combustion (Park et al., 2014) and cleaning products (Park et al., 2012) have also been identified.

Table 1. Summary of studies including information on air pollution sources in the metro system.

City	Sources and related tracers	Study
Amsterdam (The Netherlands)	- Wheels, brakes, and rails interaction (Fe, Mn, Cr, Co, Ni, V, Zn, As); - contact wires (Cu, Ag, Sn, Mg, Cd); - pantographs (Cu, Pb, Sn); - brake blocks/dumping of sand (Si); - outdoor contribution (Cl^-, NO_3^-)	Loxham et al., 2013
Barcelona (Spain)	- Brake abrasion (Cu, Ba, Sr, Sn, Mo, Pb, Mg, OC, EC, Ti, Zn, Co, Ni, As, Cd, W, Al, Mn, Li, REEs, S, Cr, V); - outdoor contribution (NO_3^-, Na, NH_4^+, K, SO_4^{2-} , Se, V); - wheel-rail abrasion (Fe, Ca, Cr, Th, Sb, Mn, Rb, Al)	Querol et al., 2012
Barcelona (Spain)	- Wheels, rails (Fe, Mn, Al, Si, Ma); - brakes (Fe, C, Ba,Mg, Ca, Cr, Co, Sr, Mo, S); - electrical supply system (Fe, Cu)	Moreno et al., 2015
Budapest (Hungary)	- Electric conducting rail and sliding collectors, rails and wheels wear (Fe, Mn, Ni, Cu, Cr); - wind erosion of construction materials (Mg, Si, K, Ti); - outdoor contribution (S, K)	Salma et al., 2007
Budapest (Hungary)	- Friction and mechanical disintegration of steel (Fe, Mn, Cr); - sparking between the electric conducting rail and collectors (Fe, Cr); - wind erosion of construction materials (Mg, Si, K ,Ti)	Salma et al., 2009
Buenos Aires (Argentina)	- Contact wires; collectors (Fe, Cu); - outdoor contribution from traffic (Zn)	Murruni et al., 2009
Fukuoka (Japan)	- Train-wheel/Rail mechanical abrasion (Fe> Si, Ca, Al); - Train-Rail melting/sparkling (Fe); - Ballast/Coated abrasive (Si>Al, Fe, Ca); - Gravel/Cement beneath track (Ca>Si, Al, Fe)	Ma et al., 2012
Helsinki (Finland)	- Wheel–rail interface; the current collector; and the conductor rail (Fe, Mn, Cu, Ti, Ni); - vehicle traffic-outdoor contribution (OC, EC)	Aarnio et al., 2005
Istanbul (Turkey)	- Wheels, brakes, rails, catenaries (Cu, Fe)	Şahin et al., 2012

