Dithiothreitol-Measured Oxidative Potential of Size-Segregated Particulate Matter in Fukuoka, Japan: Effects of Asian Dust Events

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Abstract

Oxidative potential is an important property of particulate matter (PM) that has been regarded as a more health-relevant metric than PM mass. We investigated the oxidative potential of size-segregated PM and effects of Asian dust events in Fukuoka, western Japan. Aerosol particles with diameters smaller and larger than 2.5 μm (fine and coarse particles, respectively) were collected continually from 16 March through 26 May 2016. The oxidative potential was analyzed using dithiothreitol (DTT) assay; chemical components of PM were also found. Air-volume normalized oxidative potential quantified by DTT assay (DTTv) was significantly higher during Asian dust events than during nondust-event days. The mean DTTv of fine and coarse particles during Asian dust events were, respectively, 1.5 and 2.7 times higher than that during nonevent days. DTTv of fine particles was highly correlated with elements dominated by anthropogenic combustion sources and with the elements emitted from multiple sources including mineral dust and combustion sources. DTT, of coarse particles strongly correlated with the mineral dust derived elements, suggesting concentration of mineral dust particles as an important controlling factor especially for the oxidative potential of the coarse particles. We estimated the contributions of water-soluble transition metals to the oxidative potential of PM. Water-soluble transition metals (mainly Cu and Mn) can explain only approximately 37% and 60% of the measured oxidative potential of fine and coarse particles, respectively, suggesting substantial contributions of aerosol components other than water-soluble transition metals such as quinones and insoluble minerals.

1. Introduction

Reports of epidemiological studies have described the association between exposure to ambient particulate matter (PM) and adverse health effects including increased premature mortality and increased risk of respiratory and cardiovascular diseases (e.g., Brook et al., 2010; Cohen et al., 2017; Hoek et al., 2013; Pope et al., 2004). Although the PM toxicity mechanisms remain unclear, oxidative stress has been regarded as a key mechanism of PM toxicity (Li et al., 2003; Michael et al., 2013; Nel, 2005; Xia et al., 2006). Oxidative stress is a state of imbalance between reactive oxygen species (ROS) and antioxidants in favor of the ROS in tissues and organs. When PM is deposited in the respiratory tract, then ROS, perhaps including singlet oxygen, hydroxyl radicals, superoxide radicals, hydrogen peroxide, and organic radicals, can be carried by the PM (Venkatachari et al., 2005) or generated by particle-bonded redox-active components in the epithelial lining fluid (Shiraiwa et al., 2017). Therefore, the oxidative potential of PM, which is defined as the capability of particles to deplete antioxidants and generate ROS, has been regarded as a more health-relevant metric than bulk mass concentration of PM.

Dithiothreitol (DTT) assay, a cell-free assay, is widely used to quantify the oxidative potential of PM (Cho et al., 2005; Kumagai et al., 2002). Using DTT as a surrogate of cellular antioxidants, DTT assay simulates PM-catalyzed electron transfer from cellular antioxidants (e.g., glutathione and NADPH (nicotinamide adenine dinucleotide phosphate)) to O2 and generation of superoxide radical (O2·−). In the assay, DTT is oxidized to its disulfide form. The DTT loss rate is used as a measure of the oxidative potential of PM. Pure reagents that have been identified as DTT-active components are water-soluble transition metals (e.g., Cu and Mn; Charrier & Anastasio, 2012) and quinones (Kumagai et al., 2002), although other chemical species are possibly DTT active. Charrier and Anastasio (2012) demonstrated that water-soluble transition metals...
Asian dust, a dominant component of PM in eastern Asia, derives primarily from the Taklimakan Desert and Inner Mongolian Gobi Desert (Zhang et al., 2003). The desert dust is transported eastward to populated areas of China (e.g., Sugimoto et al., 2003), Korea (e.g., Chun et al., 2001), Japan (e.g., Iwasaka et al., 1988; Shimizu et al., 2004), and occasionally even to North America and beyond (e.g., Husar et al., 2001; Uno et al., 2009). According to the volume-size distributions of Asian dust particles observed near Japan, the median diameter of Asian dust particles is in the range of coarse particles (approximately 2.5–5.5 μm; Formenti et al., 2011). Asian dust typically comprises phyllosilicate, quartz, plagioclase, K-feldspar, and calcite (Jeong, 2008). Along with the mineral components, Asian dust particles often contain sulfates or nitrates formed via heterogeneous reactions with sulfur dioxide or nitrogen oxides emitted from anthropogenic sources (e.g., Trochkine et al., 2003; Zhang et al., 2000). Moreover, Asian dust particles can contain lipopolysaccharides and β-glucan originating from bacterial cell membranes and fungal cell walls (Ichinose et al., 2005).

