Thermal and Hygroscopic Properties of Indoor Particulate Matter Collected on an Underground Subway Platform

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ABSTRACT

In order to clarify the thermal and hygroscopic properties of indoor particulate matter (PM) in a semi-closed subway space, which is critically important for understanding of the distinctive particle formation processes as well as the assessment of their health effects, the size-resolved PMs (i.e., PM2.5 and PM10-2.5) were intensively collected on the platform of Miasageori station on the Seoul Subway Line-4. The elemental concentrations in soluble and insoluble fractions were determined by PIXE from the bulkily pretreated PM2.5. The thermal and hygroscopic characteristics of individual particles were investigated via a combination of the unique pretreatment techniques (i.e., the high-temperature rapid thermal process and the water dialysis) and SEM-EDX analysis. Iron and calcium were unequaled in insoluble and soluble PM2.5 fractions, respectively, with overwhelming concentration. The SEM-EDX’s elemental net-counts for the pre- and post-pyrolyzed PMs newly suggest that magnesium and several elements (i.e., silica, aluminum, and calcium) may be readily involved in the newly generated subway fine PM by a high-temperature thermal processing when trains are breaking and starting. Through the water dialysis technique, it turned out that calcium has meaningful amount of water soluble fraction. Furthermore, the concentrations of the counter-ions associated with the calcium in subway PM10-2.5 were theoretically estimated.

Key words: Particulate matter, Subway, Individual particle, Water solubility, Dialysis, Thermal property

1. INTRODUCTION

Many previous studies have pointed out that the semi-closed underground space of subway transit systems in most metropolitan areas worldwide are a great reservoir as well as a generator of particulate matter (PM) (Abbasi et al., 2011; Kim et al. 2010; Lorenzo et al., 2006; McDonnell et al., 2000). The ultra-fine particles with a sized from 100 to 350 nm in diameter are generated by a high-temperature rapid thermal processing when train stops and starts. During braking, both the wheel-mounted disc and the brake pads are worn, then, generate very small size PM (Abbasi et al., 2011). When a train stops wheels lose their cohesive adhesion, then enormous heat is produced, and will actually generate vapors by melting both wheels and the rail. Meanwhile, relatively coarse PMs are likely generated by mechanical processes such as the shaking of train, abrasion of train body, abrasion of power cable, and abrasion of ballast and subgrade. These mechanically generated PMs are sized between 3 and 7 μm in diameter (Abbasi et al., 2011; Lorenzo et al., 2006).

Although, in a dominating amount, subway PM consists of iron, it also contains toxic heavy metals like copper, zinc, nickel, manganese, chromium, and cadmium (Kim et al., 2010). It has been reported that the respirable PM whose aerodynamic diameter is less than 10 μm and that contains heavy metals can affect the eyes and nasal mucosa and causes respiratory diseases (Lebowitz, 1996; Pope, 1991). At present, the risk assessment of subway-originated heavy metal PM to the living body has been reported that heavy metal PMs cause oxidative stress, DNA damage, and inflammatory reaction (Karlsson et al., 2005; Seaton et al., 2005).

Recently, in addition to the role of transportation, the spaces of subway tend to play parts in centers of daily activities such as various cultural events and commercial activities. Therefore, our concern about the potential exposure to the risky subway PM is growing day by day.

To know the thermal properties of indoor PM in an underground subway space is crucial for understanding of the mechanism of PM generation during train’s breaking and starting.
The PMs failed to deposit on nasal hairs, oral cavity, and nasal cavity, the larger ones will deposit in the tracheobronchial airway region and may later be eliminated by mucociliary clearance. If PMs are soluble, most of them may enter the body by dissolution, and then release potentially harmful material to the body (Morrow, 1992; Heyder et al., 1986). Moreover, if the watersoluble components dissolve in sweat and pass through the skin into the bloodstream, this can lead to more harmful health risk (Garrod et al., 1998; De Vreede et al., 1998). Therefore, in order to fully understand the health risk of subway PM and to improve the indoor air quality of underground subway, the water solubility of subway PM must be comprehensively investigated.

The purpose of the present study is to clarify the thermal and hygroscopic properties of indoor PMs (both individual and bulk) collected on an underground subway platform.

2. EXPERIMENTAL METHODS

2.1 Sampling of Size-resolved Particle

Size-resolved PM sampling was intensively performed on the platform of Miasageori station (37°36′48″N, 127°01′48″E) on the Seoul Subway Line-4 on Aug. 21st, 2012. The details on this subway station (i.e., schematic structure, tracks at a railway, ventilation, running train number and passenger number, and outdoor traffic) have been already described in our previous study (Ma et al., 2015).