Los Angeles (USA)	- Steel used in light-rail systems (Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Mo, Cd, Ba, Eu); - ware of brakes (Ba); - coating on steel (Zn, K, Ti)	Sioutas, 2011
Los Angeles (USA)	- Steel used in light-rail systems (Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Mo, Cd, Ba, Eu); - ware of brakes (Ba); - coating on steel (Zn, K, Ti)	Kam et al., 2011
Mexico city (Mexico)	- Outdoor vehicle exhausts (EC, OC, TC, S); - brakes, rubber tyres (not specified)	Gómez-Perales et al., 2004
Mexico city (Mexico)	- Friction, brake system, sparking (Fe,); - soil and tunnel construction materials (SiO_2 ,Al_2O_3, Ca, Mg); - power transmission (Cu, Cr, Mn, Ni); - outdoor contribution (Co, Pb, V, Zn)	Mugica-Álvarez et al., 2012
Milan (Italy)	- Crustal oxides (C, Si); - wheel, brake, and track wear (Fe, Ba, Sb, Mn, Cu); - electric cable wear (Cu, Zn)	Colombi et al., 2013
New York (USA)	- Frictional abrasion (Fe, Mn, Cr)	Grass et al., 2010
Seoul (Korea)	- Electrical wire (Fe, Cu); - friction between wheel and brake block (Fe, Ca); - friction of rail (Fe, Mn); - outdoor contribution (Ca, NO_3^-, SO_4^{2-}, Na, Mg)	Kim et al., 2010a
Seoul (Korea)	- Friction between the rail and the brake block (Si, Ca, Fe)	Kim et al., 2010*b*
Seoul (Korea)	- Soil and road dust (Si, Mg, Cr, Ni); - abrasion of the railroad tracks, brakes, and power supply (Fe, Mn, Cu); - secondary nitrate (NO_3^{2-}); - cleaning (Cl^-); - secondary sulphates (SO_4^{2-})	Park et al., 2012
Seoul (Korea)	- Ballast tracks (Si, Ca,); - rail–wheel–brake interfaces (Fe); - outdoor contribution (S)	Jung et al., 2012*a*
Seoul (Korea)	- Oil combustion (Cr, Ni); - soil and road dust (Ca^{2+}, K^+, Mg^{2+}, Si, SO_4^{2-}); - rail, wheel, and brake wear (Fe, Mn, Si, Ba, Ca^{2+}); - abrasion of the power supply lines (Zn, Cu); - secondary aerosols (NO_3^-, SO_4^{2-})	Park et al., 2014
Seoul (Korea)	- Ferrous related source (Fe, Cu, Cr, Mn, Cd, Ba); - soil and road dust related source (Na^+, K^+, Si, Fe); - fine secondary aerosol source (NH_4^+, SO_4^{2-})	Lee et al., 2010
Shanghai (China)	- Wheel-rail mechanical abrasion (Fe, Mn, Cr, Cu, Ni)	Zhang et al., 2011
Shanghai (China)	- Traffic-related emission through indoor/outdoor air exchange (Benzene, toluene, ethylbenzene and xylenes); - solvent emissions (tetrachloroethylene)	Zhang et al., 2012
Stockholm (Sweden)	- Concrete sleepers (Ca, Al, K, Na, Mg); - rails (Fe, Si, Mn, Cr); - wheels (Fe, Si, Mn, Cr, V, Ni); - brake discs (Fe, Si, Mn, Cr, V,Mo); - brake pads (Fe, Cu, Zn ,Si, Al, Ti, Pb, Ca, Sb, Ba, Mn, Mg, Co, Cr, Mo, V); - electrical wire (Cu, Ag, Mg)	Abbasi et al., 2012
Stockholm (Sweden)	- Rail, wheel (Fe, Cr, Mn) - brake (Fe, Ba, Cu, Zn) wear	Gustafsson et al., 2012
Stockholm (Sweden)	- Breaks, wheels (Fe, C); - infiltration of vehicle exhaust emissions (EC, BC, VOCs)	Midander et al., 2012

In spite of this broad knowledge on potential sources of particulate matter (PM) at platforms and inside trains, only a limited number of works include an analysis using well-stablished receptor/statistical models for the quantification of the contribution of the different contaminant sources. The following studies on the subway environment apply receptor/statistical models to identify and quantify the contribution of the possible PM sources.

Murruni et al. (2009) performed cluster analysis on Fe, Zn and Cu concentrations measured at subway stations and the corresponding ones at ground level sites in Buenos Aires. The cluster analysis was carried out using 1-Pearson r distance as a similarity measure among variables. Authors related Fe and Cu with processes taking place inside the subway system (contact wires, collectors), while Zn was associated with outdoor vehicular traffic. The available information did not allow a quantification of the identified sources.

Lee et al. (2010) applied a positive matrix factorization (PMF) model to identify the source of particulate matter at a platform in the metro system of Seoul. 215 samples were collected and 18 chemical species were analysed for this purpose. PM_{10} for the station was characterized by three sources: ferrous related source (Fe, Cu, Cr, Mn, Cd, Ba); soil and road dust related source (Na^+, K^+, Si, Fe) and fine secondary aerosol source (NH_4^+, SO_4^{2-}). The authors observed that after installing platform screen doors (PSD), the average PM_{10} concentration decreased by 20.5% during the study periods. In particular, the contribution of the ferrous-related source emitted during train service in a tunnel route decreased from 59.1% to 43.8% since both platform and tunnel areas were completely separated by screen doors with air exchange only occurring during train arrival. However, the contribution of fine secondary aerosol sourced from various outside combustion activities increased from 14.8 to 29.9%, probably due to ill-managed ventilation systems and confined platform space. The contribution of soil and road dust related sources remained almost the same (26.1% without PSD and 26.3% with PSD).

