



The Chemical Nature of Individual Size-resolved Raindrops and Their Residual Particles Collected during High Atmospheric Loading for PM_{2.5}

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ABSTRACT

Although it is well known that rain plays an important role in capturing air pollutants, its quantitative evaluation has not been done enough. In this study, the effect of raindrop size on pollutant scavenging was investigated by clarifying the chemical nature of individual size-resolved raindrops and their residual particles. Raindrops as a function of their size were collected using the raindrop collector devised by our oneself in previous study (Ma *et al.*, 2000) during high atmospheric loading for PM_{2.5}. Elemental analyses of solid residues and individual residual particles in raindrops were subsequently analyzed by Particle Induced X-ray Emission (PIXE) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), respectively. The raindrop number concentration ($\text{m}^{-2} \text{h}^{-1}$) tended to drastically decrease as the drop size goes up. Particle scavenging rate, $R_{\text{sc.}}$ (%), based on the actual measurement values were 38.7, 69.5, and 80.8% for the particles with 0.3-0.5, 0.5-1.0, and 1.0-2.0 μm diameter, respectively. S, Ca, Si, and Al ranked relatively high concentration in raindrops, especially small ones. Most of the element showed a continuous decrease in concentration with increasing raindrop diameter. The source profile by factor analysis for the components of residual particles indicated that the rainfall plays a valuable role in scavenging natural as well as artificial particles from the dirty atmosphere.

Key words: Raindrop, Washout, PM_{2.5}, Scavenging, PIXE, Chemical nature

1. INTRODUCTION

Fine particulate matter smaller than 2.5 micrometers (PM_{2.5}) is already a serious and growing environmen-

tal problem in China. The smog situation in China is getting even worse. Extremely high levels (several tens of times higher than the concentration of WHO's recommendation ($< 25 \mu\text{g m}^{-3}$ of 24-hour exposure) can last more than a week.

Now, the damage caused by PM_{2.5} is not just an issue for China. It has been proven that the worsening of air pollution in China affects Korea and Japan as well, with the fine particles moving with the winds. Especially, air quality in South Korea has become an increasing source of concern for the nation. According to the survey conducted by the Seoul Development Institute (Chung, 2014), 52% of the residents in Seoul consider air pollution to be the most imminent environmental issue, and 68% of them consider that the level of air pollution is serious.

In the case of Japan, in recent years, high levels of PM_{2.5} were recorded in parts of western Japan, especially Fukuoka Prefecture (The Japan Times, 2013). Under the growing concern to this pollution crisis, many regional organizations in Japan are planning various measures like providing the real-time hourly PM_{2.5} data on website.

This fiendish PM_{2.5} are removed from the atmosphere by wet and/or dry depositions, the former proceeds more efficiently in the form of precipitation such as rain, fog, and snow (Byrne and Jennings, 1993; McGann *et al.*, 1993; Flossmann *et al.*, 1985). Most people have probably experienced a clear view of the sky and landscapes after rainfall. This is a good example to understand that the rain is a great cleaner of PM_{2.5}. Therefore, in the assessment of public health risks associated with PM_{2.5}, a study of the chemical nature of the rain have fallen during high atmospheric loading for PM_{2.5} is no less important than that of the ambient PM_{2.5} itself.

One of major mechanisms of the incorporation of ambient particles into raindrops is the collision among the particles below the cloud base. The efficiency of

the collision depends on the size distributions of particles and the raindrops (Byrne and Jennings, 1993; Flossmann *et al.*, 1985). Therefore, the exposure amount of pollutants by rain is variable depend on rainfall properties (e.g., rainfall amount, rainfall duration, rainfall intensity, and raindrop size distribution). More than all, as mentioned above, raindrop size distribution is crucially important because it plays an important role in capturing pollutants.

The collection of raindrops as a function of their size has not been generalized because it is technically difficult to capture and a high degree of skill in handling of raindrops is demanded (Ma *et al.*, 2004; Tenberken and Bächmann, 1996).

This study has been carried out to improve our understanding of particle scavenging properties of size-resolved raindrops from the chemical properties of the residuals in individual raindrops.

