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Characterisation of Airborne Particulate Matter in a City Environment

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Abstract

Airborne particulate matter contains a mixture of pollutants. Identifying the source of these particles, their composition and physical/chemical properties would help to provide a clear connection between their impacts on the environment and the human health. Individual particles have a different chemical morphology and this data could provide information on the formation and reaction mechanism of these particles. It also helps to identify the source they originate from as well as their atmospheric history. Over the years, numerous studies have been conducted to characterise PM_{10} and little work has been carried out on $PM_{2.5}$. However, there is an emerging interest in identifying the effects of very fine particles such as nano-particles.

The main objective of this research project was to carry out a comprehensive characterisation study of nano-particles

collected from a city environment. Environmental monitoring samples from a local authority monitoring site were collected over a period of 7 months using a tapered element oscillating microbalance technique (TEOM). The sample filters were then analysed for their morphology and elemental compositions using SEM/EDS and LA-ICP-MS. SEM/EDS analysis was able to detect several heavy metal particulate matter while the LA-ICP-MS showed that there were more heavy metals present in the filter samples especially the heavier metals. Some of these heavier elements could have been inhibited by organic or higher amounts of the more common metals found in the EDS such as Fe, Zn, Si and Al. Nano-particles originated from high temperature sources, biological, carbonaceous and road transport were also detected in the samples. It was also found that particles containing more metallic elements tended to have a more defined shape while carbonaceous materials typically had amorphous structures. Tests showed that particles with environmental dust compositions of Ca, Al and Si were abundant. It was observed that the biological particles had very fine sizes.

Keywords: Fine-Particles, Ultrafine-Particles, Environmental Monitoring, Pollutants, Urban Environment, TEOM, SEM

1. Introduction

"Airborne suspended particulate matter may be either primary or secondary in its origins. Primary particles are those directly emitted to the atmosphere from sources such as road traffic, coal burning, industry, windblown soil and dust and sea spray. On the other hand, secondary particles are particles formed within the atmosphere by chemical reaction or condensation of gases, and the major contributors are sulphate and nitrate salts formed from the oxidation of sulphur dioxide and nitrogen oxides respectively" (QUARG, 1996).

Airborne particulate matter (PM) can cause a variety of environmental problems, and can also have a significant impact on human health (Zanobetti et al., 2000). A recent report by Brook et al., (2004) showed that the current airborne PM concentration is sufficient to cause an increased risk for cardiovascular events. Such events usually lead to increased case of hospitalisation due of coronary artery disease, stroke and other atherosclerotic diseases. Ultrafine PM from a few nanometres in diameter (d_p < 100 nm) penetrates much deeper into the lungs causing more significant damage compared to fine particles greater than 1 micrometre (d_p < 2.5 μm) (Donaldson et al., 1998; Glantz, 2002; Brook et al., 2004; Donaldson et al., 2005). Aerosol particles in the atmosphere can cause light scattering, which has a direct effect on the climate and visibility. It can also indirectly affect the climate by acting as cloud condensation nuclei which other pollutants could react with to produce other toxic and carcinogenic pollutants (Wieprecht et al., 2004). Over the years there have been numerous studies on the significance of particulate matter as a pollutant, however there is still a major need to fully characterise airborne PMs in terms of morphology, chemical composition and their origin in relation to health and environmental impact.

In the UK, the major sources of airborne particulate matter as described by the NAEI are transportation (35%), stationary fuel combustion (34%), processes (16%), agriculture and waste (14%) and others (1%) (Dore et al., 2006). There have been relatively few comprehensive studies of atmospheric particulate matter in the UK, considering the morphology and inorganic composition in detail. Often, more consideration is given to the organic components of the particulate matter, but inorganic compounds may also be significant from a health point of view, with a paper by Baulig et al., (2004) indicating that copper (and possibly iron) were significant contributors to the oxidative stress caused by fine particulate matter (Baulig et al., 2004; Limbach et al., 2005). One of the key tools selected for detailed investigation of the airborne PM samples is electron microscopy. Scanning electron microscopy with energy-dispersed analysis of X-rays (SEM/EDS) have already proven to provide information on the morphology, phase and elemental composition of individual particles (Paoletti et al., 2002; Laskin et al., 2006). The elemental composition of the samples can be analysed using laser ablation coupled with an inductive coupled plasmas mass spectrometer (LA-ICP-MS). The LA-ICP-MS is able to detect very low elemental concentrations while only requiring minute amounts of the sample.

Quantification and characterisation of particles is crucial in assessing their impact on the environment. Although airborne mass concentrations of various sizes of particulate matter are collected routinely, further information can be obtained from shape, size and chemical composition of samples, or even individual particles. Individual particles have different morphology and chemical composition, and these data will provide information on their source, atmospheric history, and their formation and reaction mechanisms. Identifying the source of airborne particles, and their composition, physical and chemical properties will help to provide a clear connection to their impact on the environment and the human health. Nevertheless, over the years, numerous studies have been conducted to characterise PM_{10} and some work on $PM_{2.5}$. Most of these studies were carried out in terms of the medical effects of particulate matter (Zanobetti et al., 2000; Baulig et al., 2004; Limbach et al., 2005). However, at the moment there is very little information on the origins of PM in the environment.

This paper presents the experimental results obtained for nano-particles collected at a local Authority monitoring site in a UK City.

2. Experimental methodology

2.1 Sampling location

Sheffield is the fourth largest city in the UK with just over half a million population. It is located in South Yorkshire and boundary to the Peak District National Park. Sheffield has a history as a major steel/metal producer in the UK. In the early 1900s, coal burning for steel production and domestic heating was a major contributor to poor air quality in the City which was associated with adverse health effects on the population (Daly and Elleker, 2004). It was the introduction of the Clean Air Act in 1956 that saw the enforcement of smokeless zone and improved air quality for residential as well as industrial areas. The location of the monitoring site used for this study is called "Groundhog 3". The site is located within a residential area and close to an A-road. This PM monitoring unit is situated within an urban commercial/residential area. The possible sources of particulate matter collected from this site are: commercial and residential heating, road transportation, and railway line. There is also a possibility that some of these airborne particulates may have migrated to this region from elsewhere. Sample filters were collected for a period of approximately 7 months (sampling duration ~ 30 to 60 days) from the local environmental monitoring unit.

2.2 Sampling technique

Samples were collected by Sheffield City Council on quartz fibre filters designed for TEOMs using Rupprecht & Patashnick Series 1400A TEOM samplers (R&P Co. Inc., 1998). Monitoring of ambient air PM_{10} mass concentration was performed using a 15-minute time resolution. The duration of the sampling was approximately 30 to 45 days from April 2006 to January 2007, and the average PM_{10} concentration during the monitoring period were approximately 24μg/m^3 to a max of 35μg/m^3.

2.3 Scanning Electron Microscopy

Characterisation of the particles in airborne PM_{10} samples were performed using scanning electron microscopy (SEM). Morphology images (shape and size) of the particles were obtained using a CamScan Series II SEM. The elemental composition of the particles was analysed using an AN10/85 Energy Dispersive X-ray Spectrometer (EDS). The CamScan SEM was capable of producing images with a resolution of 7 nm for both secondary electron (SE) and back scattered electron (BSE) compositional imaging mode. In addition, the EDS allowed qualitative and quantitative microanalysis and for X-ray mapping. Digital images captured using various image acquisition software packages enabled the images to be obtained digitally. Usage of a Be window detector however limited the ability for the EDS to analyse lighter elements (Na and below). In the EDS mode the equipment was only able to detect concentrations in ppm levels. Six sample filters were analysed and each of these samples corresponded to a monitoring period. Particulates from the sample filters were carefully transferred onto carbon film tape mounted on a SEM specimen holder. Each sample was then carbon coated under vacuum before being analysed by SEM.