Querol et al. (2012) performed Principal Component Analysis (PCA) for the quantification of sources in the metro system of Barcelona. To this end, the STATISTICA software package was used and varimax normalization was applied. Authors used 39 $PM_{2.5}$ and PM_{10} samples and analysed 42 chemical species. They identified three sources/factors of PM. Factor 1 (64% of the variance) contained Cu, Ba, Sr, Sn, Mo, Pb, Mg, OC+EC, Ti, Zn, Co, Ni, As, Cd, W, PMx, Al, Mn, Li, rare earth elements (REEs), S, Cr, V, and was associated with brake abrasion. Factor 2 (15.3% of the variance) contained NO_3^-, Na, NH_4^+, K, SO_2^{4-}, Se and V, representing the outdoor contribution to the platform ambient air and having a very low influence on the variability of PM on the platforms. Factor 3 (4.7% of the variance) contained Fe, Ca, Cr, Th, PMx, Sb, Mn, Rb, Al. Fe was the element with higher factor loading, which indicated that this group probably represented not only the wheel-rail abrasion products, but also resuspension emissions.

Park et al. (2012) identified major PM_{10} sources using PMF subway passenger cabins in Seoul. Authors collected 30 PM_{10} samples and used a matrix composed of 13 inorganic components (Mg, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ba, Pb) and four anions (Cl, NO_3^-, SO_4^{-2}). The PM_{10} sources characterized by PMF were soil and road dust sources (27.2%), railroad-related sources (47.6%), secondary nitrate sources (16.2%), and a chlorine factor mixed with a secondary sulphate source (9.1%). Overall, railroad-related sources contributed the most PM_{10} to subway cabin air. Authors observed that for the first pollution source, the explained variation values of Si, Mg, Cr, and Ni were relatively high and thus were classified as sources related to soil and road dust. The second pollution source included Fe, Mn, and Cu, with explained variation values higher than 0.5. Fe, Mn, and Cu serve as marker elements related to railroad operation and are generated by the abrasion of the railroad tracks, brakes, and power supply or draft lines during subway operation. This is the most significant of all the sources identified in this study. The third pollution source was NO_3^- which authors related to secondary nitrates present in the dust. The fourth pollution source comprised SO_4^{2-} and Cl^- ions, and was classified as Cl^- factors mixed with secondary sulphates. Cl^- in the passenger cabins was associated with residual chlorine particles from detergents used to clean the cabins or from passenger clothing.

The subway stations of Milan were investigated by **Colombi et al. (2013)**. Three PM_{10} samples were collected every day during 33 days. Samples were analysed for the determination of 19 chemical species. A cluster analysis was applied to day-time and night-time size-resolved average number concentrations and element concentrations at platform and mezzanine, in order to classify similar time trends. Authors reported that particles less than 1 micron stand alone in the classification or form a cluster with S, an element that is not emitted in the subway environment. On the platform level during the daytime on weekdays a second cluster was identified, linking particles with diameter between 1 and 3 mm with those elements that have been associated with train operation. At the mezzanine level and during the night particles between 1 and 3 mm were associated with elements of crustal origin, while the elements originating from the wear of metal parts formed an independent cluster. Cl was associated with external and occasional internal sources such as detergents used in cleaning operations. External air was found to have little influence on local PM concentrations, and its contribution was mostly observed in the sub-micron size range. In summary, at platforms Fe, Mn, Sb, and Ba oxides, related to wheel, rail, and brake wear, were reported to account for 40-73% of total PM_{10} mass on average, and Cu and Zn oxides, related to electric cable wear, for 2-3%. Total metal oxides in the urban ambient air, excluding crustal compounds, represented about 17% of total PM_{10} mass on average.

In **Park et al. (2014),** authors assessed the contribution of main PM_{10} sources in a subway tunnel in Seoul also using Positive Matrix Factorization (PMF). They collected 44 PM_{10} samples, which were analysed for 18 species. The PMF analysis identified five factors as sources of PM_{10} pollution in the subway tunnel. For the first source, the highest explained variations corresponded to Ni, Cr, SO_4^{2-} and Ca^{2+}. This source could be identified as various types of oil combustion, with a contribution of 17% to the PM_{10} level. The second source included Ca^{2+}, K^+, Mg^{2+}, Si and SO_4^{2-}, attributed to soil and road dust. These elements in outdoor soil and road dust can enter a subway tunnel through vents. The crustal particles were associated with unpaved roads, construction sites, and windblown soil dust. This source contributed 5.4% of the PM_{10}. The third source was rail, wheel, and brake wear, originating from indoor emissions due to the movement of trains. Fe, Mn, Si, Ba and Ca^{2+} were the main markers, generated by the abrasion of the railroad tracks and brakes during subway operations. Authors quantified that pollution related to rail, wheel, and brake wear accounted for 59.6% of the PM_{10} in the subway tunnel. Zn, Cu, Cl^-, and Ca^{2+} accounted for a large proportion of the fourth profile, which was identified as pollution related to electric cable wear (8.1% of the PM_{10}). Zn and Cu are markers of subway operations and are generated by abrasion of the power supply lines during subway operation. Authors quantified a fifth factor, characterized as secondary aerosols based on the presence of NO_3^- and SO_4^{2-}, with a contribution of 10% of PM_{10}.

