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Elemental Composition of Fine Particulate Matters from the Exhaust Emission of Jeepneys Plying the Route of Taft Avenue, Manila, Philippines

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Abstract: *Elemental composition of fine particulate matters coming from the vehicular exhaust emission of jeepneys plying the route of Taft Avenue, Manila, Philippines was identified using SEM/EDX technique. SEM images of each fine particulate matter were also taken for morphological analysis. Elements that were revealed by EDX include Ca, Cl, Co, Cu, Cr, Fe, Mn, Pb, Hg, Ni, P, Na, S, Si, K, V, Mn, Ni, Zn, and Sn. Hazardous elements such as Co, Cl and Cr were detected in more than 50% of the particulate matter (PM) analyzed. The PM analyzed from jeepney 1, which was manufactured in 1980 contained the most number of hazardous elements that have a high frequency of occurrence. These include Pb and Hg which were found only in one or two PM in jeepneys 2 and 3. But for jeepney 1 traces of Pb and Hg were detected in more than 50% of the PM. Another hazardous element that was found only in the PM coming jeepney 1 is Se.*

Keywords: *jeepney, diesel, fine particulate matter, SEM/EDX, elemental composition*

I. Introduction

Air pollution is one of the major environmental problems in the Philippines, especially in urban areas like Metro Manila which is densely-populated. Atmospheric particulate matter (PM) remains to be one of the major pollutants produced from human activities. They are classified according to size because of the different diameters that are associated with particles of different diameter. Fine Particulate Matters or $PM_{2.5}$ are particles that are 2.5μm or less. These particles could be also called respirable particles because it could penetrate the respiratory system further compared to other particles of larger diameters. $PM_{2.5}$ particles are primarily formed by chemical reactions in the atmosphere and through fuel combustion which come from motor vehicles, power generation, industrial facilities, residential fire places, wood stoves and agricultural burning. In the Philippines, based from the 2006 National Emission Inventory, the transport sector is the major source of air pollution in the country wherein 65% of air pollutants come from them. Most Filipinos take public transport (PT) with an estimate of about 70% of the total person trips taking PT with as high as 80% in highly urbanized cities. The most popular public transport in the Philippines is the jeepney and there are 227,493 jeepneys providing PT services throughout the country [1]. Jeepneys are predominantly fueled by diesel and most of the diesel engines are second hand and some are more than 20 years old. Diesel vehicles emit significant amount of nitrogen oxides (NOX) and also are a major source of fine particle emissions in urban locations. PM emissions in general are very hazardous and diesel PM, especially, is likely to cause cancer [2]. Hence, characterization of the composition of fine particulate emissions from diesel vehicles is very important. One method of characterizing fine particulate matter is using the Scanning Electron Microscope (SEM) with Energy Dispersive X-ray (EDX). SEM/EDX is a powerful tool in studying the size, shape, morphology, chemical and elemental composition of particulate matter. It can give us information whether the particles' origin is anthropogenic or created by natural processes. The elemental composition of atmospheric particles is sometimes more useful than their bulk elemental composition with a view to establish their origin and their potential effects on human health [3]. In the Philippines, no study has been made on the elemental composition of fine particulate matter coming from the exhaust emissions of jeepneys considering that it is the most popular means of transportation in the country and this public transport comprise 71% of the total number of vehicles registered in the country. In this study, we present to the best of our knowledge the first study on the elemental composition of fine particulate matters that came from the exhaust emissions of jeepneys plying the route of Taft Avenue, Manila, Philippines. The elemental composition and morphology of the PM was analyzed using SEM/EDX and air sampling using a personal cascade impactor is used to collect the PM.

