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Chemical Characterization of Airborne Particles Collected in an Underground Metro Station Platform in Delhi City

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Transport systems in urban land spaces are shifting to underground due to the unavailability of space on the surface. Nowadays, the underground metro system has become an imperative mode of transport. Since people spend considerable time in underground metro stations (UMS), indoor air quality (IAQ) has become an important parameter of investigation. However, maintaining IAQ at UMS has become a major issue for developing countries. Hence, the assessment and management of IAQ in UMS is important for a healthier indoor environment. The present study includes an elemental composition of indoor/outdoor (I/O) particulate matter in a UMS in Delhi city, India during winter season. The study mainly focused on metals and carcinogenic elements. Out of 41 metals analyzed, the main contributors to the indoor pollution at the UMS platform and outdoor were Iron at a concentration of 24.54 µg/cm2 and 2.58 µg/cm2, followed by Manganese 0.36 µg/cm2 and 0.08 µg/cm2, Copper 0.73 µg/cm2 and 0.15 µg/cm2, Calcium 12.77 µg/cm2 and 4.55 µg/cm2 and Silicon 34.70 µg/cm2 and 10.92 µg/cm2, respectively. Further, it has been found that indoor elemental concentrations are higher than that of outdoor environment concentrations. The results of this study will help identify the different sources from various activities within the UMS, in order to select suitable environmental management techniques to manage the IAQ in UMS better.

Keywords: *Elemental compositions, Indoor air quality, Particulate matter, Underground metro station*

Introduction

Most of the people spend their time indoors more than outdoors, either at residential, commercial, working environments or in transit and there is an increasing concern over the IAQ in different microenvironments and its effects on public health. The UMS have been considered as an important mode of transport in order to improve the quality of transport, relieve congestion, as well as to fill the gaps of insufficient public transport and the road surface capacity (Pfeiffer et al., 1996). It has a unique microenvironment because of their closed character, restricted ventilation, specific emission sources and complex indoor meteorology. The confined space in the underground metro

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environment enhances the concentration of pollutants either by infiltration from outdoor or internal generation (Boudia et al., 2006; Chan et al., 2002; Kang et al., 2008). Delhi being a metropolitan city forces millions of people to choose the underground metro systems over other road transportation systems owing to its speed and convenience. The Delhi Metro Rail Corporation (DMRC) system carries approximately 2.5 million passengers daily (www.delhimetrorail.com). Since people spend a considerable amount of time in the underground metro system daily, the IAQ has become an important apprehension for the users in metro stations (Johansson and Johansson, 2003). The sources of the different indoor air pollutants within the UMS and its health effects on the metro users (i.e. both metro staffs and commuters) are of great concern.

Numerous scientific studies show that the airborne particle concentrations in UMS differ from street-level particulate matters (PM) with respect to its particulate morphology, concentration, size distribution, and its chemical compositions. Relative to street-level particles, subway particles are generally more angular in shape, larger in diameter, more abundant by mass, and contain higher levels of the metals found in steel (Sitzmann et al., 1999; Seaton et al., 2005; Lee et al., 2012). The metallic composition of PM found in UMS includes iron (Fe), manganese (Mn), chromium (Cr), nickel (Ni), and copper (Cu) (Aarnio et al., 2005; Chillrud et al., 2005; Colombi et al., 2013; Eom et al., 2013; Frampton et al., 1999; Kam et al., 2011; Li Guo et al., 2014; Lu Senlin et al., 2015; Ripanucci et al., 2006; Salma et al., 2007). It indicates that PM at UMS is generated through the friction of wheels and rails, brake wear, and the vaporization of metals due to sparking (Pfeiffer et al., 1996; Sitzmann et al., 1999). In New York City, the concentrations of Fe, Mn, and Cr in suspended particulate matter (SPM) have been found to be more than 100 times higher in the subway station than above the ground level (Chillrud et al., 2005). These subway particles have a greater capacity to induce Deoxyribonucleic acid (DNA) damage and oxidative stress in cultured lung cells than outdoor (street-level) particles due to their high reactivity (Karlsson et al., 2005; Seaton et al., 2005; Simge Taner et al., 2013). Further, Zhang et al. (2011) carried out scientific research on the magnetic characterization and geochemistry of dust particles in the Shanghai metro system. Their results shows that the magnetic properties of the particles were of scrap-iron and spherical magnetic particulates, and that there were higher levels of Fe and Mn, and lower levels of aluminium (Al) and titanium (Ti), in metro system dusts (Lu Senlin et al., 2015).

