Characterization of heavy metal particles embedded in tire dust

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Abstract

Tire dust is a significant pollutant, especially as a source of zinc in the urban environment. This study characterizes the morphology and chemical composition of heavy metal particles embedded in tire dust and traffic-related materials (brake dust, yellow paint, and tire tread) as measured by a field emission scanning electron microscope equipped with an energy dispersive X-ray spectrometer (FESEM/EDX). In 60 samples of tire dust, we detected 2288 heavy metal particles, which we classified into four groups using cluster analysis according to the following typical elements: cluster 1: Fe, cluster 2: Cr/Pb, cluster 3: multiple elements (Ti, Cr, Fe, Cu, Zn, Sr, Y, Zr, Sn, Sb, Ba, La, Ce, Pb), cluster 4: ZnO. According to their morphologies and chemical compositions, the possible sources of each cluster were as follows: (1) brake dust (particles rich in Fe and with trace Cu, Sb, and Ba), (2) yellow paint (CrPbO\textsubscript{4} particles), (3) brake dust (particulate Ti, Fe, Cu, Sb, Zr, and Ba) and heavy minerals (Y, Zr, La, and Ce), (4) tire tread (zinc oxide). When the chemical composition of tire dust was compared to that of tire tread, the tire dust was found to have greater concentrations of heavy metal elements as well as mineral or asphalt pavement material characterized by Al, Si, and Ca. We conclude that tire dust consists not only of the debris from tire wear but also of assimilated heavy metal particles emitted from road traffic materials such as brake lining and road paint.

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Keywords: Heavy metal particles; Tire dust; Traffic-related materials

1. Introduction

Tire wear debris (tire dust) is generated by the rolling shear of tire tread against road surfaces (Rogge et al., 1993). The mass of annual emission of tire dust was estimated to be \(5.3 \times 10^7\) kg in 1996 in the UK (Environment Agency, 1998) and \(2.1 \times 10^8\) kg in 2001 in Japan (Adachi and Tainosho, 2003), and tire abrasion on urban road in Germany was estimated from 55 to 657 kg/km/year on various roads (Muschack, 1990). This large amount of tire dust is a significant cause of pollution in the urban environment (Environment Agency, 1998). Zinc oxide is added as an activator during the vulcanizing process, comprising from 0.4% to 4.3% of the resulting tire tread (Smolders and Degryse, 2002), and zinc from tire dust is a significant pollutant in soil (Smolders and Degryse, 2002; Sadiq et al., 1989), air (Rogge et al., 1993), street dust (Fergusson and Kim, 1991), and urban runoff (Davis et al., 2001). Other heavy metal elements in tire tread also pollute the environment. Fukuzaki et al. (1986) showed that tire tread contains heavy metals such as Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb, and tire dust pollution contributes to some of these elements in the form of airborne dust. Sadiq et al. (1989) analyzed the metal concentrations in tires and showed that tire dust was a soil pollutant.

The road paving aggregates embedded in tire dust have been investigated (Camatini et al., 2001; Smith and Veith, 1982), but heavy metal particles derived from other sources have not yet been examined. Heavy metal particles are emitted on the road surface as part of brake dust, road paint, diesel exhaust particles (DEP), road construction materials, or car catalyst materials. When tire tread is abraded against the road surface, the tire tread debris will assimilate these particles. In this study, we examined brake dust, yellow...
paint, and tire tread materials as possible sources of metal particles in tire dust.

Brake dust has been recognized as a significant pollutant for Cu, Sb, and Ba in the aerosols composition (Sternbeck et al., 2002), and it contributed 47% of the total loading for Cu in urban runoff (Davis et al., 2001). Yellow paint contributed from 0.3% to 1.0% of airborne dust in Niigata, Japan (Fukuzaki et al., 1986). The bulk chemical composition and manufacturing process of brake dust, yellow paint, and tire tread are well known, but detailed morphologies and individual chemical compositions of the metal particles included have not been thoroughly investigated by the scanning electron microscopy (SEM) method. The aims of this study were to characterize the heavy metal particles embedded in tire dust and the traffic-related metal particles (brake dust, yellow road paint, and tire tread) as sources of embedded particles in tire dust.

The diameter of embedded particles in tire dust and traffic-related particles ranged from several micrometers to 0.2 μm, which is too small for detection by normal SEM. Therefore, we used field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FESEM/EDX) for the single particle analysis of these metal particles. FESEM is a very useful tool for analyzing individual particles at high resolution because a field emission cathode in the electron gun of the SEM provides narrower probing beams than that found in tungsten hairpin filament SEM, resulting in improved spatial resolution.