Health effects of Asian dust have been a concern recently (Goudie, 2014; Hashizume et al., 2010; Zhang et al., 2016). Results of epidemiological studies have suggested that Asian dust exposure is associated with allergic diseases including asthma and allergic rhinitis (e.g., Chang et al., 2006; Kanatani et al., 2010; Watanabe et al., 2014) and with cardiovascular diseases (e.g., Kamouchi et al., 2012; Kashima et al., 2016; Kojima et al., 2017). In mouse models, inhalation of Asian dust particles caused increased airway inflammation (Ichinose et al., 2008) and aggravation of allergic rhinitis (Ichinose et al., 2009). Although the mechanism of PM toxicity during Asian dust events is understood incompletely, oxidative stress is suggested as a mechanism causing desert dust-induced inflammatory responses (e.g., Higashisaka et al., 2014; Kyung et al., 2012; Pardo et al., 2017). However, effects of the Asian dust storms on the oxidative potential of PM have been investigated only rarely. However, several researchers have examined Asian dust effects on the oxidative potential of water-soluble PM2.5 in China (Chen et al., 2018; Liu et al., 2014; Liu et al., 2018; Yu et al., 2019). Nevertheless, effects of Asian dust on the oxidative potential of coarse particle have not been assessed in spite of the fact that coarse particles constitute the dominant fraction of mineral dust particles, especially for particle mass. Moreover, the oxidative potential of total PM including the water-insoluble fraction has not been assessed during Asian dust events. Water-insoluble minerals are the main components of mineral dust particles.

In this study, to investigate the potential effects of Asian dust events on the oxidative potential of PM, a continuous sampling of size-segregated PM (fine and coarse particles) was performed in spring 2016 in Fukuoka, western Japan. We analyzed the oxidative potential of the collected PM samples using DTT assay and concentrations of chemical components (concentrations of total and water-soluble metals, water-soluble ions, and black carbon [BC]) in PM. This paper presents effects of Asian dust events on the DTT activity of fine and coarse particles and their correlations with chemical components. Moreover, using the measured concentrations of water-soluble transition metals, we estimate the contributions of water-soluble metals to the measured DTT activity.

2. Experimental Methods

2.1. Sampling

Ambient PM samples were collected continually during 16 March to 26 May 2016 on the rooftop (21 m above ground level) of a five-story building at Fukuoka University (130.3°E, 33.5°N) in Fukuoka, Japan (Figure 1). Fukuoka, a large city in western Japan, has large industrial and commercial areas. The greater metropolitan area is approximately 1,200 km², accommodating a population of approximately 2.6 million. Fukuoka University is in a residential area surrounding the downtown area at about 5 km. Aerosol particles with diameters smaller and larger than 2.5 μm (fine and coarse particles, respectively) were collected using four

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2.2. DTT Assay

The oxidative potential of the PM samples was measured using DTT assay in accordance with the procedure described by Cho et al. (2005), except that the sample extract was not filtered to measure the DTT activity of total particles (not of only water-soluble particles). Briefly, in the assay, the loss of 100-μM DTT in 0.10-M potassium phosphate buffer (pH 7.4) at 37 °C was measured over time. One half of the sample filter was used for DTT analysis. To extract the PM sample, the sample filter was placed in 9.0 ml of 0.11-M potassium phosphate buffer in an acid-washed polypropylene amber centrifuge tube and was sonicated for 30 min. Then, 1.0 ml of 1,000-μM DTT was added to the extract with the sample filter included. It was shaken continuously at 400 rpm at 37 °C using a dry bath incubator. At four specified times (0, 3, 6, and 10 min for the fine-particle fraction and 0, 5, 10, and 20 min for the coarse-particle fraction), a 0.50-ml aliquot of the incubated mixture was withdrawn and was added to 0.50 ml of 10% trichloroacetic acid in another tube (reaction tube) to stop the reaction. Next, 0.10 ml of 5 mM dithiobisnitrobenzoic acid solution (made in methanol) was added to the reaction tube, mixed, and allowed to react for 5 min following a recommendation by Charrier and Anastasio (2012); then 2.0 ml of Tris-HCl buffer (0.80 M, pH 8.9) was added. The reaction of DTT and dithiobisnitrobenzoic acid forms 2-nitro-5-thiobenzoic acid (TNB). To quantify the TNB concentration, its optical absorption at 412 nm was measured using a spectrophotometer (Genesys30; Thermo Scientific). Then TNB was quantified using molar absorptivity of 14,150 M$^{-1}$ cm$^{-1}$ (Eyer et al., 2003; Li et al., 2009). The DTT loss rate was ascertained from the linear regression slope of the four data points of the DTT concentration.

To reduce DTT consumption in the blank buffer solution, the potassium phosphate buffer was chelated with Chelex 100 resin (sodium form; Bio-Rad Laboratories Inc.) following the procedure described by Charrier and Anastasio (2012). The DTT loss rate in the chelated potassium phosphate buffer without a filter was negligible (<0.01 μM/min); the DTT loss rate in the extracts of a procedure blank filter was 0.06 ± 0.04 μM/min (mean ± standard deviation, N = 10). The mean DTT loss rate of the procedural blanks was subtracted from the results obtained for the PM samples. A blank without a filter or a positive control (0.20-μM phenanthrenequinone) was analyzed each day during the experiment. The DTT loss rate obtained for the positive control was quite reproducible with a mean (±standard deviation) of 3.01 ± 0.09 μM/min (N = 19).