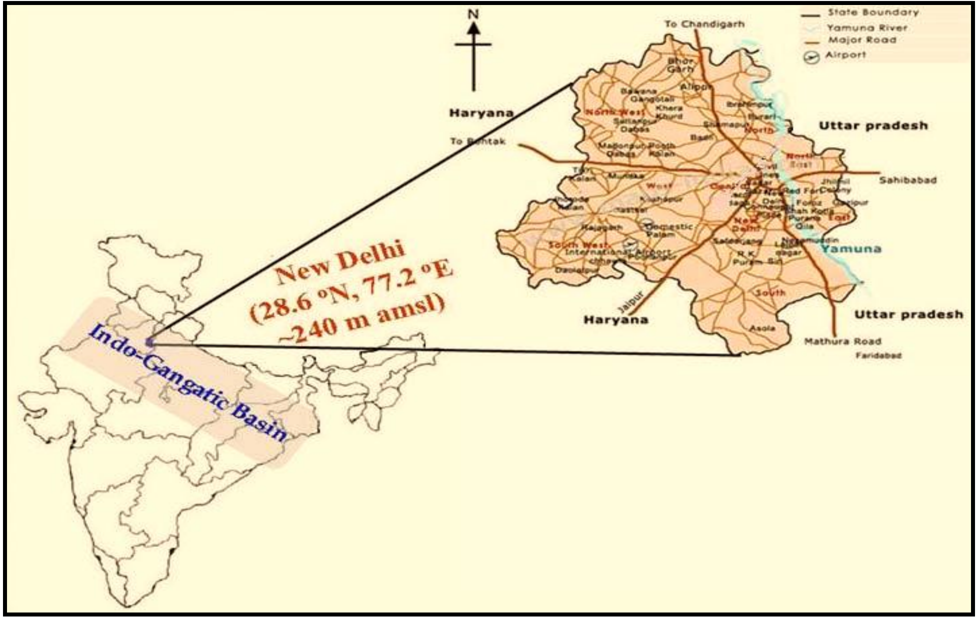
This is a novel study in the Delhi metro analyzing the chemical compositions of the respirable suspended particle (RSP) [viz., particles with diameter of 10 micrometers or less] collected at one of the selected UMS platform and outdoor environment in Delhi city, India, using a quantitative particle analysis based on Energy Dispersive X-Ray Fluorescence (EDXRF).

Materials and Methods

Study Site

Delhi is a part of the Indo-Gangetic plains at an elevation ranging from 213 meters to 305 meters above the mean sea level and lies between latitudes 28°12’ to 28°63’ N and longitudes 75°50’ to 77°23’E with a total area of 1484.46 km2 (Figure 1). The climate of Delhi is semi-arid and is mainly influenced by its inland position and prevalence of continental air all throughout the year (Mugica Alvarez et al., 2012).