2. EXPERIMENTAL METHODS

2.1 Collection and Handling of Size-resolved Raindrops

For the sampling of single raindrops as a function of their size, the raindrop collector devised by our oneself in previous research (Ma *et al.*, 2000) was applied. It was located on the rooftop of a four-story building (a height of 20 m above ground level) (33.40 N 130.26 E) at Fukuoka Women's university in Fukuoka City, Japan at a time when it was raining. The rain event lasted 14 h, with rain intensity of 0.2-1.2 mm h⁻¹, and air temperature between 9.6-16.4°C. The concentration of PM_{2.5} in that time was higher than the Japanese central government's safety standard for PM_{2.5} (i.e., a mean of 35 µg m⁻³ over a 24-hour period).

Although more details can be found in our previous papers (Ma *et al.*, 2004, 2001, 2000), the principle of our own raindrop capture device can be summarized as follows:

Fallen raindrops into the liquid nitrogen are frozen and they sink to lower sieves owing to their higher density as illustrated at the top in Fig. 1. As shown in Fig. 2, the raindrops kept their spherical shape during the freezing process, and consequently by using stainless steel sieves of different mesh widths (1.7 mm, 0.17 mm, and back-up) it is possible to separate the frozen raindrops according to their sizes.

Our previous study (Ma *et al.*, 2000) has been clearly presented that there was no meaningful size change of raindrop when it was freezing. In other words, it can be said that diameter change of frozen raindrops by liquid nitrogen did not affect the size segregation of our raindrop collector.

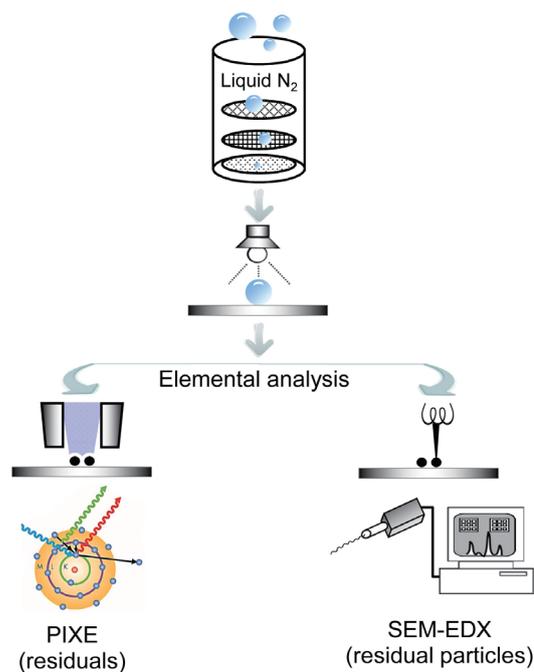


Fig. 1. Flow of collection, pretreatment, and analysis of individual size-resolved raindrops and their residual particles.

After sampling, the sieves were pulled out from the dewar vacuum flask and each frozen raindrop on each sieve was placed onto the non-hole Nucleopore[®] filter and Ag thin film (99.99% purity) by using a vacuum pipette (HAKO 392). The frozen raindrops were melted and dried under an infrared lamp for five minutes. Because every process was performed in the clean air system filled with the cooling nitrogen gas, the raindrop handling could be done successfully without any loss of some residues, evaporation, and contamination.

Moreover, in order to measure the rainfall intensity, the standard rain gauge (260-2510, NovaLynx Co.) consisting of a funnel that empties into a graduated cylinder was applied.