Final DTT activity data were presented as the DTT loss rate normalized by the sampled air volume (DTT$m$) with units of nanomole per minute per cubic meter and as the DTT loss rate normalized by the particle mass (DTT$m$) with units of picomole per minute per microgram. Then DTT$m$ was calculated by dividing the measured DTT loss rate by the PM mass concentration. Gravimetric analysis of the PM sample was not done in this study. For the fine-particle fraction, we used the mass concentration of PM$_{2.5}$ measured at the monitoring station managed by Fukuoka city (Nagao Station), which is located 2 km from Fukuoka University. The mass concentration of the coarse-particle fraction was estimated from the sum of the measured concentrations of water-soluble ions (Na$^+$, NH$_4^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, and (COO)$_2$Fe$^{3+}$) and the mass concentration of the water-insoluble fraction of mineral dust particles. The mass concentration of water-insoluble mineral dust was estimated from the measured total Fe concentration in coarse particles assuming that Fe constitutes 3.7% of mineral dust weight and that the relation does not vary among seasons or locations in Japan (Osada et al., 2014; Ura et al., 2011).
2.3. Metal Analysis

To ascertain the concentration of total metals in the PM samples, the PM sample was decomposed using the microwave acid digestion method in a mixture of 2.5 ml of concentrated HNO₃, 1.5 ml of concentrated HF, and 0.5 ml of H₂O₂ (30%) for 10 min using the microwave decomposition vessel (Type P-25; San-ai Kagaku Co. Ltd.). After microwave acid digestion, the reaction mixture was evaporated in a Teflon vessel on a hot plate to remove HF. Then the residue was diluted by 0.5 M HNO₃ to a fixed volume (20 ml).

To ascertain the concentration of water-soluble metals in the PM samples, the PM sample was extracted in 5-mMTris-HNO₃ buffer (pH 7.4) to extract the water-soluble metals at the same pH with the potassium phosphate buffer used in the DTT assay because the solubility of metals in water depends on pH. We sonicated the sample filter in 14.0 ml of Tris-HNO₃ buffer for 30 min. After sonication, the extract was filtered through a 0.45-µm PTFE (polytetrafluoroethylene) filter (DigiFILTER; SCP Science); then 150 µl of 69% HNO₃ was added to 10 ml of the filtered extract to produce a final concentration of 1% HNO₃.

The concentrations of total and water-soluble metals were measured using an inductively coupled plasma-mass spectrometer (model 7700; Agilent Technologies Inc.). We measured Na, Mg, Al, K, Ca, V, Mn, Fe, Cu, Zn, Sr, Nb, Ba, and Pb for the total metal analysis. The same elements except for Pb were measured for the water-soluble metal analysis. Two standard samples (NIES CRM no. 28, Mori et al., 2008; and NIES CRM no. 30, Nishikawa et al., 2013) were used to validate the analytical procedures. The validation results showed good agreement with the certified values. The obtained atmospheric concentrations were corrected using procedural blank levels.

2.4. Water-Soluble Ion Analysis

For water-soluble ion analysis, the sample filter was extracted in 10-ml ultrapure water (18.2 MΩ·cm, Milli-Q water). Water-soluble ions (Na⁺, NH₄⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, and (COO)₂⁻) were analyzed using ion chromatography (DX-120; Dionex Corp.). Analytical conditions and procedures were in accordance with those reported by Hara et al. (2004). The obtained concentrations of each ion were corrected using procedural blank levels.

2.5. BC Measurement

The BC concentration was measured using a multiwavelength aethalometer (AE31; Magee Scientific) with a flow rate of ~4 L/min. The aethalometer was operated in a laboratory on the fourth floor (14 m above ground level) of the same five-story building where the PM sampling was performed on the rooftop. Ambient air was taken using a stainless inlet and a conductive tube to the aethalometer. Filter-base BC measurements, including aethalometry, had measurement bias from multiscattering and shadowing effects (Bond et al., 2013; Weingartner et al., 2003). To reduce these effects, the obtained BC concentrations were corrected using optical attenuation data following a procedure described by Weingartner et al. (2003). Organic aerosols and mineral particles show strong absorption in ultraviolet and visible wavelength regions. Consequently, BC concentration in infrared channel (880 nm) was used for this study.