Figure 1. *Study Site Map*

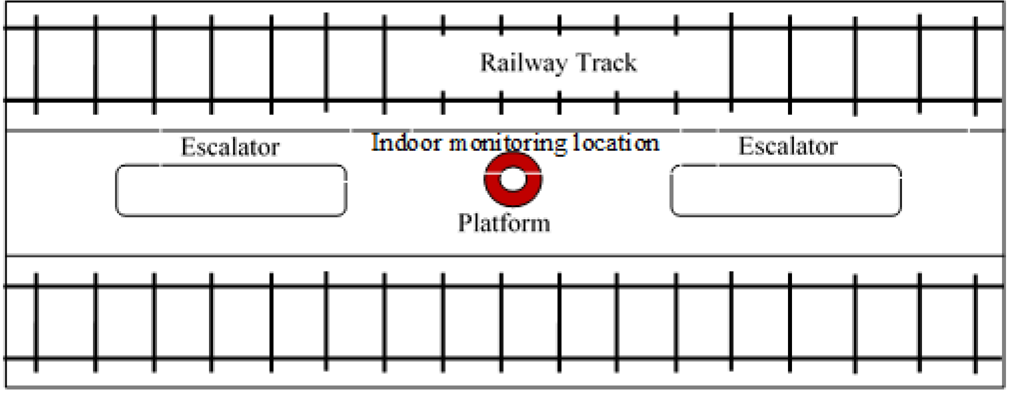


Particle Collection

We had selected one of the busiest UMS on the yellow line in the DMRC network as the number of commuters keeps increasing at a steady phase. Monitoring and collection of RSP was done simultaneously in the UMS platform and outdoor environment.

A measurement of RSP collected from indoor and outdoor environments was done at a 24 hrs average monitoring frequency at a selected UMS during winter season (i.e. December, 2013 to February, 2014). For the monitoring of RSP, an environmental dust monitor [GRIMM, 1.107 model] was used and air flow was maintained at 1.2 L min^{-1}.

Figure 2. *Monitoring Location in UMS*



The monitoring equipment was kept at the middle of the UMS platform (Figure 2) inside the metro station. The monitoring device was kept on the rooftop of the building (~ 12 m above ground level) for the measurement of the outdoor RSP. Particles were collected on 47 mm diameter polytetrafluoroethylene (PTFE) filters of pore size 1.2 µm.

Analytical Method

EDXRF spectrometry can be used for all elements (USEPA Method IO 3.3) (U.S. Environmental Protection Agency, 1999). This analysis technique is nondestructive and requires minimal sample preparation - the filter is inserted directly into the instrument for analysis (Perrino et al., 2011). In this study, a total of 41 elements were analyzed quantitatively by using XRF.

Results and Discussion

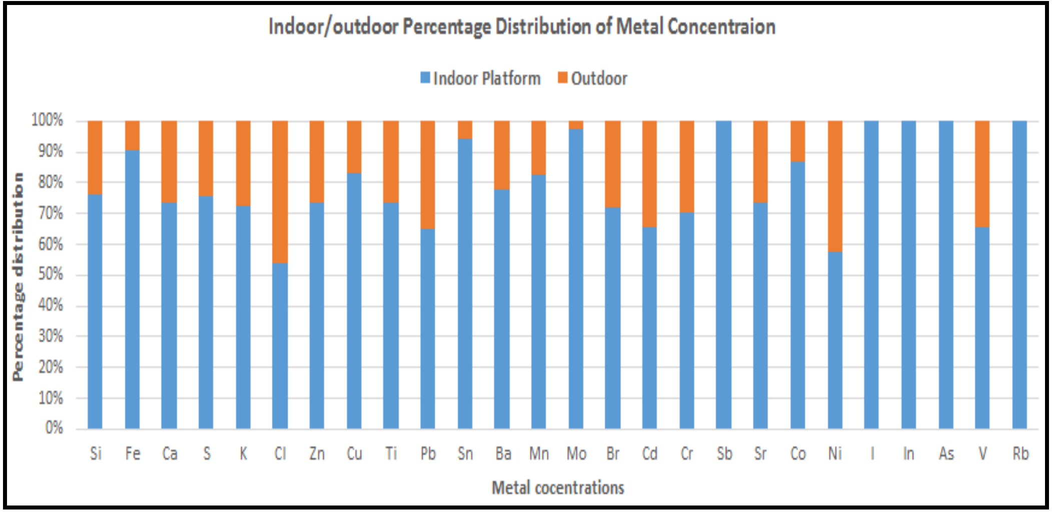
In this study, characterized metals are distributed into two categories i.e. trace (Mn, Cu and Zn) and carcinogenic (Cr, Ni and Cd). Trace elements were found to be dominant in comparison to carcinogenic metals influencing the indoor RSP collected in the UMS platform (i.e. Zn > Cu > Mn > Cd > Cr > Ni) (Table 1).