II. Air Sampling Using A Personal Cascade Impactor And Scanning Electron Microscopy

The personal 2-stage low-volume cascade impactor was made from aluminum and had a nozzle diameter of 0.4 mm. Figure 1 shows the cascade impactor plugged in with a plastic tube connecting it to the vacuum pump with a pressure gauge and flow meter. A 9V battery was used to power the vacuum pump. The flow meter was used to monitor the flow rate which is set to 4-5 L/min and the pressure gauge was used to monitor the pressure. The cascade impactor setup is placed directly in front of the tailpipe exhaust of the jeepney. Particles were impacted on an 8-mm diameter aluminum foil. The filters were prepared using a thoroughly cleaned and sonicated 8-mm hole puncher. A small amount of ethanol was applied to the aluminum foil filter after it was cut to a diameter of 8 mm to remove impurities. Morphological features and elemental composition of individual particles were analyzed with a SEM (JSM 5310 JEOL) equipped with an EDX (Oxford) Analyser. Particle size was estimated from the direct appearance of individual particles in the scanning electron micrograph.

SEM/EDX was done according to the standard operating procedure for sample preparation and analysis of particulate matter samples by scanning electron microscopy. Scanning Electron Microscope was operated at acceleration voltage of 15 kV. The SEM images and analytical data of trace elements concentration were recorded with a Link Isis 3.0 software system with a SemAfore 5.0 SA20 Scan Digitizer for digital imaging. The instrument acquires either single spot spectrum or area spectrum, in this way it is possible to identify a single particle analysis and the mean values of the constituents from a group of particles.

III. RESULTS AND DISCUSSION

3.1. SEM/EDX Results of the Blank Aluminum Foil

To differentiate the elements from PM and the aluminum foil were the PM were deposited, the EDX spectra of blank Al foils prepared in the same way as the Al foils used for the personal cascade impactor was also obtained. Figure 2 shows the blank SEM image of Al foil and the corresponding EDX spectra. In the EDX spectra, of the aforementioned Al foil, aside from Al the only other element present is Oxygen (O). This indicates that the Al foils that were prepared for impaction of fine particulate matters were not contaminated by other foreign particles

Fig. 1. The two-stage personal cascade impactor.

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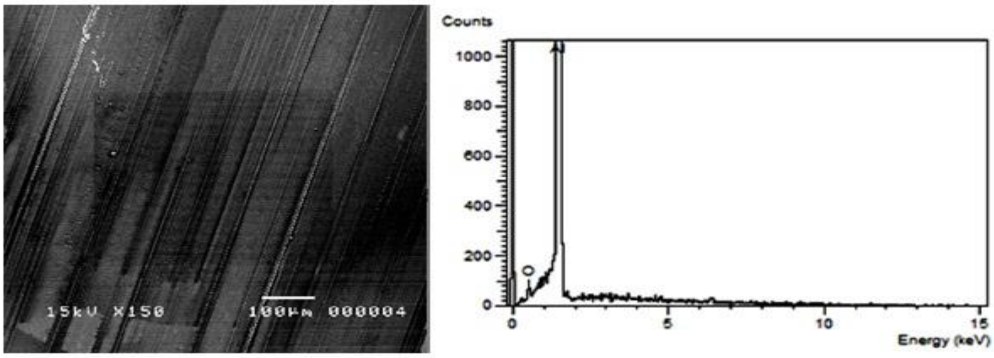

Fig. 2. SEM image of a blank Aluminum Foil Filter at a magnification of 150x with the corresponding EDS area spectrum.