2. Experimental procedures

2.1. Sampling site

Street dust samples were collected from six sites in Kobe, Hyogo Prefecture, Japan (Fig. 1) during August of 2002. The population of the city of Kobe was 1,510,000 in 2002. The northern part of the study area is a mountain, and the southern part is a harbor. The sampling sites selected were the same points at which a traffic census was carried out by the city of Kobe as a part of a national traffic census conducted in October of 1999 (Hyogo Prefecture, 1999). According to the data, the traffic volume ranged from 4944 to 50,366 vehicles per day, and the proportion of heavy truck traffic ranged from 4.7% to 22.3%. Sites 1, 2, and 6 are residential areas. Sites 3 and 4 are industrial areas, and Site 5 is a commercial area. Site 1 is located on a down slope, while the other roads are almost flat. Sites 2, 4, and 5 are crossroads. Sites 3 and 4 are different locations on the same road.

Fig. 1. Sample location map.
2.2. Sample collection

The tire dust samples investigated here were collected from street dust, which were the depositions from natural and human activities on the road (Brookman and Drehmel, 1981). The tire dust comprises a significant composition of the street dust. More than 100 g of street dust were gathered from roadsides with a nylon trowel at each sampling site. The collected samples were stored in plastic bags for subsequent sample preparation and analysis.

In addition to the tire dust samples, we collected five brake dust samples from the rim of front brake linings. The five selected cars were manufactured by three different Japanese automakers. We also picked up a yellow road paint sample from a fragment of line material painted on the road surface in the study area, and a tire tread sample was chipped off from the surface of a used tire (Bridgestone, 6.40R14, Japan).

2.3. Single particle analysis

The FESEM measurements were performed with a JSM-6330F cold field emission SEM (JEOL, Tokyo) with an energy dispersive X-ray spectroscopy (EDX) detector Link ISIS (Oxford-Instrument, Tokyo). This EDX detector is equipped with a super atmospheric thin window, which allows one to determine the low atomic number elements (from Be to U). For the single particle analysis of the heavy metal particles embedded in tire dust, we used an acceleration voltage of 15 kV, a working distance of 15 mm, and an EDX collection time of 20 s. For the bulk analysis of traffic-related materials, we used 500 or 1000 s of EDX collection time.

The street dust samples were dried at room temperature and sieved through a 149-μm nylon screen. They were affixed to a carbon tape attached to aluminum studs. All samples were coated with carbon so they would have conducting properties.

Ten larger tire dusts whose shape had not been broken were selected from each street dust sample (Fig. 2a, b). The length of the selected particles ranged from 220 to 1230 μm. Tire dust samples were distinguished from other types of debris by the following three features: (1) sausage-shaped particles (Dannis, 1974), (2) surface morphology resembling characteristic rough and ragged
tire tread wear, (3) the presence of C, Al, Si, S, Ca, Fe, and Zn (Camatini et al., 2001; Kim et al., 2001). Backscattered electron images (BEIs) were taken in the range of 0.01 mm² at ×1000 (Fig. 2c) from the middle part of each particle. Chemical compositions of the areas were also determined by EDX (Fig. 2d), and they were defined as the bulk chemical compositions of tire dust.

Heavy metal particles were brighter than silicate mineral particles in the BEI; the brightness of the BEI reflects the atomic number of the object. The BEIs were converted to show high contrast with negative images to clearly distinguish heavy metal particles from the minerals (Fig. 2e). All detected particles more than 0.2 μm in diameter were analyzed to determine their chemical composition and diameter.

The EDX quantification was determined using the standardless ZAF method, and recalculated to 100% for 24 elements (Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Y, Zr, Sn, Sb, Ba, La, Ce, and Pb). Because of the complex shape of the particles surface and their small diameters compared to the electron diffusion range, the quantification could lead to over- or underestimation. Therefore, we used a statistical method (a hierarchical cluster analysis program (HCA)) based on their major component elements to classify the particles. The HCA was based on Euclidean distances with Ward’s error sum classification. The consistent Akaike’s information criteria (AIC) were used to determine the most effective number of the cluster.