2.4 Laser Ablation ICP-MS

For solid sampling technique, Laser ablation has proven to be the most versatile sampling technique to be used in combination with an Inductive Coupled Plasma (ICP) spectrometry. It is often known as Laser Ablation Inductive Coupled Plasma-Mass Spectrometer (LA-ICP-MS). A sufficient amount of energy in the form of a focused laser beam was directed onto the surface of the sample, the material then started to sputter and vaporised. The vapour plume and particles were then transported by an argon gas carrier into the plasma flame for atomisation and ionisation. The interest and use of LA was due to its ability to sample a diverse range of materials from conducting and non-conducting inorganic and organic compounds as solids or powders (Akbar, 1998). In this experiment, PM samples were subjected to laser ablation line rasters using a New Wave RS UP-266 macro laser ablation system. This allows compositional information to be obtained from different sub-regions of the PM sample. The ablated PM was then analysed using an Agilent HP 4500 ICP-MS.

3. Results and discussion

3.1 SEM/EDS Analysis

3.1.1 Groundhog 3 PM_{10} (25/04/06 – 24/05/06)

In figure 1, the feature particle in the middle, a hollow shaped sphere, has the characteristic of particles from a high temperature source known as cenosphere. Cenospheres are typically found in fly ash and bottom ash samples of particulate matter from thermoelectric power stations (Vallack and Chadwick, 1993; Vassilev and Vassileva, 1996). It is common for particles of this nature to have compositions of alumino-silicate glass, mullite, quartz, calcite, Fe oxides, Ca silicates and sulphates (Vassilev et al., 2004). EDS result for the feature particle gave a high peak of S, which suggests high sulphate content. It also showed minor peaks of Al, Si, Ca, Fe and K. The only difference between the feature particle analysed in this study and the ones reported in the literature is the "size of particle". Typical thermoelectric power station cenospheres have sizes ranging from 5 to 500μm and since the location of particle sampling is next to a busy road with no other major high temperature activities in the surroundings; it can be concluded

that the size of this particle (slightly larger than 3μm diameter) is a result of erosion during migration. The nearest thermoelectric power station is a large Coal-fired Power Station which is approximately 40 miles downwind towards the city of Sheffield. There are also crustal materials, which could have been accumulated either during migration or sampling.

Figure 2 is an image of typical particulate matter in another region of the same filter. EDS analysis showed that the rod-like particle is composed of only elemental Fe. All the other amorphous shaped particles are either soot or carbonaceous material. This rod-like particle is around 1μm in diameter and 3μm long. The morphology of the feature particle suggests that it is a product of metal wear from vehicle tailpipe, breaks etc. It should be noted that A61 road (with an average of 20,000 vehicles using the road per day) is located next to the sampling station (Groundhog 3) (Abu-Allaban et al., 2003).

3.1.2 Groundhog 3 PM_{10} (24/05/06 – 27/06/06)

The particles in black circles in figure 3 have all been subjected to EDS analysis and the results giving varying peaks of S, Ca with moderate amounts of Cl. There were also some small amounts of Si and K present. These particles are around 10μm with round edges. The shape of the particle could be a result of accumulation and erosion in the atmospheric environment.

A high magnification of the particle in figure 4 shows evidence of particulate matter accumulation due to its morphology. The EDS analysis gave very similar elemental compositions to particles shown in figure 3.

Particle in figure 5 is around 10μm in length with high peaks of Fe and very minute counts of Si, S and Ca. The shape suggests that it is plate-like and could have been a result of brakes abrasion or rust compounds from vehicles.

In an urban environment, there are various types of particles in the form of metal, non-metals and biological particles. Particle in figure 6 is an example of a bacterium or an environmental micro-organism known as bio-film. EDS analysis of the particle surface shows that middle of the particle surface is smoother than the surround dotted surface. The results contained high counts of Cl with lower counts of S and minute amounts of K. There are reports of these particles causing allergies and infectious disease in humans. Since this particle is approximately 7μm in diameter, there is a possibility that it will penetrate into the human respiratory system, which could subsequently led to other detrimental health issues.

3.1.3 Groundhog 3 PM_{10} (20/07/06 – 05/09/06)

There are two feature particles in figure 7 labelled as “A” and “B” respectively. EDS analysis on particle A gave only a high peak of Cl. The limitation of the SEM detector as well as the EDS did not allow Na to be detected therefore it could be concluded that the “A” is a salt particle e.g. NaCl. A review of SEM images of NaCl particles from literature has shown that they are similar to the feature particle A in terms of shape and size (around 2 μm) (Ebert et al., 2002; Hoffman et al., 2004).

Feature particle B looks like a 2μm diameter spherical particle with amorphous and crustal material stuck onto it. The EDS analysis of the whole particle gave a high peak of Fe and S, which suggests that; it is a product of metal wear from vehicles or combustion processes. Signs of metal wear were further confirmed based on the minor peaks of Cr and Zn, both elements of which are used in the vehicle/steel manufacturing industries for chroming and galvanizing steel. However the shape and appearance along with the high peak in S, seems to suggest that this particle is emitted from a high temperature source such as the metal industry (there is local metal factory northeast of the sampling site). The crustal like deposit on particle B was confirmed by the EDS showing minor peaks of Ca, Cl, K and Si.

The feature particle shown in the middle of figure 8 is comprised of mainly Fe. There is also a high peak in Cl with lower concentrations of Ni and Cr. The particle in question is approximately 3μm wide and is surrounded by other amorphous-like particles, which are thought to be non-metal since under the back-scattered mode it did not show any presence of metal elements.

Figure 9 is an image of the TEOM filter fibre. EDS analysis confirms a high concentration of Si with lower concentrations of K, Ca and Ti. This type of filter media is made using silica fibre as the major component along with K, Ca and Ti. This was confirmed by the manufacturer (R&P Co. Inc., 1998).

3.1.4 Groundhog 3 PM_{10} (05/09/06 – 28/09/06)

Particle A shown in figure 10 is composed of mainly Fe with minute quantities of other environmental dust particles such as Ca, Al and Si. Since there are a lot of other smaller amorphous particles settled on top of it, it is not possible to determine the morphology or its true size. Particles B and C are salt crystals which were shown in the EDS as just a Cl peak. In the middle of the image, there is also a cube like particle, which is partially visible along with the smaller square particle on the right hand side of the image. Both particles are salt based on their morphology. Image in figure 11 has similar composition to particles B and C. Therefore based on its EDS analysis and morphology, it can be concluded that this particle is also a salt crystal.

The particles in figure 12 and 13 have a length of around 6μm and 12μm respectively. EDS analysis performed on both particles gave similar results of Si, Al and K counts with smaller quantities of Fe and Cl. These particles are environmental dust particles.

3.1.5 Groundhog 3 PM_{10} (23/11/06 – 05/01/07)

The black circle in figure 14 is a burnt spot from the EDS analysis, which gave high peaks of Ca and S along with lower counts of Si, K and Ca. It seems that environmental dust particles and most non-metals will suffer burns when electron beams are being applied. It could be due to the high 15KV energy used for EDS analysis, however under the imaging mode of 8KV the surface of the particle seemed to be melting.

Particles A and B in figure 15 are "salt particle" and "iron particle" respectively. The former particle was smaller than 1μm while the latter had a size of around 2 to 2.5μm in size.