Table 1. *Indoor/Outdoor Metal Concentration in UMS*

S. No.	Name of the elements	Symbol	Detection limit in µg/cm^2	Indoor platform µg/cm^2	Outdoor platform µg/cm^2	OSHA permissible exposure limit µg/cm^2
1	Silicon	Si	0.3531	34.6903	10.9224	NA
2	Phosphorus	P	0.0093	BDL	BDL	NA
3	Sulphur	S	0.0609	6.3082	2.0501	NA
4	Chlorine	Cl	0.0216	4.2014	3.5892	NA
5	Potassium	K	0.0024	5.0885	1.9202	NA
6	Calcium	Ca	0.003	12.7726	4.5459	NA
7	Scandium	Sc	0.0069	BDL	BDL	NA
8	Titanium	Ti	0.0042	0.6902	0.2461	NA
9	Vanadium	V	0.0012	0.0148	0.0078	NA
10	Chromium	Cr	0.0021	0.1205	0.0501	1
11	Manganese	Mn	0.006	0.3585	0.0762	0.2
12	Iron	Fe	0.0081	24.5378	2.5765	1
13	Cobalt	Co	0.0027	0.0466	0.0072	0.1
14	Nickel	Ni	0.0027	0.0354	0.0261	0.1
15	Copper	Cu	0.0036	0.7324	0.1499	1
16	Zinc	Zn	0.006	1.0397	0.3734	5
17	Gallium	Ga	0.015	BDL	BDL	NA
18	Germanium	Ge	0.0084	BDL	BDL	NA
19	Arsenic	As	0.0048	0.0159	BDL	0.01
20	Selinium	Se	0.0096	BDL	BDL	0.2
21	Bromine	Br	0.0048	0.2383	0.092	NA
22	Rubidium	Rb	0.0018	0.0133	BDL	NA
23	Strontium	Sr	0.0099	0.0656	0.0233	NA
24	Yttrium	Y	0.0096	BDL	BDL	NA
25	Molybdenum	Mo	0.0078	0.3475	0.0084	15
26	Rhodium	Rh	0.0192	BDL	BDL	NA
27	Palladium	Pd	0.0171	BDL	BDL	NA
28	Silver	Ag	0.0132	BDL	BDL	NA
29	Cadmium	Cd	0.0186	0.1339	0.0708	0.01
30	Indium	In	0.0189	0.0244	BDL	NA
31	Tin	Sn	0.0249	0.5077	0.03	2
32	Antimony	Sb	0.0231	0.0917	BDL	0.5
33	Tellurium	Te	0.0222	BDL	BDL	NA
34	Iodine	I	0.0264	0.0265	BDL	NA
35	Caesium	Cs	0.0375	BDL	BDL	NA
36	Barium	Ba	0.0441	0.5052	0.146	0.5
37	Lanthanum	La	0.0831	BDL	BDL	NA
38	Tungsten	W	0.0387	BDL	BDL	NA
39	Gold	Au	0.009	BDL	BDL	NA
40	Thallium	TI	0.0063	BDL	BDL	NA
41	Lead	Pb	0.0072	0.5303	0.2816	0.05