3. Results and Discussion

3.1. DTT Activity of Fine and Coarse Particles

Figures 2 and 3 portray temporal variations of (a) DTTᵥ, (b) DTTₘ, and (c) the mass concentrations of fine and coarse particles. We defined an Asian dust event sample as one in which the sum of Al concentrations in fine and coarse particles (Figures 2d and 3d) was larger than 2 µg/m³. Broken red lines in Figures 2 and 3 show Asian dust events. Table 1 presents the mean DTTᵥ of all samples and of samples collected during Asian dust events and nondust event days. Figure S1 in supporting information is a graphical summary of the same data presented in Table 1. Statistical summaries of concentrations of chemical composition in particulate matter are presented in Tables S1–S4. Table 1 shows that the mean DTTᵥ of all the fine-particle samples (0.75 nmol min⁻¹ m⁻³) was larger than that of the coarse-particle samples (0.35 nmol min⁻¹ m⁻³) by about a factor of 2.1. Mean DTTₘ of all the fine-particle samples (45.3 pmol min⁻¹ µg⁻¹) were also higher than those of the coarse-particle samples (23.9 pmol min⁻¹ µg⁻¹) by about a factor of 1.9. The DTTᵥ during Asian dust events was significantly higher (p < 0.01) than those during the nonevent days. The mean DTTᵥ during the Asian dust events were 1.04 and 0.73 nmol min⁻¹ m⁻³, respectively, for the fine- and coarse-
Figure 2. Temporal variations of (a) DTTv, (b) DTTm, and (c) bulk mass; total (d) Al, (e) Fe, (f) Mn, (g) K, (h) Cu, and (i) Zn; and water-soluble (j) Mn and (k) Cu (gray vertical bars) in the fine-particle fraction. Pink triangles and blue circles in (f), respectively, represent Cu/Mn ratio and solubility of Mn. Pink triangles and blue circles in (g), respectively, represent the Cu/K ratio and solubility of K. Red broken lines represent Asian dust events. DTTv = dithiothreitol loss rate normalized by sampled air volume; DTTm = dithiothreitol loss rate normalized by particle mass.
Figure 3. Temporal variations of (a) $\text{DTT}_v$, (b) $\text{DTT}_m$, and (c) bulk mass; total (d) Al, (e) Fe, (f) Mn, (g) K, (h) Cu, and (i) Sb; and water-soluble (j) Mn and (k) Cu in the coarse-particle fraction. Red broken lines represent Asian dust events. $\text{DTT}_v$ = dithiothreitol loss rate normalized by sampled air volume; $\text{DTT}_m$ = dithiothreitol loss rate normalized by particle mass.
particle fractions, which are higher than those during nonevent days by factors of about 1.5 and 2.7, respectively. The mean DTT$_m$ during the Asian dust event days were 47.0 and 21.1 pmol min$^{-1}$ µg$^{-1}$, respectively, for the fine- and coarse-particle fractions. No significant difference ($p > 0.1$) was found between the DTT$_m$ during Asian dust events and nonevent days for fine- or coarse-particle fractions.

We compared the observed DTT activities to results described in reports of earlier studies. The respective DTT$_m$ of fine and coarse particles reported at urban background sites are typically 20–80 and 10–20 pmol min$^{-1}$ µg$^{-1}$ (Shiraiwa et al., 2017). For both size fractions, DTT$_m$ observed in this study were within the ranges that have been typically described in reports of earlier studies. In Japan, Fujitani et al. (2017) reported DTT$_m$ of approximately 40–50 pmol min$^{-1}$ µg$^{-1}$ for fine particles collected at a traffic intersection and at a residential site, which resemble our results obtained for the fine-particle fraction. Chirizzi et al. (2017) reported DTT$_m$ of water-soluble PM$_{2.5}$ and PM$_{10}$ (particles with diameter smaller than 10 µm) collected during Saharan dust events in southern Italy (9.2- and 3.1-pmol min$^{-1}$ µg$^{-1}$ mean, respectively), which is much lower than our results observed during the Asian dust events. After they compared DTT activity of water-soluble PM during Saharan dust events and nondust events, they inferred that Saharan dust has a lower DTT activity than the other sources on the site. Lovett et al. (2018) also examined the effects of Saharan and Arabian dust on the oxidative potential of PM in Beirut, Lebanon, although they used an assay that differs from DTT assay (alveolar macrophage assay) to measure the oxidative potential. They concluded that Saharan and Arabian dust events contribute minimally to the oxidative potential of PM in Beirut. Results of these studies related to Saharan and Arabian dust are not consistent with ours. In contrast, our results are consistent with a source apportionment study (Yu et al., 2019) conducted at Beijing, China, which implicated the mineral dust as a dominant source (~40%) of DTT$_v$ of water-soluble PM$_{2.5}$ in Beijing in spring. Asian dust particles might have some characteristics causing the high oxidative potential of PM during Asian dust events.

### 3.2. Correlations of DTT Activity With Measured Chemical Species

In this section, we discuss sources of the measured chemical species in PM and correlations between the chemical species and DTT$_v$, to elucidate sources of DTT activity of PM. The elemental ratios in the sample PM can provide qualitative information related to the sources of the elements. The enrichment factor (EF) of an element $X$ was calculated using the following equation.

\[
EF = \frac{([X]/[Al])_{PM}}{([X]/[Al])_{crust}}
\]

In that equation, ([X]/[Al])$_{PM}$ and ([X]/[Al])$_{crust}$, respectively, represent the relative concentrations of the element of interest ($X$) to Al in PM and the crust. The crustal composition given by Wedepohl (1995) was used for this study. The enrichment factors of the elements derived from the continental crust are close to unity, whereas the enrichment factors of metals derived from anthropogenic sources are known to be much higher than 10.