3.2 LA-ICP-MS Analysis

Most of the elements shown in figure 16 were less than 85ppm with the exception of Pb with at a surprising peak of nearly 140ppm in the final sample. Mn, Ni and Cr averaged around 15ppm while a gradual increase in Zn and Fe was observed. In figure 17, the concentrations of Sb, Mo and As were also less than 15ppm throughout the sampling dates. Ca and Na concentrations were expected to be high due to busy roads and high dust concentrations within the vicinity of the sampling location. The toxic metal concentrations of Co, Tl and Hg in figure 18 were all less than 2ppm while Cd concentrations were less than 4.5ppm. Concentration of elements illustrated in figure 19 was lower than 20 ppm except Si, which had a peak of approximately 30ppm in the third sample. From all four figures there were several elements, which exhibit similar concentration trends. One such trend observed was elements of Ca, Al and Si, which are the composition of typical crustal or dust particles.

3.3 Discussion

The SEM analysis of each sample filters showed that there were particles, which could have originated from the surrounding activities and environment but it also showed that some particles could have migrated from high temperature processes further upwind. In most of the images there were some particles, which had an amorphous structure, but EDS analysis did not detect any elemental composition. This could have been due to the sensitivity of the equipment or the Be window detector. However, the appearance and morphology of amorphous particles suggests that they could be soot particles produced from the combustion of petrol and diesel in internal combustion engines (Moreno et al., 2004). It was not unusual to find high amounts of carbonaceous or soot particles since the monitoring location is within the vicinity of a busy A-road with an approximate traffic of 20000 vehicles/day. There were also some particles, which were biological in nature. These micro-organisms are known as bio-films. Crustal material was also one of the major components found in this analysis. The sources of these crustal materials are industrial fly ash, dust from transportation and soil. The compounds usually exist naturally as oxides of aluminium, silica, calcium, titanium, iron, magnesium, sodium and potassium with moisture contributing to more than 80% of the soil sediments (Chan et al., 1997; Suzuki, 2006). However, the high content of Fe, Cr, Zn and other heavy metals detected by the EDS analysis could have been released by the steel and metal industries or wear and tear metals parts of vehicles. The majority of the chlorine found in the EDS analysis was thought to be sea salt particles, which could have travelled inland from the oceans or from road gritting during the winter seasons. Generally chlorine was detected more in PM_{10} samples since marine aerosols are much more dominant in the coarse particle range (Kouimtzis and Samara, 1995).

Analysis from the elemental composition of all the filters showed that the concentrations of Cd, Co, Tl and Hg were lower than 4.5ppm. Concentrations of Mn, Ni, Cr, Sb, Mo and As were less than 15ppm. All these heavy/toxic metal elements are highly regulated due their effects on human health. It was expected that the concentrations of Al, Na and Ca would be very high since they exist in the environment as crustal material (dusts, soil, sand etc) and salt. Some elements such as Pb, Zn and Fe were found to be very high such as Pb at nearly 140ppm, but these could have originated from wear of vehicles or from high temperature processes in the North-east region of Sheffield. The metals detected in the samples such as Ni, Zn, Fe, Mn, Mo, Pb and Cu are all the known metallic elements which are widely used in the metal/steel industries. Some of trends exhibit in the figures also proved that some metals tend to condense or agglomerate close to each other.

4. Conclusions

The main findings from this research project are as follows:

- SEM/EDS analysis was only able to detect some heavy metal particulate matter while the LA-ICP-MS showed that there were other heavy metal elements present in the filter sample. Some of these heavier elements could have been inhibited by organic or higher amounts of the more common metals found in the EDS such as Fe, Zn, Si and Al.
- However, SEM analysis was able to show the characteristics and morphology of individual particles and thus

enabled one to understand its origin and airborne activity.

- Individual particles could have originated from high temperature sources, biological, carbonaceous and road transportation were detected in the samples. It was also found that particles containing more metallic elements tended to have a more defined shape while carbonaceous material typically had an amorphous structure.
- Some metals and their elemental compositions detected in the samples were traced back to the common metallic-elements widely used in the steel and metal industries.
- The analytical techniques used in this study were able to provide valuable information on the morphology and elemental composition of the samples collected. This information was used to identify the sources of origin of the particle emission.

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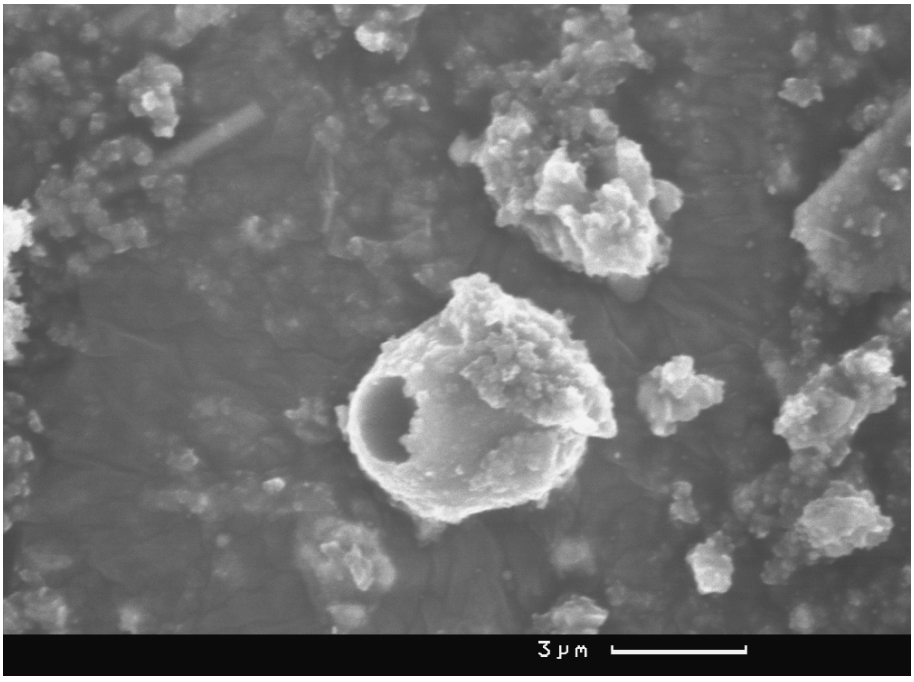