3.2. SEM/EDX Results of the Fine Particulate Matter from Exhaust Emission of Jeepneys

Three jeepneys were used in this study differing in manufacturing year, 1980, 2003, and 2006, which will be referred to as jeepney 1, jeepney 2, and jeepney 3, respectively. Twenty (20) particles with a diameter not greater than 2.5 μm were selected for each jeep for analysis and detection of elemental composition and concentration. Figure 3 shows the SEM image and the EDS spectrum of some PM analyzed in the study. As can be seen from fig. 3, particles have different morphologies. We observed agglomerates, aggregates, floccules, sphere, strips, triangle, and irregularly shaped carbonaceous particles. From fig. 3, it can also be seen that PM with different morphologies have different elemental composition. EDX analysis of the PM collected for the three jeepneys revealed the presence of hazardous air pollutants, as classified by US/EPA, such as Cl, Co, Cr, Mn, Pb, Hg, Ni, and P. Figure 4 shows a box plot of the concentration in wt% of elements detected on the PM collected from the exhaust emissions of (a) jeepney 1, (b) jeepney2, and (c) jeepney 3. As can be seen from fig. 4, the major elements in all the PM for all the three jeeps are C and O. PM from jeepney 1, the oldest jeep, contains the most number of elements with high frequency of occurrence. The hazardous element, Se, was detected only in jeepney 1 with concentration of 1 wt % to 15 wt % which means that in some PM it is a major element. In a recent study by Atikul et. al, Se could not be traced to the gasoline itself but traceable to the engine chambers and emissions from other mechanical activities within the operation zones of the engine [4]. However, the mean concentration of Fe is lower for jeepney 1 compared to jeepneys 2 and 3. Another source of Fe in diesel exhaust PM is the lubricating oil. Si is also a minor