2.2 Elemental Analyses of Residues in Raindrops

Elemental analyses of solid residues and individual residual particles in raindrops were subsequently analyzed by Particle Induced X-ray Emission (PIXE) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), respectively. The PIXE installed at the Cyclotron Research Center of Iwate Medical University was applied and it has the great advantages such as an excellent sensitivity, a nondestructive technique for multielement with a wide range of elements ($Z > 10$). The sensitivity, if defined by the ratio between PIXE yield per unit dose and

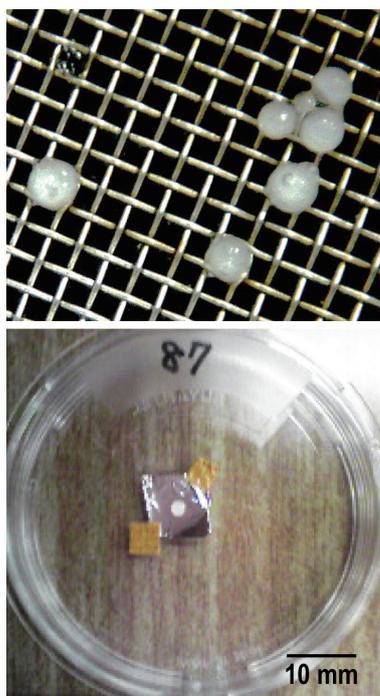


Fig. 2. Several frozen raindrops lying on the sieve with 1.7 mm mesh size (top) and a raindrop on Ag film (bottom).

mass thickness, can be determined for all objective elements both experimentally and theoretically. For instance, the sensitivity of calcium was calculated to be $1700 \text{ (counts} \cdot \text{cm}^2/\mu\text{C} \cdot \mu\text{g)}$ with a detection limit of $9.4 \times 10^{-3} \text{ (}\mu\text{g/cm}^2\text{)}$. The more detailed analytical procedures and experimental setup for PIXE analysis were described elsewhere (Sera *et al.*, 1999).

The overall process of collection and handling of size-resolved raindrops, and their elemental analyses is shown in Fig. 1.

2.3 Monitoring of Sulfate, $\text{PM}_{2.5}$, and Particle Number Concentration

In addition to the raindrop collection, the highly time-resolved (10-minute cycle) $\text{PM}_{2.5}$ sulfate was monitored during a whole research period by the ambient particulate sulfate monitor (8400S, Rupprecht & Patashnick Co.). A detailed description of design, operation, and data reduction and processing can be found elsewhere (Drewnick *et al.*, 2003). In order to measure $\text{PM}_{2.5}$ mass concentration, a light scattering $\text{PM}_{2.5}$ monitors (Dust scan Scouts 3020, Rupprecht & Patashnick Co.) was simultaneously operated. Details on this $\text{PM}_{2.5}$ monitoring system was previously described (Ma and Kim, 2013).

The number concentrations of size-selective particulate matters (i.e., 0.3-0.5 μm , 0.5-1.0 μm , 1.0-2.0 μm ,

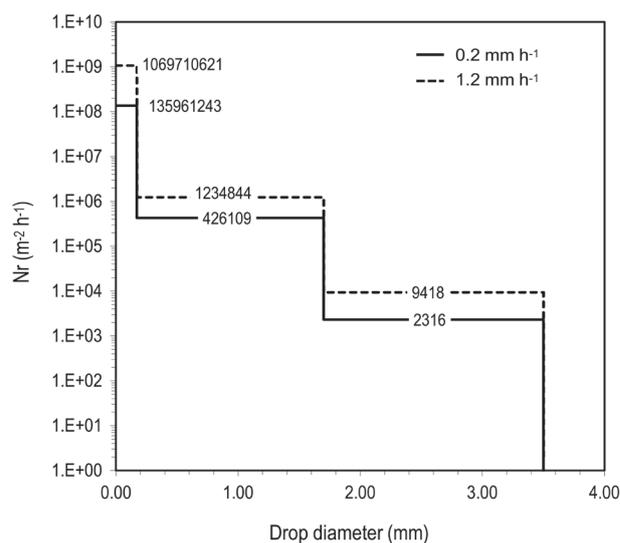


Fig. 3. Raindrop number size distribution at the beginning (0.2 mm h^{-1}) and subsequent (1.2 mm h^{-1}) rainfalls.

and 2.0-5.0 μm) were also monitored by an optical particle counters (OPC) (RION, KC-01D).