3. Results and discussion

3.1. Brake dust

Three or four fragments from each brake dust sample were analyzed to determine their bulk chemical compositions and the particulate compositions by FESEM/EDX. The BEI and distribution of Cu, Sb, S, and Fe of brake dust are shown in Fig. 3a and b, respectively. The diameter of particles in the brake dust was about 1 μm, which was within the range of average mass median diameters of brake dust measured under several condition tests (from 0.62 to 2.49 μm) (Garg et al., 2000).

The brake dust consisted mainly of particulate Al, Si, S, Ti, Fe, Cu, and Sb (Fig. 3b). Iron particles also contained slight amounts of S, Cu, Sb, and Ba. Some brake dust samples contained particulate BaSO₄ and Zr. When we averaged the bulk compositions of the brake dust fragments, we found that Fe was the most abundant heavy element, followed by Ba, Cu, Sb, and Zr (Table 1). Sternbeck et al. (2002) proposed diagnostic criteria for brake wear particles that included a ratio of 4.6 ± 2.3 for Cu/Sb. The ratio in our analysis was 1.3. The low ratio compared to the criterion was because of the presence of Cu-free brake dust samples in this study.

Cu is used to control heat transport, and Sb is used to enhance stability (ORNL, 2001). BaSO₄ is used to increase the density of the brake pad (ORNL, 2001).

3.2. Yellow paint

The typical morphology and EDX spectra of yellow paint are shown in Fig. 4. The bulk chemical composition is high in Si, Ca, Cr, and Pb (Table 1). The yellow
Table 1
Chemical compositions of clusters and traffic related materials (mean wt.% ± standard deviation)

<table>
<thead>
<tr>
<th></th>
<th>B.D. (^a)</th>
<th>Y.P. (^b)</th>
<th>T.T. (^c)</th>
<th>T.D. (^d)</th>
<th>Cluster 1</th>
<th>Cluster 2</th>
<th>Cluster 3</th>
<th>Cluster 4</th>
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<td>ND</td>
<td>1.9 ± 0.5</td>
<td>0.9 ± 1.2</td>
<td>1.3 ± 0.9</td>
<td>1.2 ± 1.5</td>
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<td>Al</td>
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<td>2.7</td>
<td>7.5 ± 2.7</td>
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<td>4.6 ± 2.1</td>
<td>3.5 ± 2.6</td>
<td>2.5 ± 1.4</td>
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<td>Si</td>
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<td>6.1 ± 4.1</td>
<td>2.8</td>
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<td>5.8 ± 3.3</td>
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<td>ND</td>
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<td>S</td>
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<td>0.9 ± 0.8</td>
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<td>ND</td>
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<td>Ca</td>
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<td>5.8 ± 4.1</td>
<td>4.0 ± 5.2</td>
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<td>0.2 ± 1.0</td>
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<td>Fe</td>
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<td>ND</td>
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<td>13.1 ± 10.3</td>
<td>1.2 ± 1.9</td>
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<td>ND</td>
<td>ND</td>
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<td>0.3 ± 3.5</td>
<td>0.1 ± 0.2</td>
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<td>Cu</td>
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<td>ND</td>
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<td>0.2 ± 0.6</td>
<td>4.8 ± 12.1</td>
<td>0.1 ± 0.4</td>
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<td>Zn</td>
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<td>ND</td>
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<td>1.8 ± 4.4</td>
<td>57.9 ± 10.4</td>
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<td>ND</td>
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<td>0.1 ± 0.4</td>
<td>0.4 ± 0.9</td>
<td>1.8 ± 9.7</td>
<td>0.1 ± 0.5</td>
</tr>
<tr>
<td>Y</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>0.0 ± 0.1</td>
<td>0.0 ± 0.1</td>
<td>0.2 ± 1.8</td>
<td>0.0 ± 0.1</td>
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<tr>
<td>Zr</td>
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<td>ND</td>
<td>ND</td>
<td>0.1 ± 0.2</td>
<td>0.1 ± 0.4</td>
<td>0.1 ± 0.5</td>
<td>1.6 ± 5.7</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>0.1 ± 0.5</td>
<td>0.7 ± 3.8</td>
<td>0.1 ± 0.3</td>
</tr>
<tr>
<td>Sb</td>
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<td>ND</td>
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<td>0.3 ± 0.8</td>
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<td>0.1 ± 0.4</td>
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<td>Ba</td>
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<td>ND</td>
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<td>0.5 ± 1.5</td>
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<td>7.2 ± 12.0</td>
<td>0.1 ± 0.4</td>
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<td>La</td>
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<td>ND</td>
<td>ND</td>
<td>0.0 ± 0.1</td>
<td>0.1 ± 0.4</td>
<td>0.1 ± 0.7</td>
<td>0.7 ± 3.3</td>
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<td>ND</td>
<td>0.0 ± 0.1</td>
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<td>1.7 ± 7.2</td>
<td>0.1 ± 0.4</td>
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<td>26.3 ± 10.2</td>
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<td>O</td>
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<td>33.7 ± 4.5</td>
<td>36.0 ± 6.2</td>
<td>27.2 ± 3.4</td>
</tr>
<tr>
<td>(n)</td>
<td>17</td>
<td>3</td>
<td>1</td>
<td>60</td>
<td>1246</td>
<td>162</td>
<td>344</td>
<td>536</td>
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<td>(d)</td>
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<td>0.42</td>
<td>1.05</td>
<td>0.52</td>
<td></td>
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</tr>
</tbody>
</table>