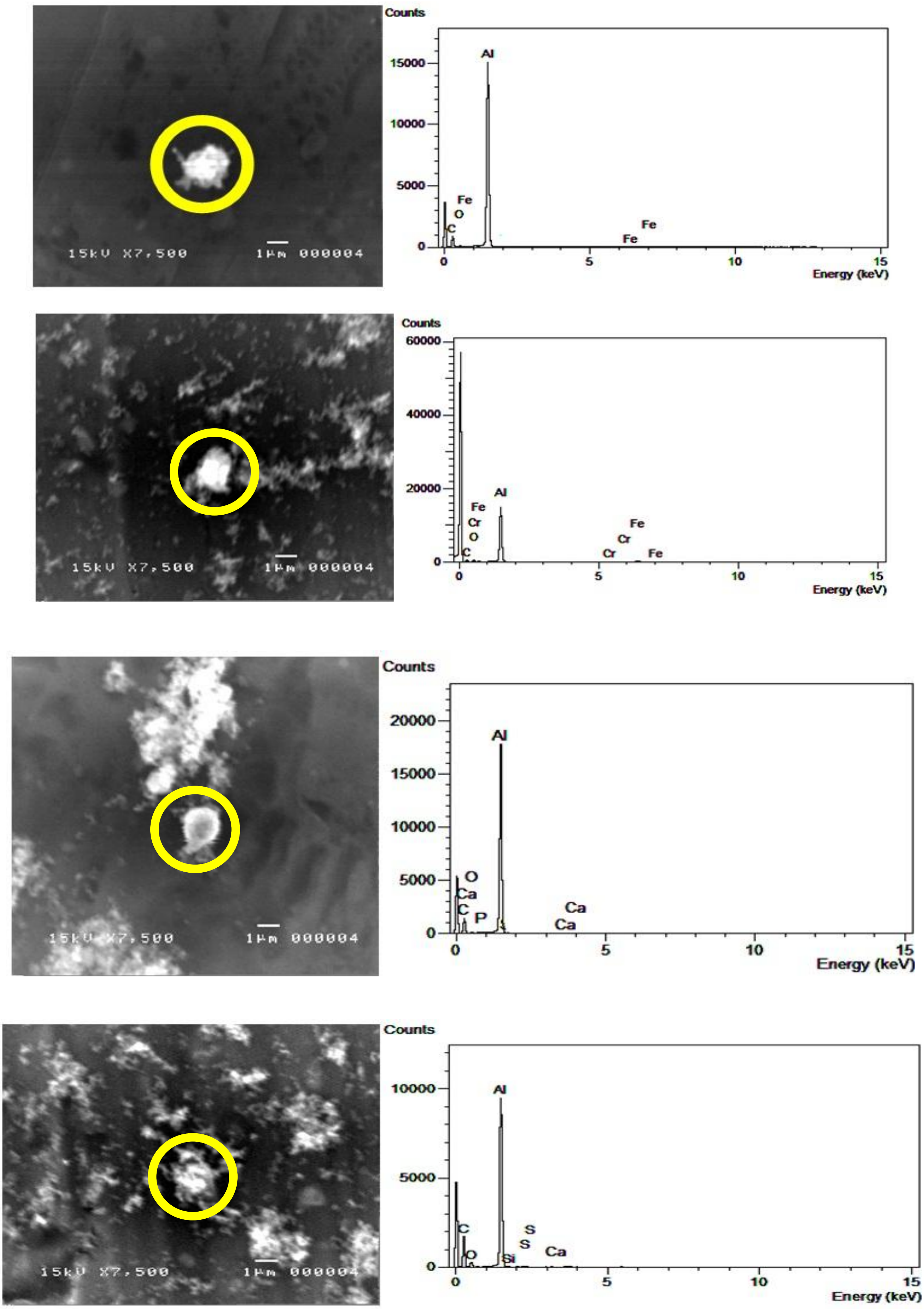

Fig. 3. SEM image of a $PM_{2.5}$ collected from the exhaust emissions of jeepneys and the corresponding EDS spectrum. The magnification used is 7500x.