3. RESULTS AND DISCUSSION

3.1 Number Size Distribution of Raindrops

The number size distribution of raindrops collected at two different rainfall intensities was estimated by the volume of melted raindrops and that of calculated single raindrop from its average size. Fig. 3 shows the raindrop number size distribution at the beginning (0.2 mm h^{-1}) and subsequent (1.2 mm h^{-1}) rainfalls. The raindrop concentration $\text{Nr} \text{ (m}^{-2} \text{ h}^{-1}\text{)}$ is the total number of drops falling per square meter of surface per hour. Raindrop number tended to drastically decrease as the drop size goes up at both hourly rain rates (i.e., rain intensity). Needless to say, it showed higher number concentration when the higher rainfall intensity. This result indicates that the increase in the rain rate stemmed mainly from the increase in the number concentration of raindrops with drop diameter $< 0.94 \text{ mm}$.

3.2 Calculation of Particle Scavenging Efficiency of Size-resolved Raindrops

Prior to the interpretation of the actual measurement data about particle scavenging properties of size-resolved rain drops, the collection efficiency of ambient particles as a function of raindrop size was theoretically calculated.

Slinn and Hales (1971) proposed three particle collection efficiencies (E), i.e., E by Brownian diffusion (E_{dif}),

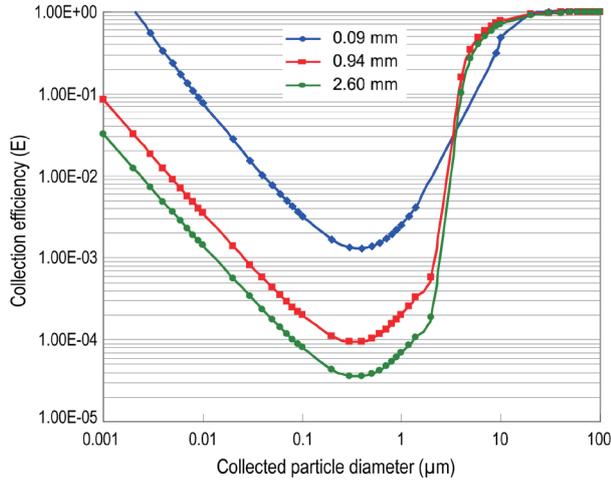


Fig. 4. Theoretically calculated collection efficiency of ambient particles as a function of raindrop size.

E by interception (E_{int}), and E by inertial impaction processes (E_{imp}). Subsequently, Strauss (1975) suggested a more advanced equation for particle collection efficiency (E_{integ}) of raindrops that integrated three kinds efficiencies as follows:

$$E_{integ} = 1 - (1 - E_{dif}) (1 - E_{int}) (1 - E_{imp})$$

In this study, the collection efficiency of ambient particles for three kinds of raindrop sizes (i.e., 0.09, 0.94, and 2.60 mm diameter) was theoretically computed using this integrated E_{integ} . Details for calculation like variable settings and computation processes were already described in our earlier articles (Ma *et al.*, 2005, 2004). Fig. 4 shows the below-cloud scavenging coefficients of ambient particles by falling raindrops as a function of aerosol radius and collector rain drop size. There are several features that appear in the particle capturing efficiency curves. As the first outstanding feature, the smaller raindrop can scavenge particles more efficiently. Another peculiarity for particle scavenging efficiency curves is that the efficiency is rapidly degraded in the central part of each curve. This is well-known phenomenon as the term of “Greenfield gap” (Slinn and Hales, 1971). Although, the margin is varied from 0.01 μm to 2 μm (Henzing *et al.*, 2006), this gap has been reported in various studies.