Figure 1. SEM image of PM at 3μm

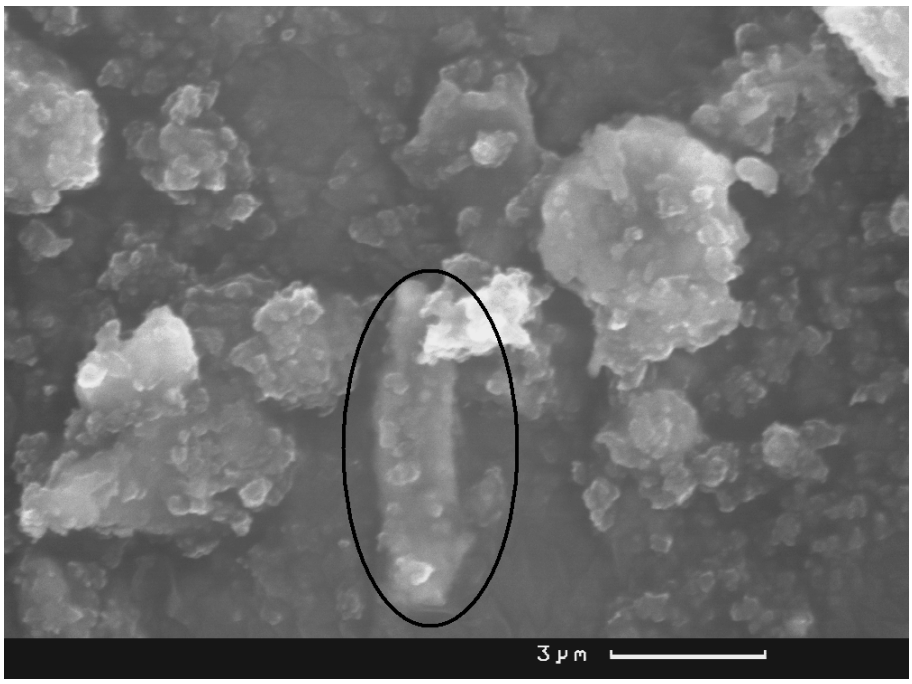

Figure 2. SEM image of PM at 3μm

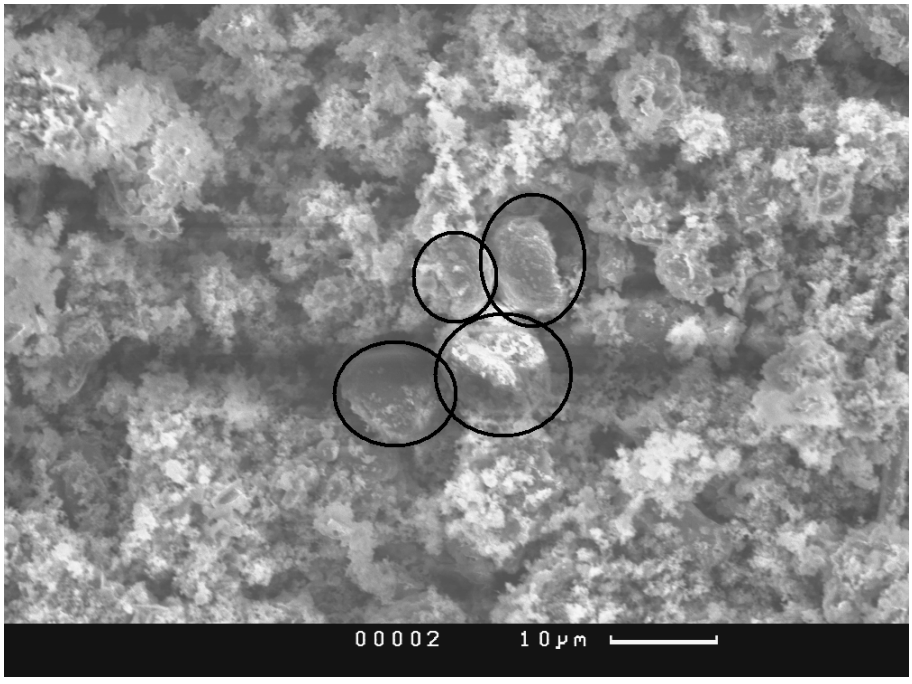

Figure 3. SEM image of PM at 10μm

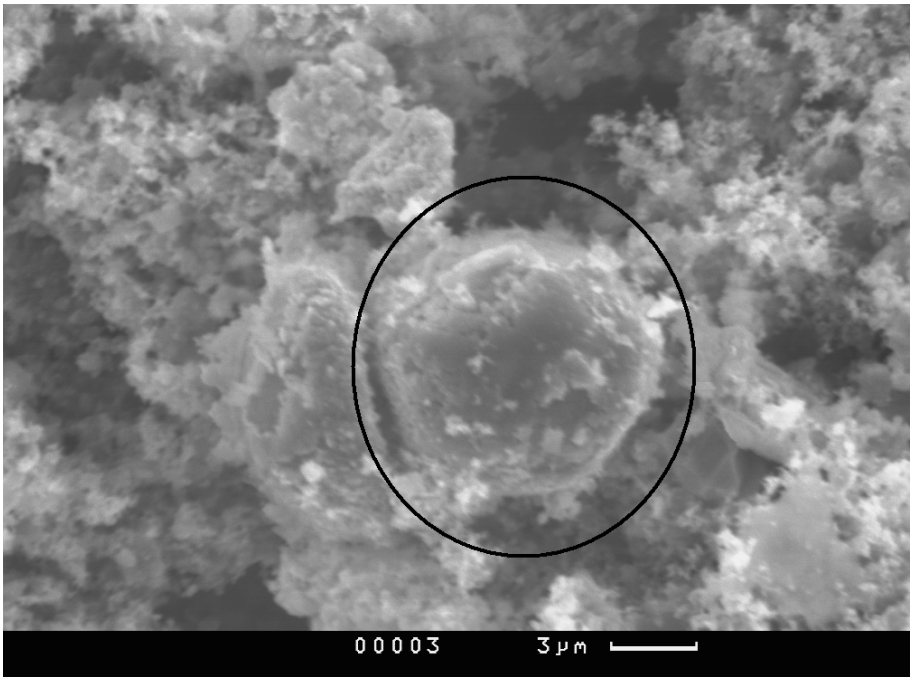

Figure 4. SEM image of PM at 3µm

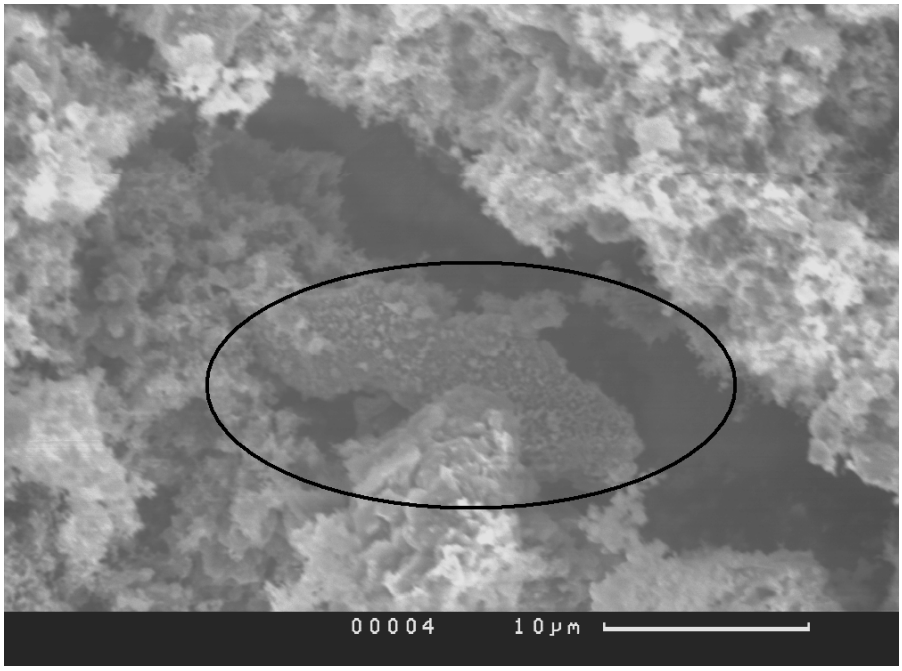