BDL-Below detection level; NA-Not available

Figure 3. *Indoor/Outdoor Percentage Distribution of Metal Concentration*



Out of the 41 metals analyzed from RSP, Fe was the second most abundant metal. Fe may have originated from wear of steel during the friction periods between wheels and rail, wear of brakes and the vaporization of metals due to sparking between the rail and wheel (Gutierrez et al., 2006). Further, Eom et al. (2013) have found that the Fe concentration is the most enriched metal in the underground metro systems, iron species in subway particles are of prime interest because of their different toxicity and magnetic properties according to the iron species (Eom et al., 2013). The concentration of Mn was less consistent. High levels of Mn were measured in some metro stations and the contribution from outside traffic is suspected (Awad, 2002), while other studies (Cheng et al., 2008; Okeson et al., 2004) reported the contribution of Mn from friction erosion of the metro rails. Furthermore, dust re-suspension was linked with passenger activities, effect of train piston effects (airflow at the front of the platform) and floor cleaning (Aarnio et al., 2005).

In this analysis, high mass concentration of Fe was found the most abundant element in the UMS platform, i.e. nearly 9.5 times higher than that measured in ambient RSP. Other scientific studies also confirmed that a high concentration of Fe has also been found in the London (Seaton et al., 2005; Vasconcellos, 2001), Mexico City (Mugica Alvarez et al., 2012) and Helsinki (Aarnio et al., 2005) subway particles. The Mn is likely to be produced from processes at rail wheel brake interfaces, because Mn is another component of rail steel (Li Guo et al., 2014). The crustal species such as K, Ca and Ti are mainly originated from soil (Kam et al., 2011). Furthermore, the re-suspension of particles was linked with commuters activities, piston effect (airflow at the front of the platform), and floor cleaning (Awad, 2002). Other important determinants of the increasing levels of exposure to RSP may also derive from improper maintenance ventilation systems in UMS (i.e. supply ducts), tunnels and train movements within UMS (Furuya et al., 2001). The indoor/outdoor percentage distribution of the elemental concentration also confirms that most of the elements are released within the UMS. Out of 41 elements, only 26 elements were plotted, others are BDL (Figure 3).

Numerous scientific studies have found that the particles from the UMS are mainly from the rail wheel brake, particle re-suspensions due to internal activities and the infiltration of particles from outdoor environments (Jung et al., 2012; Querol et al., 2012).

The element concentrations measured in this study were compared with international regulations and guidelines and were found to be considerably lower than the limit values stipulated by the Occupational Safety and Health Administration (OSHA) regulations in the US (eg. As, Cr, Co, Cu, Pb, Ni and Mo). The accepted limit values for different metals recommended by OSHA for As = 10 µg/m3, Cr = 1 mg/m3, Co = 0.1 mg/m3, Cu = 1 mg/m3, Pb = 50 µg/m3, Ni = 1 mg/m3, Mo = 15 mg/m3 and the international guidelines (e.g., WHO Air Quality Guideline for Pb = 500 ng/m3 and Cd = 5 ng/m3) (Crump et al., 2000).

The evidence implicates that transition metals are mediators of inflammation and cytotoxicity via oxidative mechanisms. Ambient air particles contain ionizable metals that produce reactive oxygen species in aqueous solutions generating oxidative stress (Colombi et al., 2013). Soluble transition metals such as Co, Cu, Fe, Mn, V and Zn participate in various metabolic and signaling pathways and have been related with DNA damage and oxidative stress (Furuya et al., 2001; Kim et al., 2008).

Conclusions

This is the first comprehensive IAQ study in UMS in Delhi city, which could serve to build up a better understanding of the mass/chemical speciation and its negative health effects of RSP on commuters and workers in the UMS. The results of this present study show that the indoor elemental concentrations in UMS platform have a higher than the above ground level. Trace elements were found to be dominant in carcinogenic metals influencing the indoor RSP collected in UMS platform (i.e. Zn > Cu > Mn > Cd > Cr > Ni). Further, the present analysis provided a comprehensive assessment of RSP and its chemical characterization in selected UMS in Delhi city. In addition, this study may ultimately provide a unique database and systematic methodology for carrying out the IAQ study in the UMS. In India, the comprehensive IAQ study in the UMS is not done so far.

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