CONCLUSIONS

The review presented in this report highlights the lack of works quantifying the contribution of indoor sources at underground metro systems under different platforms designs or ventilation conditions, with mostly of these studying only the PM_{10} size fraction. The metro system of Seoul is the only one which includes a detailed characterization of factors affecting the air quality, while this information is very limited in European cities. According to the considered studies, the contribution of indoor-generated sources at platforms ranges between 44 and 69 % (Figure 1), with the lowest percentage corresponding to a station with platform screen doors (PSD).

In order to more fully characterize passenger's exposure in metro systems, reduce emissions and propose a good practice guide for future subway lines constructions, more detailed source apportionment studies based on a large number of samples and analysed chemical species is needed.

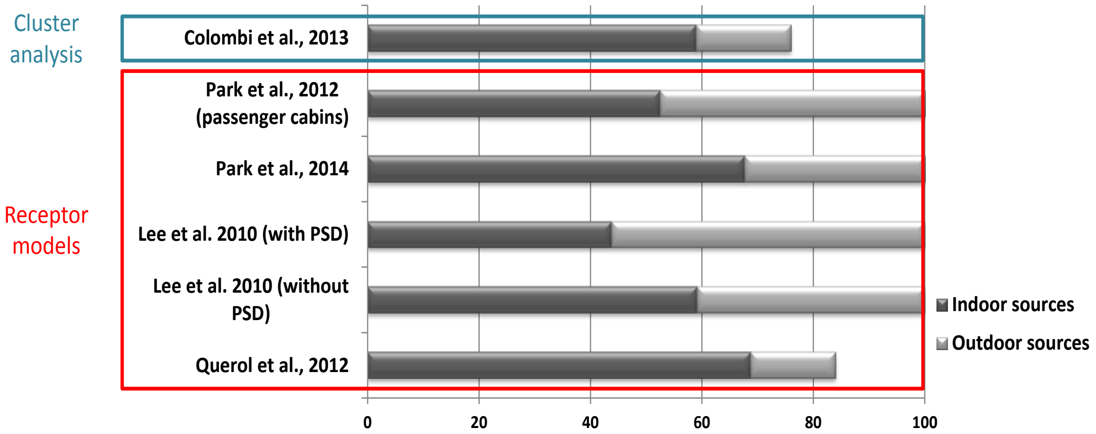

Figure 1. Contribution of indoor and outdoor sources reported in different studies. The methodology employed for the quantification has been indicated.

Following the results from a total of 62 studies, carried out in 30 different cities, shown in both the "Historical PM levels and chemical composition database" (deliverable action A1) and this report, the main parameters to be considered in future subway air quality studies are as follows:

- particle mass concentrations,
- inorganic and organic chemical composition,
- black carbon concentrations,
- particle number concentrations and size distribution,
- microscopy (for size, shape and chemical composition of individual particles),
- toxicity,
- bioaerosol concentrations,
- concentration of gases such as NO, NO_2, CO, CO_2 and ozone concentrations,
- and identification of contaminant source (source apportionment).

The examination of these reports has facilitated the determination of the main parameters on which to focus in IMPROVE LIFE, and revealed the existence of obvious gaps in knowledge. In order to obtain the most comprehensive database in IMPROVE we will need to monitor the maximum number of parameters, including not only those most commonly shown in other studies (i.e. particle concentrations and inorganic chemistry), but also others less frequently studied such as particle numbers, size distribution, organic chemistry, microscopy studies, bioreactivity, gaseous components, combined with a detailed source apportionment study based on a large number of samples. The selection and analysis of these parameters to be tested will then enable us to move on to the development of the implementation actions.

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