In order to estimate the thermal property and water solubility of individual and semi-bulk subway PMs as a function of their size, multi kinds of filter media (i.e., the non-hole Nuclepore® filter (GE Healthcare Whatman) for PM_{10.2,5} and the Nucleporefilter® (GE Healthcare Whatman) with 0.2 μm pore size for PM_{2.5} and backing materials (i.e., the Ag film with 99.99% purity (Kojundo Chemical Lab. Co.) and the semipermeable membrane fixed at a Pt grid (3 mm diameter) (Spectrum Lab. Co.) were arranged on the stage of a two-stage multi nozzle cascade impactor (MCI) samplers (Tokyo Dylec Co.) sampler. The details of MCI sampler including its particle cut-off have been described elsewhere (Ma et al., 2015). To take account of PM’s health effect, an MCI sampler was installed at 1.6 m above platform surface and operated for 4 h.

2.2 Pretreatment and Elemental Analysis of Bulk PM_{2.5}

In order to separate PM_{2.5} into soluble and insoluble fractions and to make them closer to uniform, the PM_{2.5} sample was pretreated by the following procedures. The filter was extracted ultrasonically with 10 mL of deionized water (18.2 MΩ·cm²/cm). And then the extracted water was filtrated through a 25 mm diameter Nuclepore® filter with 0.08 μm pore size to separate into the soluble and insoluble fractions. After filtration, the filtrate and residue were considered to be soluble and insoluble fractions, respectively. Both fractions of PM_{2.5} were irradiated by the proton beam of Particle Induced X-ray Emission (PIXE) installed at the Cyclotron Research Center of Iwate Medical University. This PIXE analytical system has the great advantages such as an excellent sensitivity, a nondestructive technique for multielement with a wide range of elements (Z>10), and a short measuring time (3-10 minutes for typical environmental samples). The sensitivity, if defined by the ratio of (PIXE yield per unit dose)/(mass thickness), can be determined experimentally and theoretically for all objective elements. For instance, the sensitivity of calcium was calculated to be 1700 (counts·cm²/μC·μg) with a detection limit of 9.4×10⁻³ (μg/cm²). The more detailed analytical set-up and the procedures on sample pretreatment for PIXE analysis were described elsewhere (Sera et al., 1999).

2.3 Pretreatment for Single Particle Analysis

From a health effect perspective, it would be absolutely necessary to make clear assessment about water-soluble fraction of subway PM. In order to separate the water-soluble fraction from individual subway PM_{10.2,5}, the technique of water-dialysis was applied. Water-dialysis method is effective to remove water-soluble components from individual particles (Zhang, 2003). If a mixture of dissolved ions and insoluble portion is placed on a semipermeable membranes suspended in water, the ions pass through the pores of membranes. Fig. 1 demonstrates a portion of the Pt grid with 3 mm diameter (left) and the structure of semipermeable membrane fixed at Pt grid (right). The individual particles collected on this semipermeable membrane were the target of dialysis. Diagram of dialysis process for individual subway particles is illustrated in Fig. 2. The dialysis procedure was well established by Zhang et al. (2003) and it can be summarized as follows: (1) fix Pt grid on a stainless steel mesh stand (Okenshoji Co. Ltd.); (2) put the stand in a stainless steel settlement dish (Okenshoji Co. Ltd.), which has a drain tap at its bottom; (3) input gradually distilled water into the dish and stop before water reaches the top of the stand; (4) cover the dish and leave it for one hour; (5) remove the cover of the dish and add distilled water with a syringe slowly into the dish until the grid was completely got into water; (6) cover the dish and leave it for another hour; (7) remove slowly the water in the dish from the drain tap; and (8) transfer the stand to a desiccator (Rh <30%) for dehydration.
The more details of dialysis processes employed in this study have been described elsewhere (Zhang et al., 2003).

Meanwhile, in order to clarify the thermal property of individual subway particles, the particle collected on the Ag film was placed in an electric furnace (Labotechno Co.) and exposed at 500°C atmosphere for 20 seconds.

2.4 Morphological Observation and Elemental Analysis of Individual Particle

A Scanning Electron Microscope (SEM) (SS-550) equipped with an Energy Dispersive X-ray Detector (EDX) (Genesis 2000) was employed on the analysis of individual particles in PM$_{10-2.5}$. Before the pretreatment (i.e., dialysis and heating), the morphological observation and elemental analysis of the randomly-selected original individual particles were carried out under 15-20 kV working conditions. After the pretreatment, the residue particles experienced dialysis and heating processes were also analyzed again using the SEM-EDX system under the same analytical conditions. And then, the morphological and elemental natures of individual particles were compared with those before pretreatments.