3.3 Particle Scavenging Properties of Size-resolved Raindrops

Fig. 5 shows time series variation of relative humidity and four-size resolved (0.3-0.5, 0.5-1.0, 1.0-2.0, and 2.0-5.0 μm) particle number concentration throughout a whole rainfall duration. As previously mentioned, it was a relatively weak rainfall with the rainfall intensi-

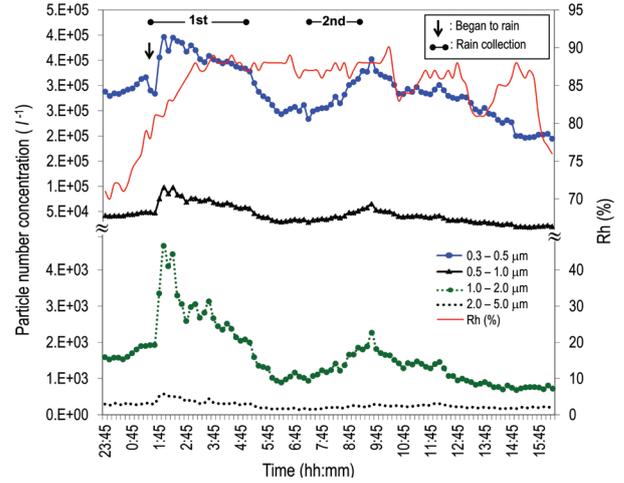


Fig. 5. Time series variation of relative humidity and size-resolved particle number concentration.

ty varied from 0.2 to 1.2 mm h^{-1} .

Particles of all sizes were getting lower concentrations when the rain started. Although this was the expected result, an unusual thing was that particle number concentration was temporarily increased immediately after the rain.

Decreasing relative humidity increases scavenging in the Greenfield gap since the evaporating raindrops are cooler at the surface, and this sets up a thermal gradient that induces motion of the aerosols towards the cooler raindrop surface (Croft *et al.*, 2009). In the condition of initial rainfall, falling raindrops can be exposed to the dry air of near the surface. According to Croft *et al.* (2009), this situation will reduce the levels of atmospheric particles because the particle removal efficiency can be improved by increasing scavenging in the Greenfield gap. Nevertheless, the reason for a temporarily increasing of particle concentration might be that new particles were created in the early stage of precipitation because small size rain droplets cloud be easily evaporated in the dried low altitude air.

A continuous decrease of the particle number concentration over most of the range of particle diameter during a whole precipitation was not seen. There was a modest increase in particle number concentration from 07:00 to 09:30 (see Fig. 5). Such increases might be caused by a decline of rainfall intensity and the influx of pollutants to our measurement site.

Scavenging rate, R_{sca} (%), of three-size resolved (0.3-0.5, 0.5-1.0, and 1.0-2.0 μm) particles showing an obvious reduction was calculated by below equation:

$$R_{sca} (\%) = \frac{N_{p_{max}} - N_{p_{min}}}{N_{p_{max}}} \times 100$$

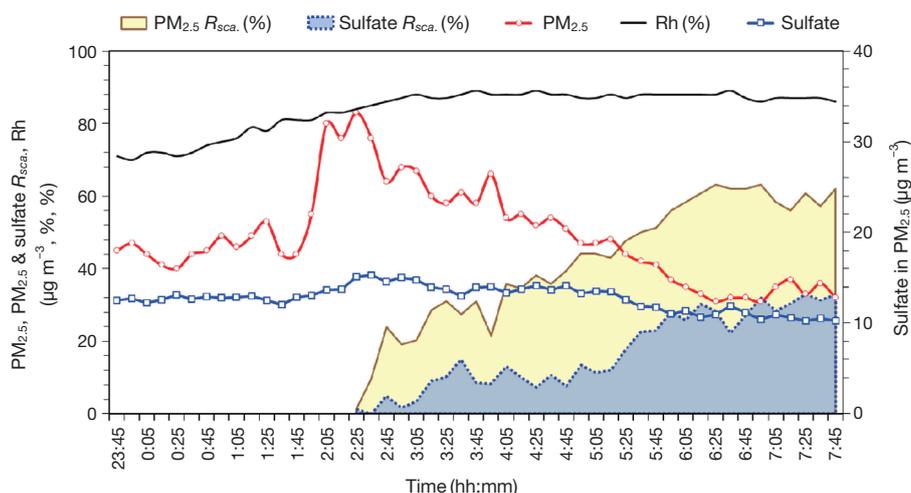


Fig. 6. Time series variation of $PM_{2.5}$ ($\mu\text{g m}^{-3}$), sulfate in $PM_{2.5}$ ($\mu\text{g m}^{-3}$), their $R_{sca.}$ (%), and relative humidity (%).

where, $N_{p_{max}}$ and $N_{p_{min}}$ are the maximum and minimum particle number concentration for target particle size, respectively.