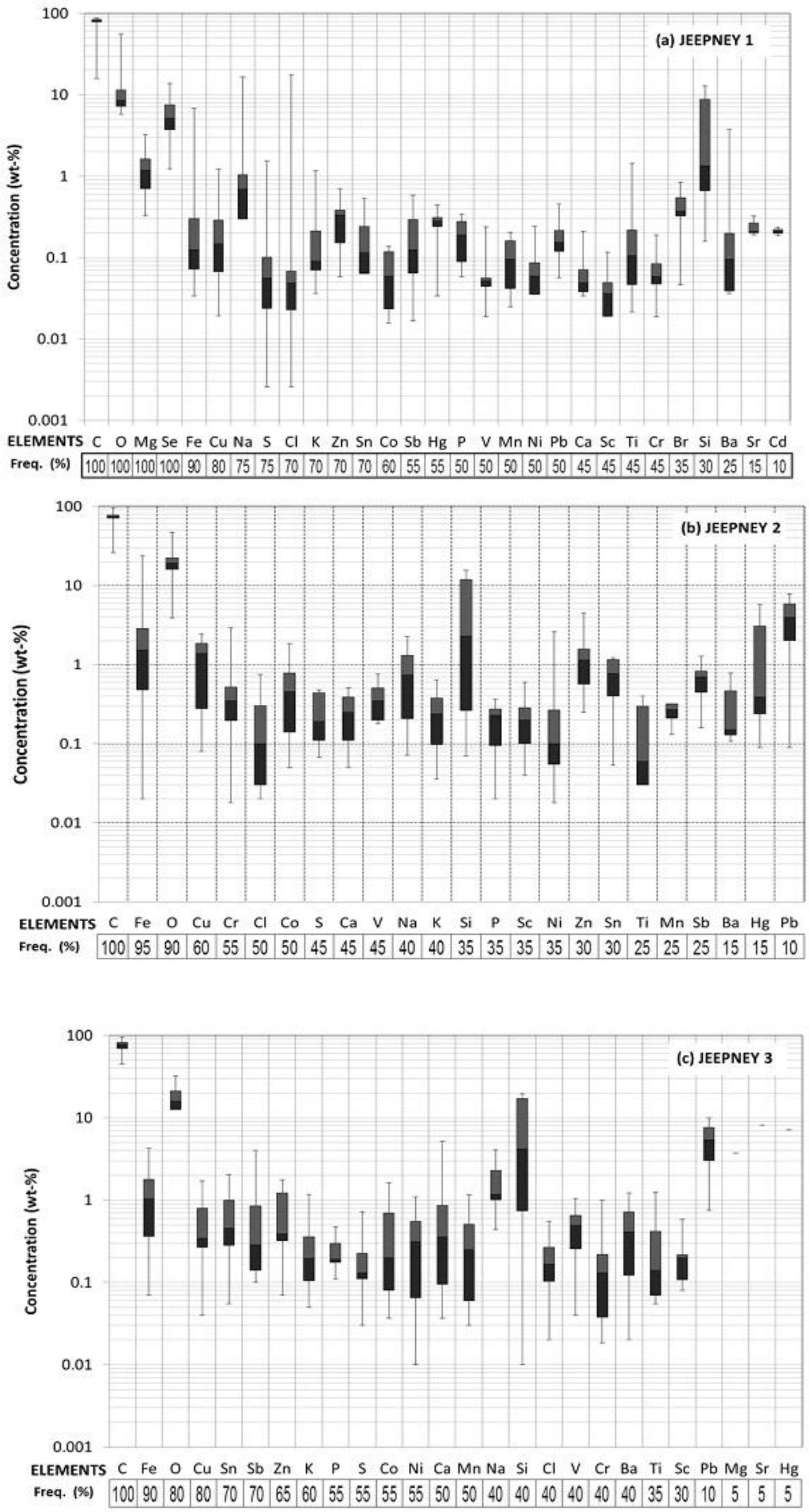

Fig. 4. Concentration (in wt%) of elements found in fine particulate matters collected from the exhaust emissions of (a) Jeepney 1; (b) Jeepney 2; (c) Jeepney 3.

element in all the three jeeps occurring in one-third of all the particles analyzed for each jeepney. It may have come from sintered silicon nitride that is used in automobile industry as a material for engine parts. More than 40% of the particles analyzed for all the jeepneys contain trace amounts of Cu, Co, Cl, Cr, Ca, Na, S, K, and V. Hazardous elements, Mn, Ni, Zn, and Sn were detected in more than 50% of the PM in jeepneys 1 and 3 in trace amounts. Several engine lubricating oil additives include metallo-organic compounds resulting in some metal oxide emissions including such metals as P, Zn, Cr, and Ca, and fuel additives can result to emission of Cu and Fe and some other metals [5]. Among the three jeepneys, jeepney 1 contains the most number of hazardous elements with high frequency of occurrence. In 2001, leaded gasoline was phased out but inspite of this, trace amounts of Pb and Hg were detected in 50% of the PM of jeepney 1 whereas it was only detected in just one or two PM of jeepneys 1 and 2. Jeepney 1 was manufactured in 1980. Ar, Ba, Co, and Sr are inorganic exhaust components that are products of engine and component wear, or are trace contaminants of the fuel and/or lubricant oil which usually vaporize in the combustion chamber and then "plate" themselves to particles in the exhaust stream [6].

IV. Conclusion

Elemental composition of fine particulate matters from the exhaust emission of jeepneys, which uses second hand diesel engine, was determined using SEM/EDX technique. Several hazardous elements were detected in minor or trace amounts in most of the fine PM collected for all the three jeepneys. Morphological images from the SEM revealed various shapes and sizes of PM from diesel exhaust emissions of the three jeepneys. Most of the PM had sizes less than 2.5 μm which is typical for diesel particulate matter. The major element is C for all the PM analyzed. EDX analysis of the PM from all the three jeepneys revealed the presence of several elements like Ca, Cl, Co, Cu, Cr, Fe, Mn, Pb, Hg, Ni, P, Na, S, Si, K, V, Mn, Ni, Zn, and Sn. Hazardous elements such as Co, Cl and Cr were detected in more than 50% of the PM analyzed. The PM analyzed from jeepney 1 contained the most number of hazardous elements that have a high frequency of occurrence. These include Pb and Hg which were found only in one or two PM in jeepneys 2 and 3. But for jeepney 1 traces of Pb and Hg were detected in more than 50% of the PM. In April 2000, Pb was completely phased out in Metro Manila. But since jeepney 1 was manufactured in 1980, that could have explained the presence of Pb in its PM emission. Another hazardous element that was found only in the PM coming jeepney 1 is Se. Again this could have been due to the age of the engine. This element could serve as tracer for very old jeepneys that were still on the streets of Manila.

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