3. RESULTS AND DISCUSSION

3.1 Soluble and Insoluble Fractions of Subway PM$_{2.5}$

Fig. 3 displays the elemental concentration of soluble and insoluble fractions of bulk PM$_{2.5}$. As might be expected, in Fig. 3, the main peculiarity is the enrichment of insoluble iron. It is well-known that iron is the most abundant composition in subway PM. The iron-rich small-size PM might be formed from the thermal metamorphism of numerous train wheels and the me-
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Mechanical friction of electrical wires. When a train stops and starts an enough heat is produced to melt iron (Kim and Ro, 2010; Mori et al., 2007; Lorenzo et al., 2006).

As the next enrich element, calcium and silica were detected in soluble and insoluble fractions, respectively. Most of them in PM$_{2.5}$ were also probably derived from the thermal processes occurred between train wheels and rail during train stopping and starting. During braking and stopping a heavy train system is the great input of heat flux into rain and break disc in a very short time. Iron, calcium, silica, and magnesium are mainly involved in cement as Fe$_2$O$_3$, CaO, SiO$_2$, and MgO, respectively (Institute of Environmental Research at Kangwon National Univ., 2006). Since Seoul subway has been used cement as common sleeper for bridging underneath the railway tracks, the powder of cement and the cement origin coarse PM are easily deposited on rails as well as on wheels by vibration and train induced wind. Then they have experience of thermal metamorphism. Fig. 4 illustrates the new fine-particle generation from the frictions between train wheel and rail as well as between brake pad and train wheel.

Meanwhile, several toxic components such as manganese and chromium also show a meaningful detection from subway PM$_{2.5}$. Chillrud et al. (2004) pointed out that the exposure levels of these harmful metals with together iron among high-school students were substantially increased while they were commuting via the NYC subway system.

3.2 Thermal Properties of Individual Subway PM$_{10-2.5}$

When a brake is working, the transformation of kinetic energy of moving masses into thermal energy takes place. As mentioned above, to clarify the thermal property of coarse PM in subway is of great importance to understand the distinctive processes of the secondary fine PM formation as well as to find means of controlling of indoor air quality in subway space. In order to gain knowledge on the mechanism of fine PM generation by thermal heating, the particles collected on the Ag film experienced a heat treatment (i.e., 500°C for 20 sec.).

Tudor et al. (2003) evaluated the maximum tempera-
Fig. 5. Variation of relative elemental wt% of individual PM_{10.2.5} (n = 550) before and after heating (500°C for 20 seconds).

Fig. 6. Morphological change of individual particles (PM_{10.2.5}) before (left) and after (right) dialysis.

Fig. 7. Box plots for the net count of three major elements (i.e., calcium, silica, and iron) in individual PM_{10.2.5} before and after dialysis.
body, health effects resulting from exposure to water-
soluble subway PM have to be obviously investigated. 
A variety of actions for the improvement of the indoor 
air quality of underground subway should also be car-
ried out simultaneously.

3.4 Theoretical Calculation of Counter Ions of Calcium in PM_{10-2.5}

It was apparent from the previous results that calcium 
was the most abundant water-soluble fraction in sub-
way PM. It is therefore critically important to clarify 
the amount of counter ions of calcium for the assess-
ment of their risks to human health.

The major solid salts containing calcium can be clas-
sified into two groups based on their water solubilities. 
CaCO_3, CaC_2O_4, and Ca_3(PO_4)_2 belong to the water 
insoluble group because of the lower values of their 
solubilities. Their water solubilities are 6.1 × 10^{-4} g, 
6.7 × 10^{-4} g, and 2.5 × 10^{-3} per 100 g-H_2O, respectively. 
On the other hand, Ca(NO_3)_2, CaCl_2, and CaSO_4 can 
be classified as water-soluble. Although CaSO_4 has 
low solubility (2.4 × 10^{-3} g/100 g-H_2O), in this study it 
was accounted as water soluble.

Therefore, under the assumption that calcium ion 
mainly combines with three-kind of counter ions (i.e., 
chloride, nitrate, and sulfate), the concentrations of 
chloride, nitrate, and sulfate in PM_{10-2.5} can be theoret-
cally calculated.