Calculated $R_{sca.}$ based on the actual measurement values were 38.7, 69.5, and 80.8% for the particles with 0.3-0.5, 0.5-1.0, and 1.0-2.0 μm diameter, respectively. The results show a good match to that of model calculation shown in Fig. 4.

Fig. 6 shows the time series variation of $PM_{2.5}$, sulfate in $PM_{2.5}$, their $R_{sca.}$, and relative humidity in the first half of rainfall. Here, let's pay attention to the $R_{sca.}$ for $PM_{2.5}$ and sulfate in $PM_{2.5}$. $R_{sca.}$ shows a gradual increase in both. However, that of $PM_{2.5}$ (63.1%) was overwhelmingly high compared to sulfate in $PM_{2.5}$ (33.0%).

Despite sulfate particles are water soluble, unexpectedly they have a low $R_{sca.}$. Most of the sulfate in fine particles are forming $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 and they are generally appearing in the fine mode at 0.5-0.6 μm (Taiwo *et al.*, 2014). Therefore, Greenfield gap is the reason for the low $R_{sca.}$ of sulfate in $PM_{2.5}$.

Meanwhile, there was a very high rain washing efficiency for $PM_{2.5}$. This result should be welcomed by people, particularly living in East Asia, who suffer from $PM_{2.5}$.

3.4 Chemical Properties of the Residuals in Size-classified Raindrops

Fig. 7 shows the elemental concentration of individual raindrops classified in three steps (i.e., 0.09, 0.94, and 2.6 mm) in order of size. The data were the elemental concentration in the raindrops at the beginning (0.2 mm h^{-1}) rainfall and they were determined by PIXE analysis. S, Ca, Si, and Al ranked relatively high

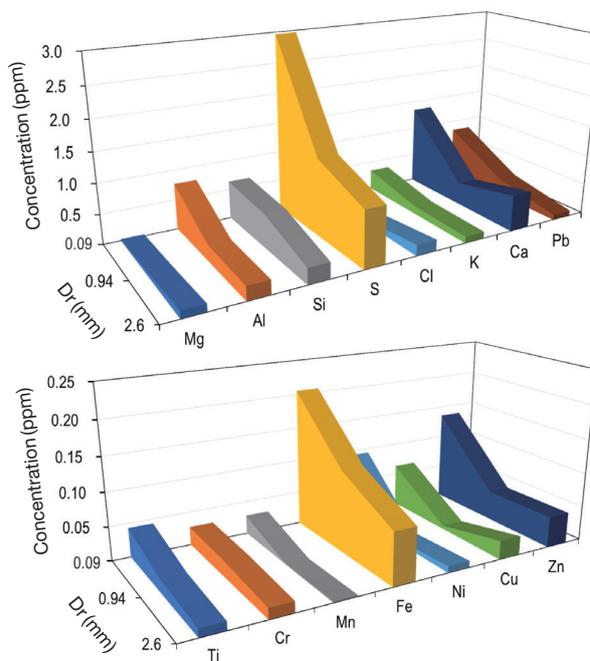


Fig. 7. Elemental concentration of size-resolved raindrops determined by PIXE analysis.

concentration in raindrops, especially small ones. Most of the element showed a continuous decrease in concentration with increasing raindrop diameter. Especially, there was a marked decrease in the range of between 0.09 and 0.94 mm raindrop diameter. Although little is known at present, it is expected that smaller raindrops should have higher elemental concentration because they have lower falling velocities

and consequently they can effectively remove pollutants during longer lifetimes than larger ones. On the other hand, in some of the elements (e.g., Cl, Ca, Cu, and Zn), a slight increase was found between 0.94 and 2.6 mm raindrop diameter. If the elemental constituent were originated from large size particle (> 4 mm in diameter), it has some possibility of the increasing for