Figure 2 shows the temporal variations of total (Figure 2h) Cu and (Figure 2i) Zn in the fine-particle fraction. A group of elements, total Cu, Zn, Sb, and Pb, showed mutually similar trends of variation. Table 2 presents a correlation matrix of all pairs of DTT$_v$, bulk mass concentration, and selected chemical species in the fine-
| Parameter | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 |
|-----------|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 1. DTTv   | 1 |   |   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 2. Bulk mass | 0.82 | 1 |   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 3. Total Na | 0.12 | 0.19 | 1  |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 4. Total Mg | 0.56 | 0.48 | 0.36 | 1  |   |   |   |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 5. Total Al | 0.59 | 0.50 | 0.20 | 0.98 | 1  |   |   |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 6. Total K | 0.77 | 0.77 | 0.34 | 0.87 | 0.86 | 1  |   |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 7. Total Ca | 0.43 | 0.36 | 0.29 | 0.88 | 0.84 | 0.75 | 1  |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 8. Total V | 0.56 | 0.56 | −0.04 | 0.47 | 0.53 | 0.43 | 0.41 | 1  |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 9. Total Mn | 0.68 | 0.64 | 0.18 | 0.91 | 0.93 | 0.88 | 0.85 | 0.61 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 10. Total Fe | 0.64 | 0.56 | 0.20 | 0.96 | 0.99 | 0.87 | 0.85 | 0.58 | 0.96 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 11. Total Cu | 0.77 | 0.72 | 0.05 | 0.56 | 0.58 | 0.73 | 0.54 | 0.50 | 0.76 | 0.67 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 12. Total Zn | 0.71 | 0.80 | 0.19 | 0.56 | 0.57 | 0.76 | 0.54 | 0.50 | 0.76 | 0.66 | 0.91 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 13. Total Sr | 0.50 | 0.40 | 0.19 | 0.85 | 0.84 | 0.74 | 0.84 | 0.44 | 0.82 | 0.84 | 0.55 | 0.52 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |
| 14. Total Pb | 0.72 | 0.70 | −0.02 | 0.40 | 0.43 | 0.62 | 0.33 | 0.46 | 0.61 | 0.52 | 0.87 | 0.80 | 0.36 | 1  |    |    |    |    |    |    |    |    |    |    |    |
| 15. Total Ba | 0.61 | 0.54 | 0.16 | 0.93 | 0.94 | 0.86 | 0.88 | 0.53 | 0.95 | 0.95 | 0.72 | 0.69 | 0.85 | 0.55 | 1  |    |    |    |    |    |    |    |    |    |    |
| 16. Total Pb | 0.64 | 0.72 | 0.19 | 0.45 | 0.43 | 0.69 | 0.41 | 0.32 | 0.65 | 0.51 | 0.87 | 0.90 | 0.39 | 0.83 | 0.55 | 1  |    |    |    |    |    |    |    |    |    |
| 17. Soluble Na | −0.05 | 0.05 | 0.94 | 0.18 | 0.03 | 0.14 | 0.12 | −0.17 | 0.01 | 0.03 | −0.12 | 0.03 | 0.04 | −0.17 | −0.02 | 0.04 | 1  |    |    |    |    |    |    |    |    |
| 18. Soluble K | 0.65 | 0.73 | 0.33 | 0.30 | 0.27 | 0.70 | 0.28 | 0.03 | 0.40 | 0.31 | 0.61 | 0.66 | 0.25 | 0.58 | 0.35 | 0.73 | 0.20 | 1  |    |    |    |    |    |    |
| 19. Soluble Ca | 0.45 | 0.37 | 0.28 | 0.89 | 0.87 | 0.76 | 0.98 | 0.42 | 0.87 | 0.87 | 0.55 | 0.54 | 0.84 | 0.35 | 0.89 | 0.40 | 0.13 | 0.29 | 1  |    |    |    |    |
| 20. Soluble V | 0.46 | 0.48 | −0.12 | 0.22 | 0.28 | 0.21 | 0.19 | 0.95 | 0.39 | 0.34 | 0.38 | 0.37 | 0.26 | 0.36 | 0.31 | 0.21 | −0.20 | −0.04 | 0.21 | 1  |    |    |    |
| 21. Soluble Mn | 0.81 | 0.72 | 0.11 | 0.79 | 0.83 | 0.86 | 0.64 | 0.57 | 0.92 | 0.87 | 0.85 | 0.82 | 0.67 | 0.72 | 0.83 | 0.75 | −0.04 | 0.52 | 0.69 | 0.40 | 1  |    |    |
| 22. Soluble Fe | 0.30 | 0.38 | −0.13 | 0.13 | 0.16 | 0.24 | 0.07 | 0.19 | 0.25 | 0.18 | 0.29 | 0.31 | 0.21 | 0.30 | 0.19 | 0.34 | −0.17 | 0.28 | 0.06 | 0.17 | 0.31 | 1  |    |
| 23. Soluble Cu | 0.72 | 0.73 | 0.00 | 0.34 | 0.37 | 0.60 | 0.38 | 0.42 | 0.61 | 0.46 | 0.93 | 0.88 | 0.36 | 0.81 | 0.51 | 0.85 | −0.13 | 0.68 | 0.40 | 0.36 | 0.75 | 0.35 | 1  |
| 24. Soluble Zn | 0.60 | 0.75 | 0.12 | 0.26 | 0.26 | 0.55 | 0.26 | 0.33 | 0.51 | 0.37 | 0.81 | 0.92 | 0.25 | 0.75 | 0.39 | 0.89 | 0.02 | 0.71 | 0.27 | 0.29 | 0.66 | 0.37 | 0.89 | 1  |
| 25. BC     | 0.62 | 0.76 | −0.18 | 0.09 | 0.15 | 0.40 | 0.03 | 0.49 | 0.38 | 0.25 | 0.74 | 0.73 | 0.13 | 0.72 | 0.26 | 0.68 | −0.27 | 0.52 | 0.04 | 0.49 | 0.54 | 0.34 | 0.78 | 0.79 | 1  |