Figure 5. SEM image of PM at 10µm

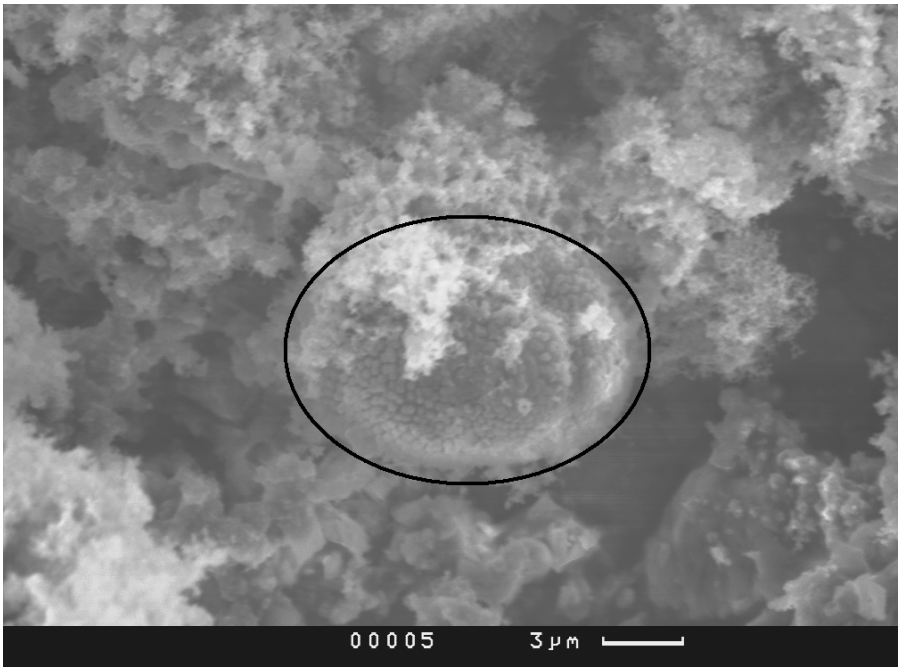

Figure 6. SEM image of PM at 3µm

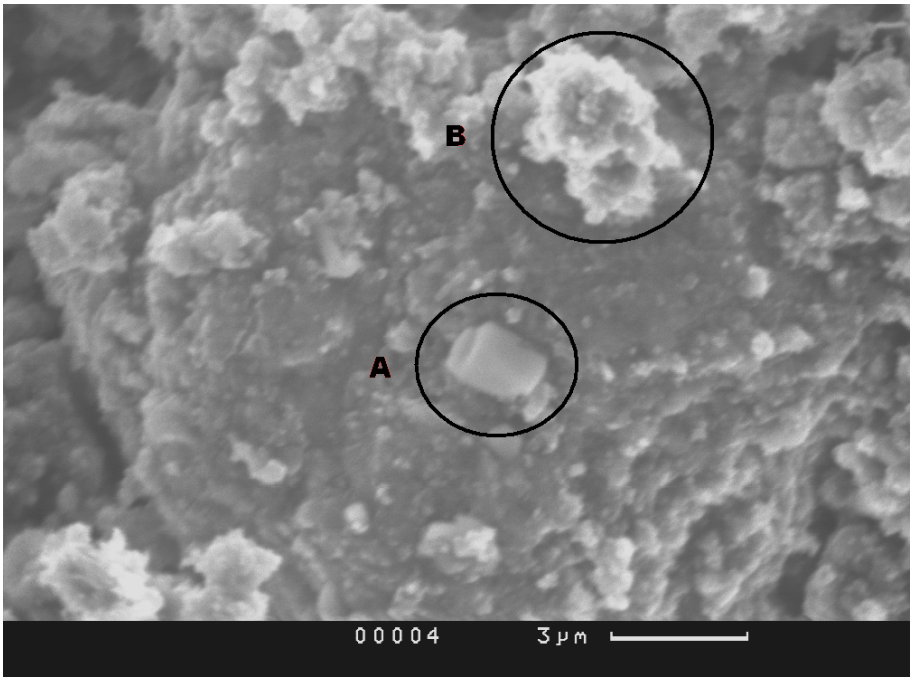

Figure 7. SEM image of PM at 3µm

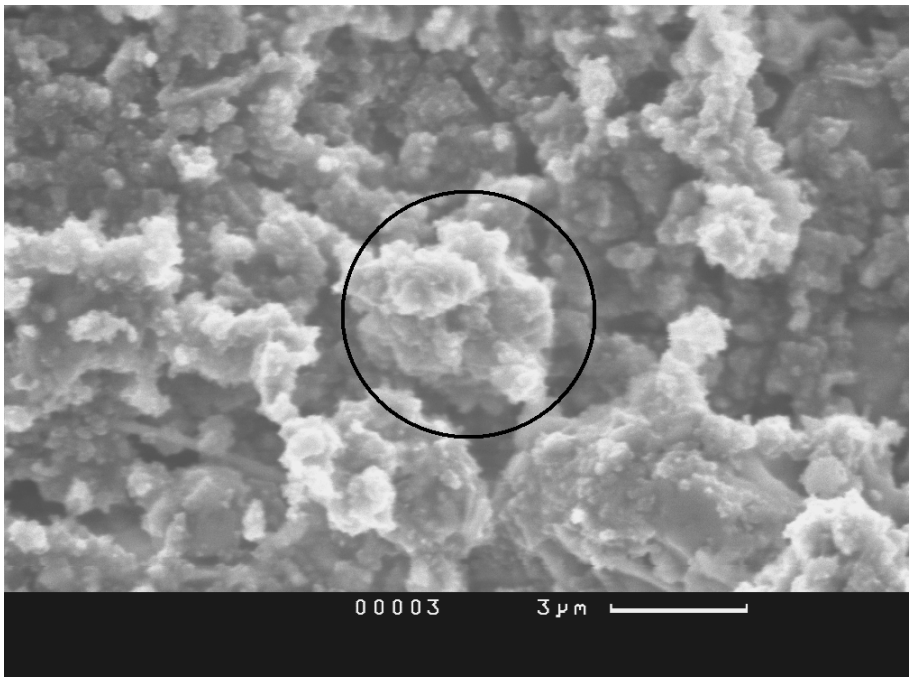

Figure 8. SEM image of PM at 3µm

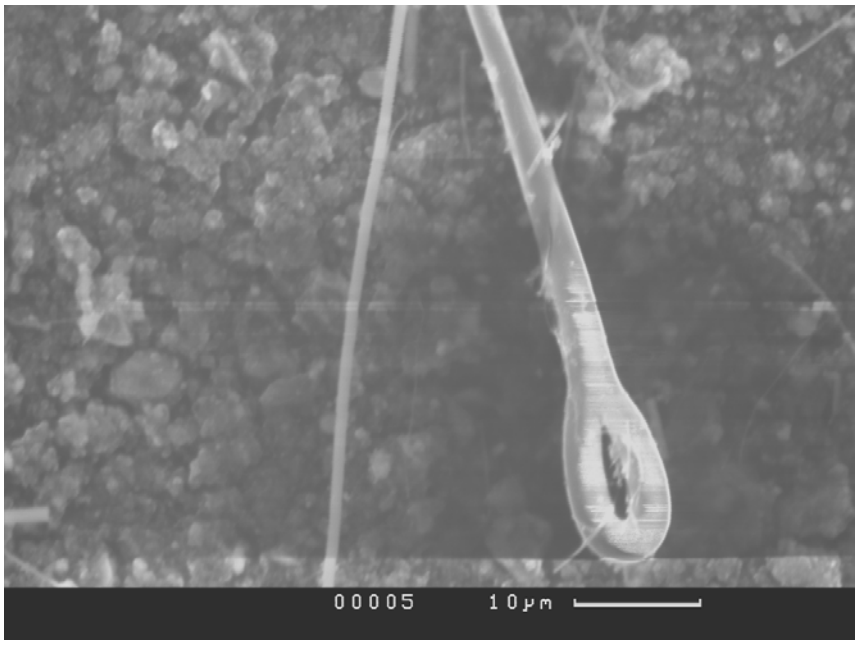