ND: not detected.

\(^a\) B.D.: Brake Dust.
\(^b\) Y.P.: Yellow Paint.
\(^c\) T.T.: Tire Tread.
\(^d\) T.D.: Tire Dust.
\(^n\) \(n\): number of particles.
\(^d\) \(d\): averaged diameter.

paint consists of beads, Ca material, and PbCrO\(_4\) particles. The PbCrO\(_4\) is a particulate about 0.5 \(\mu\)m in diameter with an oval morphology (Fig. 4a). The PbCrO\(_4\) in yellow paint is one of the Pb contributors in street dust (Fukuzaki et al., 1986; Fergusson and Kim, 1991).

3.3. Tire tread

A cross-section image of tire tread and EDX spectra is shown in Fig. 5. Detected elements in tire tread were O, Al, Si, S, Ca, and Zn (Table 1). The diameter of particulate ZnO was about 1 \(\mu\)m or less, and the morphology was multi-angular (Fig. 5a). Zinc oxide is added to activate vulcanization in the tire tread. Much of the Zn forms chelates with the accelerators, but the major part of the Zn in tire tread is excess ZnO and ZnS (Fauser et al., 1999).

3.4. Heavy metal particles embedded in tire dust

We detected 2288 heavy metal particles in 60 tire dust samples. The bulk chemical composition of the surface of tire dust debris was rich in mineral or asphalt pavement material characterized by Al, Si, K, and Ca, and smaller amounts of Fe, S, Mg, Zn, and Ti (Table 1). The chemical composition was quite different from that of tire tread. Mineral materials were found at high levels compared to the composition of tire tread, and some heavy metal elements were detected.

The embedded particles were divided into four clusters based on the consistent AIC and on particle compositions. Iron-, Cr/Pb-, and Zn-rich particles were classified into clusters 1, 2, and 4, respectively. The particles with multi-elemental composition were classified into cluster 3. Typical morphology and EDX spectra of the heavy metal particles are shown in Fig. 6. In each EDX spectrum, Al, Si, and Ca may reflect neighboring material of the targeted heavy metal particles, such as asphalt pavement material, soil minerals, or tire tread itself.

3.5. Cluster 1

Cluster 1 is characterized by high Fe composition. Other heavy metal elements such as Mn, Cu, Zn, Sb, and Ba are contained in slight amounts in this cluster (Table 1). The average particle diameter is relatively large (1.17 \(\mu\)m). Iron is the most abundant heavy metal element in street dust.
The possible sources of Fe particles are brake lining material (brake dust) (Hopke et al., 1980; Hildemann et al., 1991; ORNL, 2001; Garg et al., 2000), automobile rust (Hopke et al., 1980), and motorcar exhaust (Weber et al., 2000).

In this study, the rich Fe content in the brake dust showed that it is an important contributor of this cluster, as noted by the consistent particle diameter and chemical composition that was rich in Fe with a low level of Cu, Sb, and Ba. The ratio of Cu/Sb was 2.5 in this cluster, which was within the diagnostic criteria for brake wear particles (4.6 ± 2.3) (Sternbeck et al., 2002).

A steel plant located in the southern part of the study area is also a source of Fe particles (Adachi and Tainosho, 2001). The chemical composition of most Fe particles derived from the steel plant was Fe and little Mn (several weight percent or less) (Adachi and Tainosho, 2001).