Note: Correlation coefficients larger than 0.70 are shown as bold. DTTv = dithiothreitol loss rate normalized by sampled air volume; BC = black carbon.
particle fraction. Table 2 shows that correlation coefficients of each pair of total Cu, Zn, Sb, and Pb were larger than 0.85. Their enrichment factors were high (Cu, 91; Zn, 187; Sb, 1,097; and Pb, 164 on average). Consequently, these elements are likely to originate predominantly from similar anthropogenic sources. The volatile and semivolatile metals including Cu, Zn, Sb, and Pb are known to be emitted to the atmosphere from combustion sources, such as coal combustion and waste incineration (e.g., Iijima et al., 2009; Pavageau et al., 2002). Therefore, total Cu, Zn, Sb, and Pb are likely to originate mainly from anthropogenic combustion sources. Correlation coefficients of DTTv, with the combustion-dominated elements were high (Cu, r = 0.77; Zn, r = 0.71; Sb, r = 0.72; and Pb, r = 0.64), suggesting that combustion-derived particles are a dominant source of DTT activity of fine particles.

Figure 2 shows the temporal variation of total (Figure 2d) Al, (Figure 2e) Fe, and (Figure 2f) Mn in the fine-particle fraction. A group of elements in the fine-particle fraction (total Al, Fe, Mn, Mg, and Ba) shows mutually similar trends of variation. As presented in Table 2, the correlation coefficient of each pair of these elements was quite high (r > 0.9). Their enrichment factors were low (<10), indicating that these elements originate predominantly from mineral dust. The correlation coefficient of DTTv with total Al (r = 0.59), Mg (r = 0.56), and Ba (r = 0.61) was lower than that with the combustion-dominated elements although the correlations were significant (p < 0.01). The correlation coefficient of DTTv, with total Mn (r = 0.68) and Fe (r = 0.64) was not lower than that with total Pb (r = 0.64), but it was lower than that with the other combustion-dominated elements. Mineral dust is suggested as less important as a source of DTT activity of fine particles than anthropogenic combustion sources.

In addition to the combustion-dominated elements, DTTv of the fine-particle fraction was highly correlated also with water-soluble Mn (Figure 2j), total K (Figure 2g), and bulk mass (Figure 2c). The correlation coefficients of DTTv, with water-soluble Mn and bulk mass were 0.81 and 0.82, respectively, which are higher than that with the combustion-dominated elements. The correlation coefficient of DTTv, with total K of 0.77 was the same with that with total Cu and higher than that with the other combustion-dominated elements.

The possible sources of Mn in the atmosphere are, generally speaking, mineral dust and combustion sources. Solubility of Mn depends on its emission sources, which are low for Mn derived from mineral dust but high for Mn derived from anthropogenic sources (Deguillaume et al., 2005). Blue circles and pink triangles in Figure 2f represent variations of solubility of Mn ([soluble Mn]/[total Mn]) and Cu/Mn ratios ([total Cu]/[total Mn]). Solubility of Mn varied from 19% to 88%, which tended to increase concomitantly with the increasing Cu/Mn ratio and to decrease concomitantly with the decreasing Cu/Mn ratio. Considering high dominance of combustion-derived Cu, the Cu/Mn ratio can be regarded as an index of the relative contribution of combustion-derived Mn against total Mn. The large variation of Mn solubility and its relation with Cu/Mn ratio suggest that anthropogenic combustion sources contribute considerably to water-soluble Mn, whereas the mineral dust is the primary source for total Mn.

Potassium also has multiple emission sources in the atmosphere such as sea salt, biomass burning, coal combustion, and mineral dust (Andreae, 1983; Watson et al., 2001; Yu et al., 2018). According to a rough estimation of the source contribution of K in PM$_{2.5}$ in Beijing (Yu et al., 2018), coal combustion, biomass burning, and dust contribute, respectively, 49%, 32%, and 19% of K in PM$_{2.5}$ on average in spring. Solubility is known to be high (~50–100%) for K emitted from coal combustion and biomass burning (Yu et al., 2018) but low (~10%) for K originated from mineral dust (Nishikawa et al., 2016; Yu et al., 2018). Water-soluble K in the fine-particle fraction was highly correlated with total Pb (r = 0.73), but it was not correlated significantly with total Al (r = 0.27; Table 2). However, total K was highly correlated with both total Pb (r = 0.69) and Al (r = 0.86). Solubility of K varied from 4% to 199% (Figure 2g). High solubility exceeding 100% is probably attributable to measurement errors because large solubility was obtained when the total and water-soluble K concentrations were low. Therefore, we converted solubility greater than 100% into 100% in Figure 2g. Similar to the variation of Mn solubility, K solubility tended to increase concomitantly with the increase in the Cu/K ratio and decrease concomitantly with the decreasing Cu/K ratio (Figure 2g). The large variation of the solubility of K related to the Cu/K ratio suggests that total K originates from multiple sources including anthropogenic combustion sources and mineral dust particles. Bulk mass concentration of fine particles is also likely to originate from multiple sources; it was highly correlated with DTTv, (r = 0.82). These results suggest that the DTT activity of fine particles originates from multiple sources including anthropogenic
### Table 3
**Correlation Matrix for DTTv, Bulk Mass Concentration, and 22 Chemical Components of the Coarse-Particle Fraction**