elemental concentration between 0.94 and 2.6 mm raindrops in diameter. Among many elements determined from individual raindrops, sulfur that showed the highest concentration was probably derived from gaseous SO₂ and particulate sulfur taken up by falling raindrops. As another remarkable thing, unexpectedly, relatively high levels of lead were detected. Their concentration were 0.83, 0.28, and 0.088 ppm in 0.09, 0.94, and 2.6 mm raindrops, respectively. In dealing with the health hazards of lead like neurologic and behavioral disorders, it is something that we ought to be talking about. In general, major sources of ambient lead are piston-engine aircraft operating on leaded aviation fuel, metals processing, waste incinerators, and lead-acid battery manufacturers. Although, because of its serious impacts on public health, leaded gasoline was permanently banned in Japan long time ago, the metal contaminations of roadside soils were included in ambient particles until now (Chen *et al.*, 2010; Christoforidis and Stamatis, 2009).

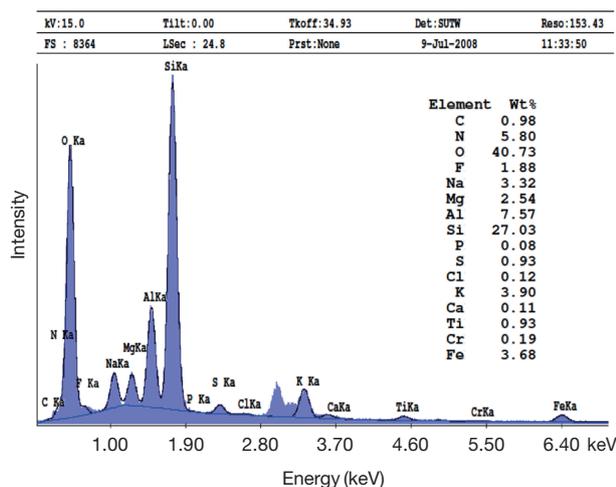


Fig. 8. EDX spectrum and elemental Weight% of a single residual particle in a raindrop ($D_r = 2.5$ mm).

3.5 Chemical Properties of the Residual Particles in Size-classified Raindrops

When melt and evaporation of frozen raindrops were completed, it was possible to maintain residual materials on the Ag thin film. These retained matters could be the targets of SEM-EDX analysis. An example of EDX

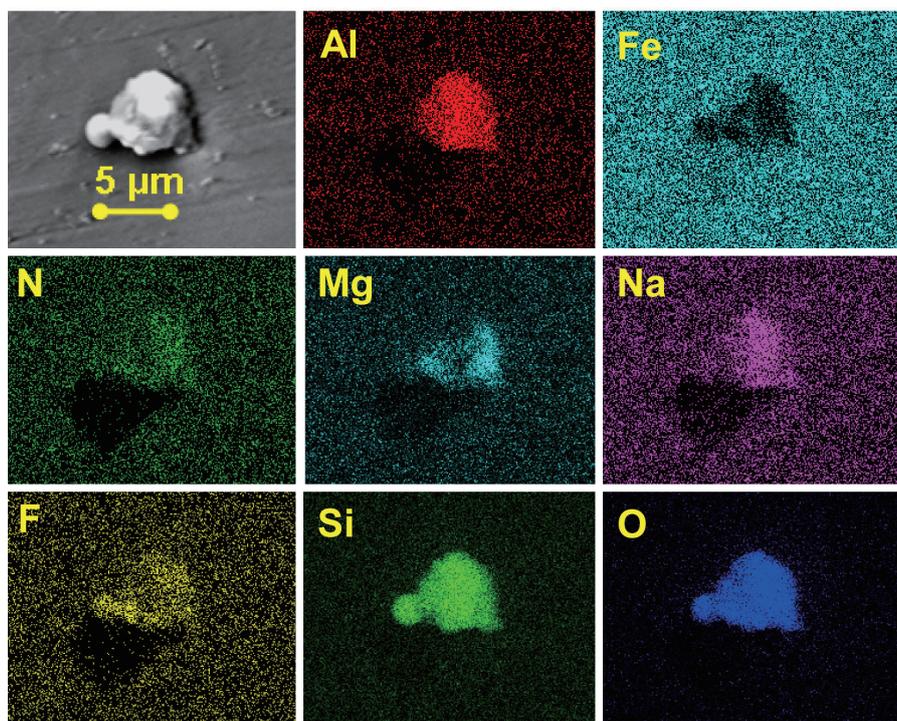


Fig. 9. SEM image (top left) of a single residual particle in a raindrop ($D_r = 2.5$ mm) and its elemental maps.