### 3.6. Cluster 2

This cluster is rich in Cr/Pb. The average particle diameter is 0.42 μm. The morphology, shown in Fig. 6b, is an aggregate of oval particles, which is similar to that of yellow paint shown in Fig. 4a. Because the chemical composition, diameter, and morphology agree with that of PbCrO₄ in yellow paint material, we conclude that a large part of this cluster is abraded particles of yellow paint. The average molar ratio of Cr/Pb is 0.92, whereas the ideal ratio of PbCrO₄ should be one. This decrease means a minor presence of Pb-rich particles in this cluster. One of the possible sources of Pb particles is lead used in motor vehicle wheel balance weights (Root, 2000).

The abundance ratio of this cluster in each tire dust samples showed large variation among individual tire dusts (Average: 7%; S.D.: 7%; Max: 32%; Min: 0%) but not among sampling sites. This means that heavy metals embedded in tire dust need not indicate the sampling location. Additional investigation is needed to learn when tire dust assimilates metal particles and when tires abrade, and how far tire dusts are distributed in the environment.

### 3.7. Cluster 3

Cluster 3 is characterized by multiple elements (Ti, Cr, Fe, Cu, Zn, Sr, Y, Zr, Sn, Sb, Ba, La, Ce, and Pb) (Table 1). The average particle diameter in this cluster is 1.05 μm. The typical morphology and EDX spectra of this cluster are shown in Fig. 6c. Because the brake dust has many Ti, Fe, Cu, Sb, Zr, and Ba particles, these particles are significant contributors to this cluster. The ratio of Cu/Sb (3.8), which was in good agreement with the diagnostic criteria for brake wear particles (4.6 ± 2.3) (Sternbeck et al., 2002), also suggests the contribution of brake dust.

De Miguel et al. (1997) has classified the elements in street dust (La, Sr, Y) as natural elements, and Sternbeck et
al. (2002) showed that rare earth elements such as Ce, La, and Pr are hosted in a mineral phase in airborne particles. We found some heavy minerals such as allanit (Ca, Ce, Fe, Al, Si), zircon (Zr, Si), and monazite (P, Ce, La, Y, Th) by single particle analysis. This study area has a granite geological background, which includes these heavy minerals (Huzita and Kasama, 1983), so one of the possible sources of these elements is a natural source.
Classification into cluster 3 indicates multiple sources. Because the classification in this analysis was based on only major components of the particles, it is difficult to distinguish the particles with multi-elemental composition with exactness. Further division based on elementary ratios or detailed morphological analysis will help to classify them.

3.8. Cluster 4

Cluster 4 mainly consists of ZnO with an average particle diameter of 0.52 μm. The most typical morphology of the particles is square or multi-angular (Fig. 6d). These characteristics agree with that of ZnO in tire tread (Fig. 5a), so we conclude that most of the particles in this cluster come from ZnO in the tire tread. The abundance ratio of Cluster 4 was very different in each tire dust sample (Average: 22%; S.D.: 17%; Max: 56%; Min, 0%). Some tire dusts samples contained no particulate ZnO. The presence of particulate ZnO may depend on the manufacturing process of tire tread.

Other possible sources of particulate Zn are metal plating, galvanized iron roofs (Fergusson and Kim, 1991), and brake dust (Davis et al., 2001; Fauser et al., 1999).

4. Conclusion

In this study, we characterized the morphology and chemical composition of traffic-related material (brake dust, yellow paint, and tire tread) and heavy metal particles embedded in tire dust. Brake dust contains heavy metal particles such as Fe, Cu, Zr, Sb, and Ba with a particle diameter of about 1 μm. Yellow paint contains Cr/Pb particles with an oval morphology and a diameter of about 0.5 μm. Tire tread has multi-angular ZnO particles 1 μm or less in diameter. A total of 2288 heavy metal particles were found embedded in tire dust and were classified into four groups by cluster analysis. Cluster 1 is rich in Fe, cluster 2 is rich in Cr/Pb, and cluster 3 is characterized by multiple elements. Cluster 4 consists mainly of ZnO. Judging from its chemical composition, particle diameter, and morphology, brake dust is a possible contributor of clusters 1 and 3, and yellow paint is a possible contributor of cluster 2. Zinc oxide in tire tread is a significant source for cluster 4.

These results suggest that tire dust assimilates traffic-related metal particles when the dust is rolled between surfaces and abraded. The interactions between tire wear debris and heavy metal particles may give the heavy metal risk to the tire dust. Further study that discusses the risk of heavy metal particles embedded in tire dust is needed.

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