Figure 9. SEM image of PM at 10µm

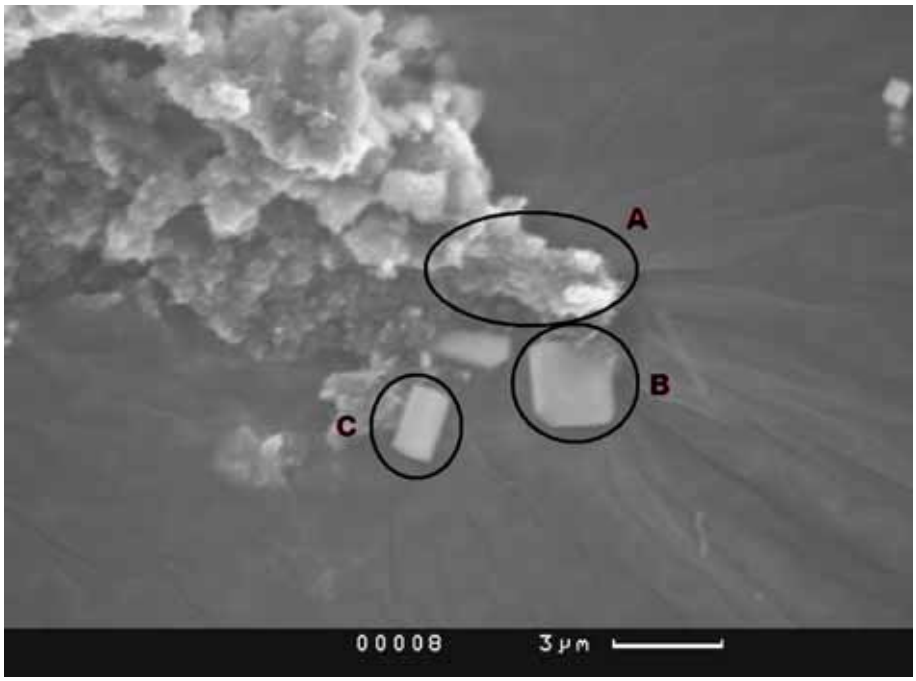

Figure 10. SEM image of PM at 3µm

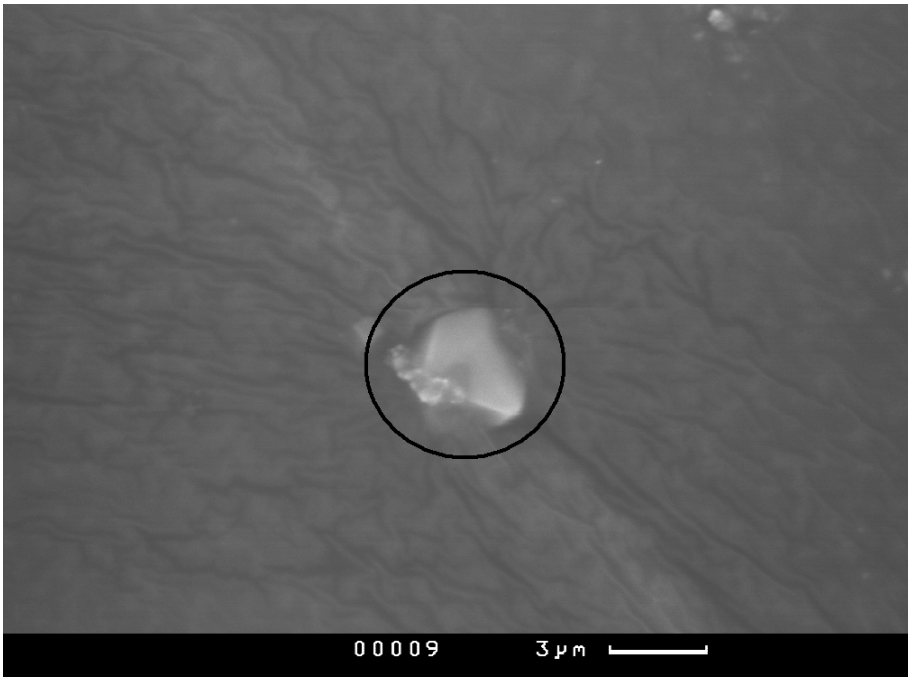

Figure 11. SEM image of PM at 3µm

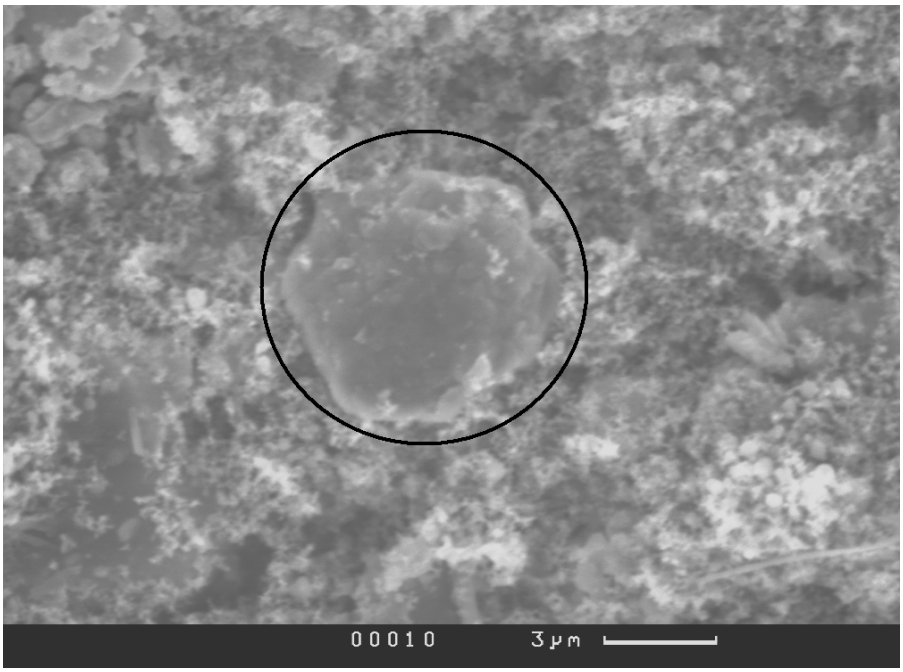

Figure 12. SEM image of PM at 3µm

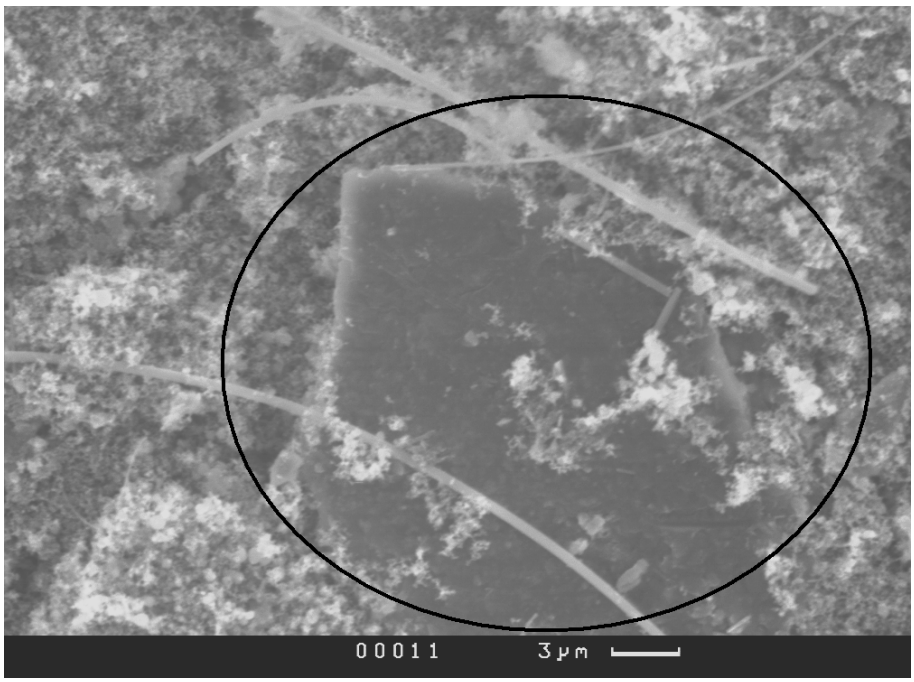