| Parameter | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
|-----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 1. DTTv   | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 2. Bulk mass | 0.77 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 3. Total Na | 0.25 | 0.60 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 4. Total Mg | 0.57 | 0.89 | 0.83 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 5. Total Al | 0.87 | 0.95 | 0.39 | 0.79 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 6. Total K | 0.87 | 0.75 | 0.40 | 0.61 | 0.78 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 7. Total Ca | 0.63 | 0.92 | 0.48 | 0.83 | 0.89 | 0.61 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 8. Total V | 0.79 | 0.55 | 0.18 | 0.38 | 0.63 | 0.94 | 0.43 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 9. Total Mn | 0.91 | 0.81 | 0.28 | 0.62 | 0.88 | 0.94 | 0.71 | 0.89 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 10. Total Fe | 0.90 | 0.91 | 0.35 | 0.72 | 0.96 | 0.90 | 0.84 | 0.80 | 0.96 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 11. Total Cu | 0.44 | 0.34 | −0.07 | 0.11 | 0.37 | 0.63 | 0.32 | 0.73 | 0.62 | 0.58 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 12. Total Zn | 0.40 | 0.62 | 0.31 | 0.48 | 0.54 | 0.57 | 0.67 | 0.56 | 0.62 | 0.66 | 0.76 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 13. Total Sr | 0.69 | 0.97 | 0.66 | 0.93 | 0.91 | 0.69 | 0.95 | 0.47 | 0.74 | 0.85 | 0.27 | 0.61 | 1  |    |    |    |    |    |    |    |    |    |    |    |    |
| 14. Total Sb | 0.31 | 0.29 | −0.04 | 0.09 | 0.27 | 0.52 | 0.28 | 0.63 | 0.50 | 0.47 | 0.96 | 0.77 | 0.22 | 1  |    |    |    |    |    |    |    |    |    |    |    |
| 15. Total Ba | 0.81 | 0.93 | 0.35 | 0.72 | 0.95 | 0.81 | 0.90 | 0.68 | 0.89 | 0.96 | 0.56 | 0.72 | 0.89 | 0.48 | 1  |    |    |    |    |    |    |    |    |    |    |
| 16. Total Pb | 0.67 | 0.87 | 0.43 | 0.68 | 0.80 | 0.77 | 0.84 | 0.66 | 0.80 | 0.86 | 0.59 | 0.84 | 0.84 | 0.56 | 0.89 | 1  |    |    |    |    |    |    |    |    |    |    |
| 17. Soluble Na | 0.25 | 0.52 | 0.97 | 0.78 | 0.32 | 0.38 | 0.37 | 0.17 | 0.24 | 0.29 | −0.13 | 0.20 | 0.57 | −0.11 | 0.26 | 0.33 | 1  |    |    |    |    |    |    |    |    |    |    |
| 18. Soluble K | 0.55 | 0.67 | 0.87 | 0.79 | 0.54 | 0.70 | 0.48 | 0.54 | 0.57 | 0.57 | 0.19 | 0.38 | 0.68 | 0.17 | 0.52 | 0.57 | 0.89 | 1  |    |    |    |    |    |    |    |    |    |    |
| 19. Soluble Ca | 0.86 | 0.89 | 0.36 | 0.72 | 0.92 | 0.81 | 0.88 | 0.71 | 0.90 | 0.94 | 0.45 | 0.65 | 0.86 | 0.37 | 0.91 | 0.87 | 0.31 | 0.56 | 1  |    |    |    |    |    |    |    |    |    |
| 20. Soluble V | 0.56 | 0.63 | 0.49 | 0.59 | 0.56 | 0.50 | 0.48 | 0.41 | 0.54 | 0.54 | 0.27 | 0.44 | 0.56 | 0.26 | 0.56 | 0.50 | 0.49 | 0.59 | 0.55 | 1  |    |    |    |    |    |    |    |    |    |
| 21. Soluble Mn | 0.93 | 0.72 | 0.20 | 0.52 | 0.82 | 0.93 | 0.59 | 0.92 | 0.97 | 0.91 | 0.60 | 0.54 | 0.63 | 0.48 | 0.81 | 0.74 | 0.20 | 0.56 | 0.87 | 0.52 | 1  |    |    |    |    |    |    |    |    |    |
| 22. Soluble Fe | −0.03 | 0.00 | 0.07 | 0.03 | −0.03 | −0.04 | −0.01 | −0.01 | −0.02 | −0.01 | 0.10 | 0.20 | −0.01 | 0.13 | 0.02 | 0.00 | 0.11 | 0.07 | −0.04 | 0.34 | −0.01 | 1  |    |    |    |    |    |    |    |    |    |
| 23. Soluble Cu | −0.14 | −0.03 | −0.07 | −0.12 | −0.13 | −0.05 | 0.00 | 0.05 | −0.03 | −0.03 | 0.52 | 0.48 | −0.07 | 0.60 | 0.08 | 0.16 | −0.08 | −0.04 | 0.00 | 0.33 | −0.03 | 0.48 | 1  |    |    |    |    |    |    |    |    |    |
| 24. Soluble Zn | 0.16 | 0.45 | 0.40 | 0.43 | 0.31 | 0.32 | 0.48 | 0.28 | 0.34 | 0.38 | 0.49 | 0.78 | 0.46 | 0.59 | 0.48 | 0.61 | 0.30 | 0.35 | 0.39 | 0.45 | 0.25 | 0.41 | 0.53 | 1  |    |    |    |    |    |    |    |    |