Table 1. Result of factor analysis for the elements detected from individual residues in raindrops with diameters between 1.17 and 3.5 mm

	Factor 1	Factor 2	Factor 3	Factor 4
S	0.901	0.128	-0.030	-0.026
P	0.853	0.113	0.011	-0.060
Cu	0.780	0.057	-0.052	0.033
Ca	0.756	-0.039	0.084	0.148
Cr	0.565	0.502	0.042	-0.037
C	-0.056	0.976	-0.059	-0.012
N	0.430	0.786	-0.110	0.303
F	0.037	-0.015	0.960	0.101
Fe	-0.098	-0.078	0.936	-0.234
K	0.177	0.096	-0.144	0.805
Cl	0.467	0.425	0.064	0.688
Mg	-0.200	-0.039	0.140	0.597
Na	-0.141	0.168	-0.198	0.493

Extraction method: Principal component analysis
 Rotation method: Varimax with Kaiser normalization

spectrum and elemental Weight% of a single residual particle in a raindrop ($D_r = 2.5$ mm) was drawn in Fig. 8.

Fig. 9 illustrates the SEM image (top left) of a single residual particle in a raindrop ($D_r = 2.5$ mm) and its elemental maps. These visualized elemental maps for several elements including oxygen enable us not only to presume the chemical mixing state of raindrop residual particles, but also to estimate their source profiles.

To obtain the source profile information for aerosol components, factor analysis, which is one of the multivariate statistical techniques, was carried out. It was possible to construct the matrix of 450-set of 13 components by the result of SEM-EDX analysis for residual particles in a total of 150 individual raindrops. The factor loadings (Varimax with Kaiser normalization) are shown in Table 1. The data matrix (450 variables \times 13 cases) constructed in the present study was successfully classified into four factors. The first factor (34% of the variance) shows high loadings for S, P, Cu, Ca, and Cr. Although typical soil component like Al and Si were excluded because of their missing data, the first factor was associated with soil components (Ca and other minors). The second factor, which explains 26% of the variance, seemed to express the sources of fossil fuel combustion. The third factor grouped F and Fe were the components originated from biomass burning (or volcanoes) (Jayarathne *et al.*, 2014) and iron industry. The fourth factor dominantly made up of typical marine components. The cumulative variance of these three factors was 85.2%. This result indicates that the rainfall plays a valuable role in scavenging natural as well as artificial particles from the dirty atmosphere.

4. CONCLUSION

Ambient particles are ultimately removed from the atmosphere by the natural processes generally referred to as wet precipitation and dry deposition. The former is the most important natural removal mechanism of ambient air pollutants including $PM_{2.5}$. The clear landscapes after the rain is a good proof of this wet precipitation. In this study, the scavenging properties of ambient particles were investigated by collection of raindrops as a function of their size and clarifying their chemical nature. Particle scavenging rates based on both the actual measurement and the theoretically calculated values indicated that raindrops, especially small raindrops, played a great role to remove ambient particles including both naturally and artificially formed ones. On the other hand, through the PIXE analytical technique for the residuals in and/or on individual raindrops, it was obvious that several hazard components like Pb, Cr, and Mn had meaningful amount. Therefore, we must thank for the role of the rain, at the same time, we should be avoided to get wet to protect our health from heavy metals. Further study on a comparison of the real measured data with the calculated result for the particle scavenging by raindrops is being planned in the near future.

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(Received 16 March 2017, revised 5 April 2017, accepted 10 April 2017)