Figure 13. SEM image of PM at 3µm

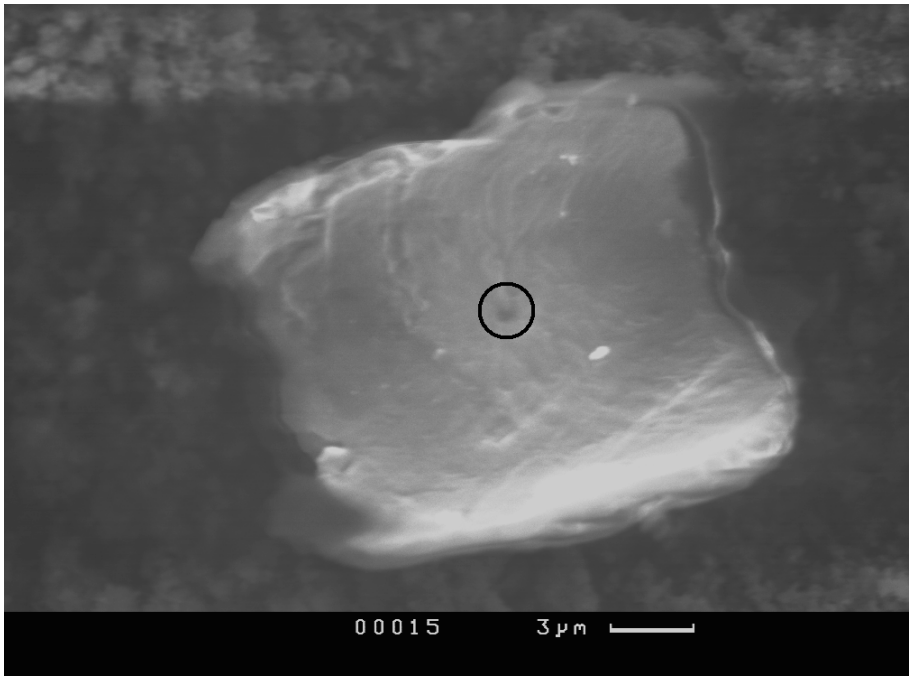

Figure 14. SEM image of PM at 3µm

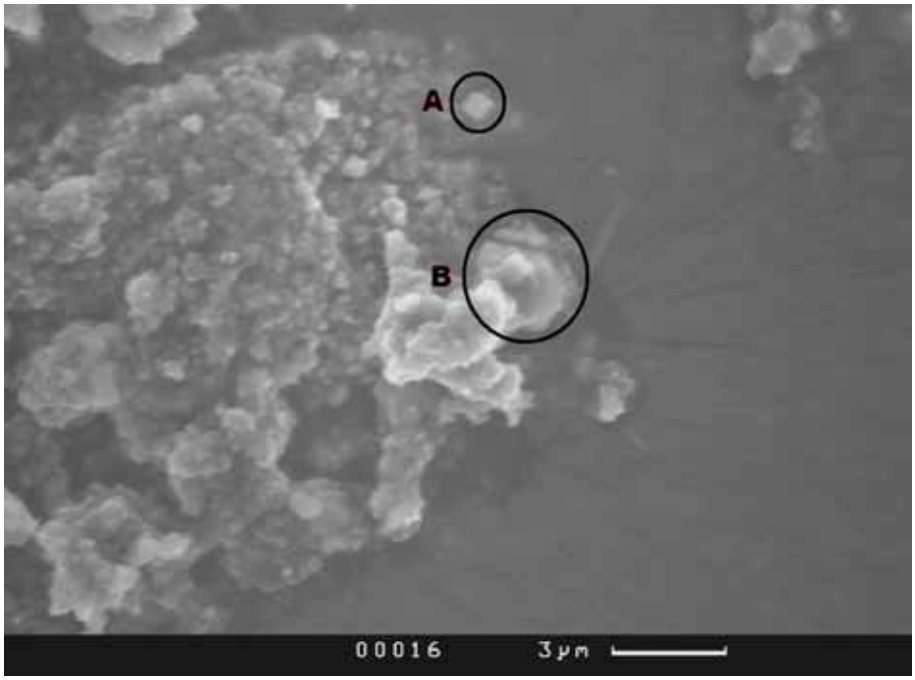

Figure 15. SEM image of PM at 3µm

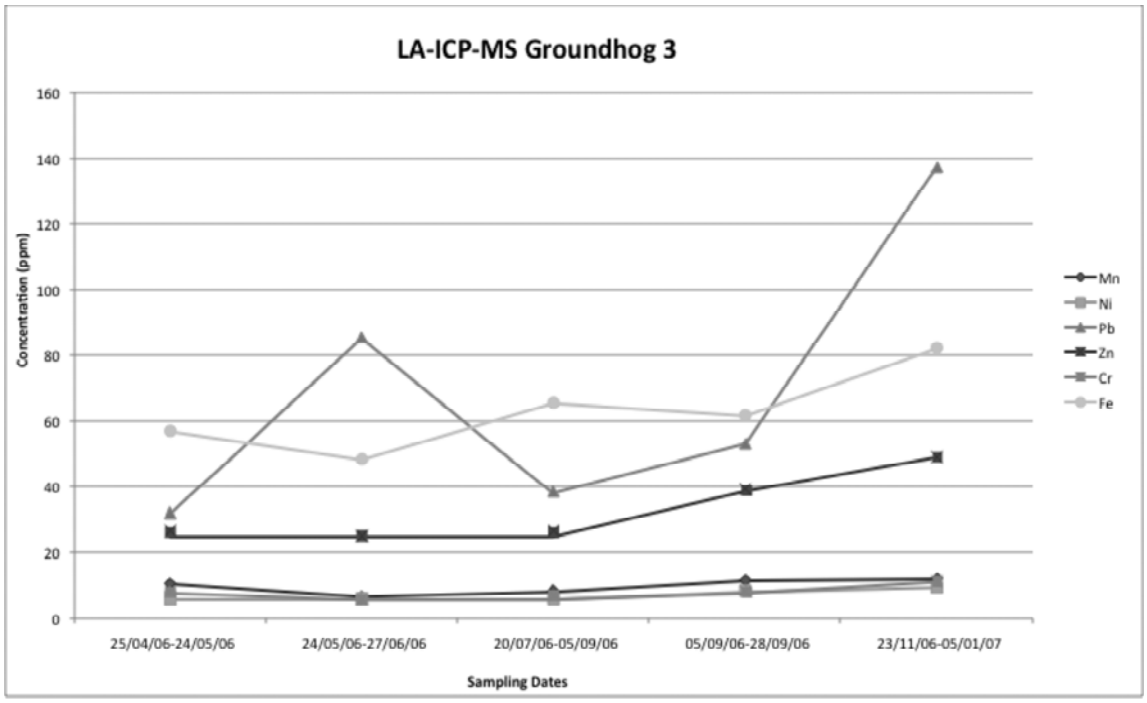

Figure 16. LA-ICP-MS Groundhog 3 for Mn, Ni, Pb, Zn, Cr and Fe