**Note.** Correlation coefficients larger than 0.70 are shown as bold. DTTv = dithiothreitol loss rate normalized by sampled air volume.
Figure 4. Measured DTT$_{v}$ (black lines) and DTT$_{v}$ estimated from water-soluble Mn, Cu, Fe, and V concentrations (stacked color bars) of the (a) fine- and (b) coarse-particle fractions. DTT$_{v}$ = dithiothreitol loss rate normalized by sampled air volume.

3.3. Contributions of Water-Soluble Transition Metals to DTT Activity

To quantify the contributions of water-soluble transition metals to DTT activity of PM, we estimated the DTT loss rates from the concentrations of the water-soluble transition metals (Cu, Mn, Fe, and V) measured in this study. The DTT loss rates by individual transition metals were calculated using regression equations for Cu (II), Mn (II), Fe (II), and V (V) provided by Charrier and Anastasio (2012). Figure 4 shows DTT$_{v}$ estimated from water-soluble Cu, Mn, Fe, and V concentrations (stacked color bars) with the measured DTT$_{v}$ (black lines) of the fine- and coarse-particle fractions. On average (±standard deviation), the soluble transition metals can explain, respectively, 37 (±11)% and 60 (±16)% of the measured DTT$_{v}$ of the fine- and coarse-particle fractions. Soluble Cu and Mn were mostly responsible, accounting for 18 (±6)% and 16 (±6)% of the measured DTT$_{v}$ of the fine-particle fraction and 33 (±14)% and 26 (±8)% of the measured DTT$_{v}$ of the coarse-particle fraction, respectively, on average. These results indicate that water-soluble Cu and Mn are important contributors to DTT activity of PM in Fukuoka in spring. However, a large fraction (approximately 63% for the fine-particle fraction and 40% for the coarse-particle fraction on average) of the measured DTT activity was not explained by the water-soluble transition metals. This result implies that redox-active species other than the water-soluble transition metals contribute considerably to DTT oxidation. The redox-active species that are responsible for the remaining DTT loss might be organics including quinines (Charrier & Anastasio, 2012; Kumagai et al., 2002) and water-soluble organic carbon (Lin & Yu,
water-insoluble fractions of mineral dust (Schoon et al., 2006) and brake abrasion dust (Simonetti et al., 2018). Especially for the coarse-particle fraction, water-insoluble mineral dust is likely to contribute considerably because DTT of coarse particles strongly correlated with the mineral elements, as described earlier.

4. Summary and Conclusions

This study investigated the effects of Asian dust events on the oxidative potential of ambient PM using DTT assay in Fukuoka, Japan, in spring. Results show that DTT activity normalized by air volume (DTTv) is higher during Asian dust events than during nonevent days for both fine and coarse particles. In contrast, no significant difference was found in the DTT activities normalized by PM mass (DTTv) observed during Asian dust events and nonevent days. Those findings indicate that Asian dust events engender a significant increase in the exposure amount of PM oxidative potential, but they show little effect on PM toxicity causing oxidative stress. The oxidative potential of fine particles is highly correlated with bulk particles mass and elements originated from anthropogenic combustion sources and mineral dust particles such as water-soluble Mn and total K, although it is also highly correlated with the element group that is emitted dominantly from anthropogenic combustion sources such as total Cu, Zn, Sb, and Pb. This result suggests that multiple sources influence the oxidative potential of fine particles, although anthropogenic combustion sources might be more important than mineral dust as a controlling factor. The oxidative potential of coarse particles strongly correlated with the element group originated predominantly from mineral dust particles such as total Al, Fe, K, and Mn. The result implicates mineral dust concentration as the main controlling factor for oxidative potential of coarse particles in Fukuoka in spring. Finally, we estimated the contribution of water-soluble transition metal to the measured PM oxidative potential based on the DTT loss rates by individual water-soluble transition metal quantified by Charrier and Anastasio (2012). Water-soluble transition metals can explain only approximately 37% and 60% of the measured oxidative potential of the fine- and coarse-particle fraction. Results demonstrate that chemical components other than water-soluble transition metals, such as organics and insoluble minerals, contribute considerably to the oxidative potential of PM in Fukuoka in spring.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

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