In the first place, the mass concentration of water 
soluble calcium (M_{sol.Ca}) can be calculated by the fol-
lowing equation:

\[ M_{sol.Ca} = M_{PM_{10-2.5}} \times \left( \frac{Ca_{wt\%}}{100} \times \frac{Ca_{N.C.D_{Pr.}} - Ca_{N.C.D_{Po.}}}{Ca_{N.C.D_{Pr.}}} \right) \]

where \( M_{PM_{10-2.5}} \) is mass concentration of PM_{10-2.5} mea-
sured by filter weighing. \( Ca_{wt\%} \) is the SEM-EDX wt\% of Ca in untreated PM_{10-2.5}, \( Ca_{N.C.D_{Pr.}} \) and \( Ca_{N.C.D_{Po.}} \) are the SEM-EDX net counts of Ca in PM_{10-2.5} before 
and after dialysis, respectively.

Then, the mass concentrations of chloride (M_{Chloride}), 
nitrate (M_{Nitrate}), and sulfate (M_{Sulfate}) as the counter ions 
of calcium can be calculated based on the following formulas:

\[
M_{Chloride} = M_{sol.Ca} \times \left( \frac{2Cl_{A.W.}}{\sum_{i=1}^{3} C.I.M.W.} \cdot \frac{2Cl_{A.W.}}{Ca_{A.W.}} \cdot \frac{Sol.CaCl_2}{Sol.Ca(NO_3)_2} \right)
\]

\[
M_{Nitrate} = M_{sol.Ca} \times \left( \frac{2NO_3_{3.M.W.}}{\sum_{i=1}^{3} C.I.M.W.} \cdot \frac{2NO_3_{3.M.W.}}{Ca_{A.W.}} \right)
\]

\[
M_{Sulfate} = M_{sol.Ca} \times \left( \frac{SO_4_{4.M.W.}}{\sum_{i=1}^{3} C.I.M.W.} \cdot \frac{SO_4_{4.M.W.}}{Ca_{A.W.}} \cdot \frac{Sol.CaSO_4}{Sol.Ca(NO_3)_2} \right)
\]

where A.W. is atomic weight, C.I. is counter ions, M.W. is 
molecular weight, \( [Sol.CaCl_2/Sol.Ca(NO_3)_2] \) is the ratio 
(0.615) of CaCl_2 solubility to Ca(NO_3)_2 solubility, 
\( [Sol.CaSO_4/Sol.Ca(NO_3)_2] \) is the ratio (0.0019) of CaSO_4 
solubility to Ca(NO_3)_2 solubility. The ratio of solubili-
ty is the value of saturated liquid state.

Fig. 8 shows the theoretically estimated mass concen-
tration of counter ions of calcium in PM_{10-2.5}. The
concentrations of chloride, nitrate, and sulfate in PM$_{10:2.5}$ could be estimated as 74.9 ng m$^{-3}$, 164.9 ng m$^{-3}$, and 0.42 ng m$^{-3}$ respectively.

It is difficult to accurately assess the adverse health effect for these water-soluble components because the limits of exposure to the polluted air have not yet been established. However, the exposure to them at levels above the risk values of drinking-water based has been reported to have adverse health effects. WHO (2006) reported that exposure to higher levels of nitrates has been associated with increased incidence of cancer in adults, and possible increased incidence of brain tumors, leukemia, and nasopharyngeal tumors in children. The major health effect observed with sulfate ingestion exposure was laxative action (Daniels, 1988). In the case of calcium chloride, aqueous solutions or solid in contact with wet skin might cause severe irritation (WHO, 2010).

4. CONCLUSIONS

The mechanisms for particle generation at subway rail-system are very complex and poorly understood. It is really important to clarify the thermal properties of indoor PM collected on an underground subway for understanding of the distinctive particle formation processes in a semi-closed subway space. To know the hygroscopic properties of indoor subway PMs is critically important for the assessment of health effects. In the present study we took new attempts, i.e., heat treatment and water-dialysis, for the individual subway particles and uncovered new facts about thermal and hygroscopic properties. The results of present study newly pointed out that preceded by magnesium, several elements (i.e., silica, aluminum, and calcium) may be readily involved in the newly generated subway fine PM by a high-temperature thermal processing when trains are breaking and starting. Through the water dialysis technique, it was obvious that calcium has meaningful amount of water soluble fraction. The mass concentrations of counter ions of calcium in PM$_{10:2.5}$ found in the subway were newly estimated. Although this study was restricted by the number of sample, especially the particles treated by individually, the results obtained from new efforts may throw light on not only the subway PM formation, but the hygroscopic properties of subway PM that are highly significant for the improvement of indoor air quality in subway space as well as health impact assessment.

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