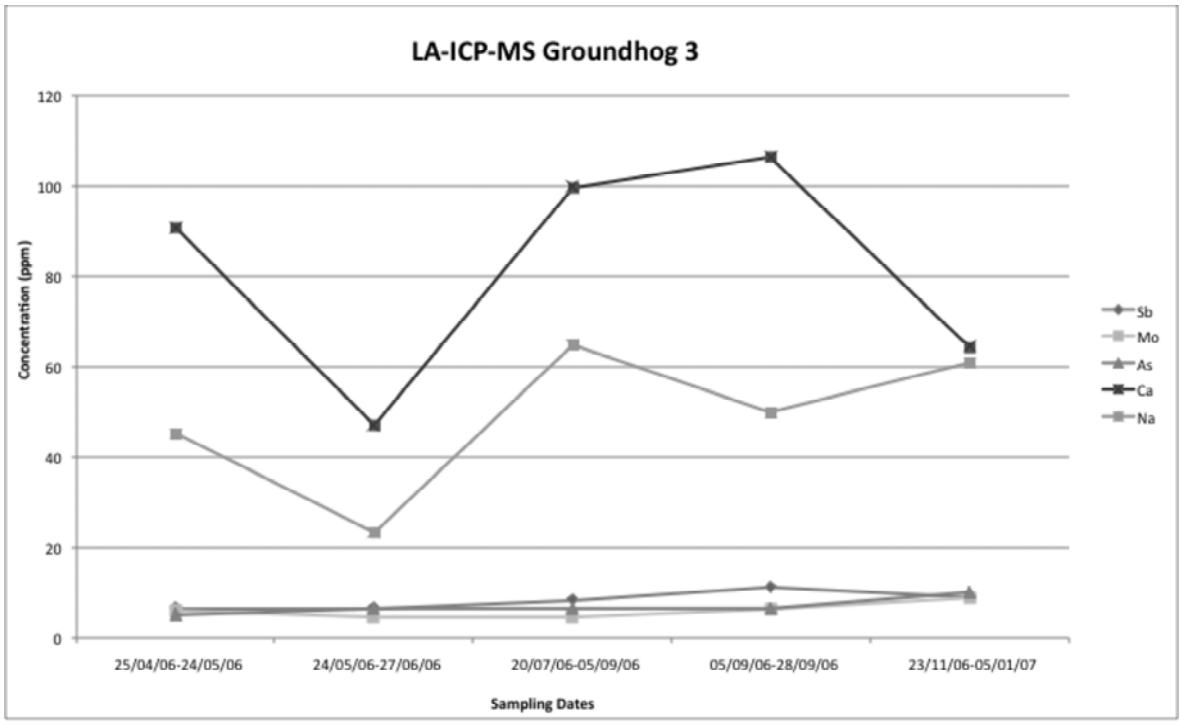

Figure 17. LA-ICP-MS Groundhog 3 for Sb, Mo, As, Ca and Na

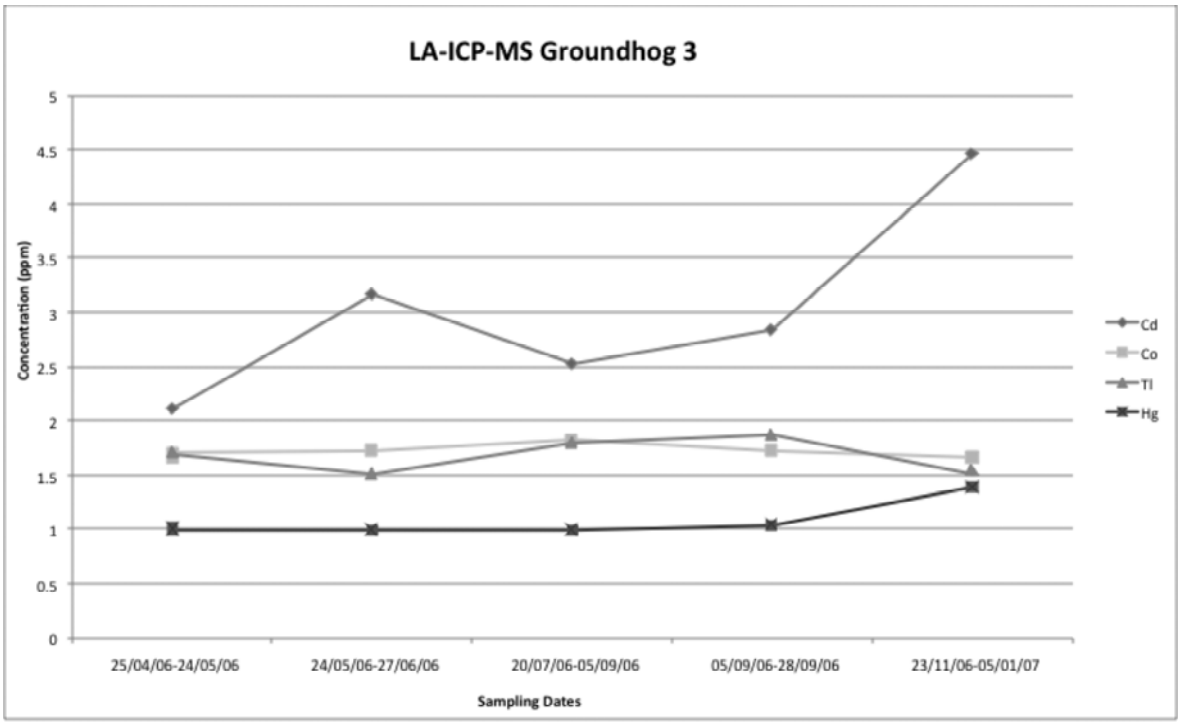

Figure 18. LA-ICP-MS Groundhog 3 for Cd, Co, Tl and Hg

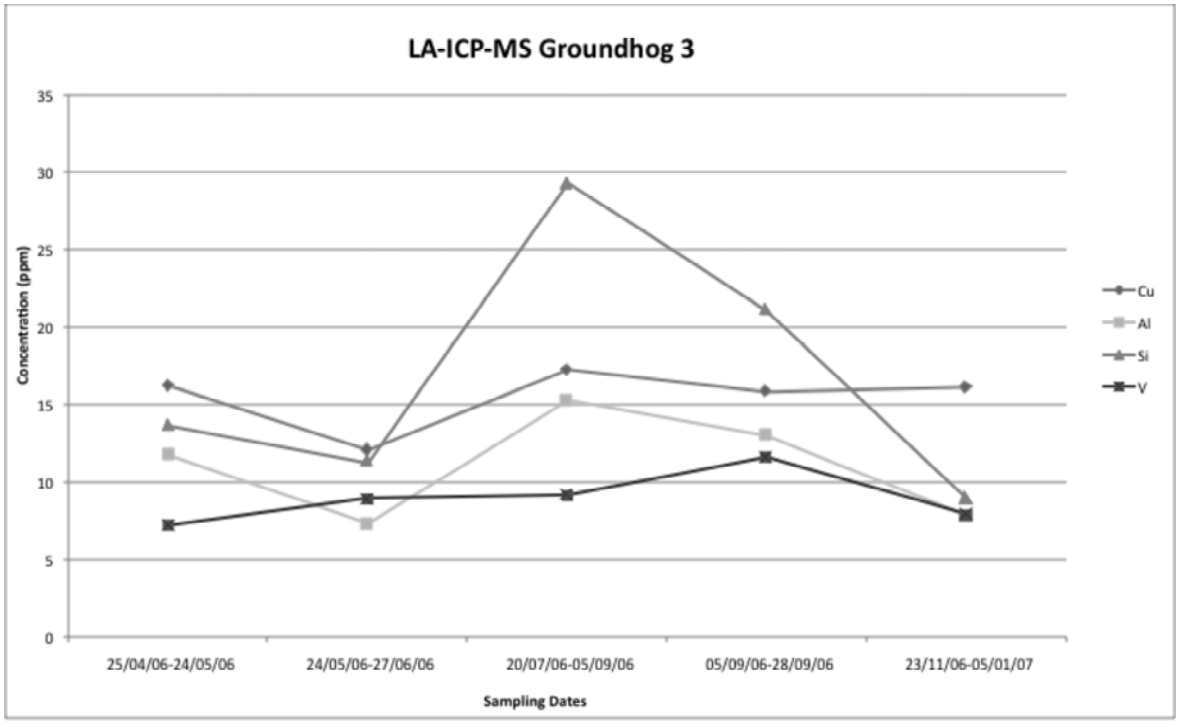

Figure 19. LA-ICP-MS Groundhog 3 for Cu, Al, Si, and V