Evaluation of $PM_{2.5}$ Emitted in Environmental Contingency in the urban area of Tijuana, B.C. (Mexico)

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Abstract

From October 22 to 29, 2007, there was an environmental contingency in the city of Tijuana. This contingency generated environmental conditions that did not allow citizens to have a clear sky. With the purpose of identifying elemental contents and morphological composition of $PM_{2.5}$ particulate material, which was generated during such period, a sampling was carried out in two areas of the city: one with constant traffic activity and a residential area. Particle Induced X-Ray Emission (PIXE) techniques was applied for the quantitative determination of micro-elemental contents, while Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to study the morphology. Based on the results obtained, it is estimated that the analyzed particulate material comes from different generating sources, mainly from mineral and soil, as well as that resulting from biomass burning and traffic activity. Regarding $PM_{2.5}$ and in compliance with the Mexican Official Regulation, the limit allowed was not surpassed.

Keywords: $PM_{2.5}$, Particulate material, Fine particles, Environmental contingency, AFM application, Morphological characterization

1. Introduction

Environmental and public health organisms consider particulate material as a pollutant due to the harmful effects on human and environmental health. Particles with dimensions below 2.5 µm ($PM_{2.5}$ fine particulates) are especially under consideration due to its relationship with respiratory illnesses, cardiovascular conditions and an increase of mortality indexes (Sousa, et al; 2012). Additionally, the environmental impact of $PM_{2.5}$ is reflected on the quality of local and regional air, depending on aspects such as the meteorological issues, the particle size or, chemical composition (Fang, et al; 2005).

Emission sources that contribute to the generation of particulate material can be of anthropogenic type: emitted by industrial processes, agricultural activity, transportation and forest fires. Thus, they can be naturally generated by: volcanic emissions, marine breeze, forest fires caused naturally, and the combination of pollutants emitted to the atmosphere (secondary pollutants). The chemical composition and the morphological characterization of $PM_{2.5}$ are essential factors in order to identify the source of the particulate material. Therefore, a significant stage within public health evaluation regarding air quality, it can be said that fine particles are formed by elements such as sodium, magnesium, aluminum, silicon, potassium (Beebe, et al; 2001), or they are constituted by chemical or mineral components such as sulfates, nitrates, metallic oxides, silicates, calcium carbonates, and high-carbon particles (it represents 20-40%; Zhuang, et al; 2004). Likewise, some authors indicate that fine particles represent 60-70% of the particulate material whit dimensions below 10 µm (Fang, et al; 2005, Lin, et al; 2004).

2. Experimental Development

2.1. Study Area: Two study areas, located northeast and southeast of the city of Tijuana, B.C. The first area has constant traffic activity of mobile sources (cars, buses, etc.) (A-I), with commercial and school land usage --such as CONALEP Tijuana Campus II Highschool, this site is adjacent to Via Rapida Poniente where vehicles move at high speed and it is parallel to the area of Río Tijuana (Lat- 32°30'48.00"N Lon. 116°58'12.37"O). The second area of study is located in a residential zone known as Cuesta Blanca Seccion Loma Blanca (A-II), to the north and southeast, where land movement occurs due to heavy machinery operation used for the construction of residential developments (Lat- 32°25'4.43"N Lon. 117° 1'38.56"O). It also limits with the city of Playas de Rosarito. Location of both sampling areas is shown in Figure 1.

Figure 1: Location at the Sampling Areas; A-I and A-II

2.2. Sampling and Analytical Techniques

The sampling was carried out for a period of seven consecutive days; during such period, fog was appreciated in the area as a result of an accumulation of particles and gases in the city of Tijuana, B. C. For sites A-I and A-II, 7 and 6 samples were studied respectively, derived from micro-fiber filters of 37 mm diameter ringed teflon (PTFE) for 2.5 μm particles, obtained through Minivol low-volume samplers and with a flow rate 5 L min^{-1}, programmed to carry out a 24 h sampling consecutively from October 22 to 29, 2007. By Particle Induced X-Ray Emission (PIXE) was used to determine the micro-elemental composition. For the morphological study, the Scanning Electron Microscopy (SEM) technique was applied and a circular section of approximately 5 mm diameter was selected in each filter. Besides, in each case a sample was taken by contact. The Atomic Force Microscope (AFM) technique was used for selecting a sample of 1 cm^2 of the same filter paper and placing a double-glue copper sample holder in order to conduct the direct contact analysis of collected samples.

3. Results

3.1. Micro-Elemental Analysis (PIXE)

The identification of elements is carried out: Sulfur, calcium, zinc, chlorine, copper, iron, manganese, potassium, silicon, titanium, and vanadium. It is possible to estimate the following elements in a quantitative manner: Iron, calcium, chlorine, potassium, silicon, titanium, and manganese. They are contributed in a predominant manner for the material generated by the earth's crust as clay, feldspar, or micas, etc., and the re-suspension of dust (Almeida, et al; 2005, Hopke, et al; 2007, Viana, et al, 2007). The contribution of sulfur, zinc, copper and vanadium is attributed by a mobile source providing an incomplete combustion of gasoline and diesel fuel (Almeida, et al, 2005, Godoy, et al, 2009, Hopke et al; 2004). It should not be ruled out that a number of identified elements are products contributed by its surrounding industry. Likewise, the potential sources of forest fires might be potassium, chlorine, and carbon (Alves, et al; 2010, Chan, et al; Hopke, et al; 2007, Kim, et al; 2007, Reche, et al; 2012,). Table 1 shows the relationship of micro-elemental composition of the identified elements.

Table 1: Micro-Elemental Composition of Particulate Material (μm/m^3)

Sampling Area	Si	S	Cl	K	Ca	Ti	V	Mn	Fe	Cu	Zn
A-I	0.363	0.427	0.366	0.653	0.951	0.047	0.000	0.021	0.495	0.000	0.094
	0.635	1.095	1.113	1.477	1.681	0.114	0.017	0.000	1.640	0.455	0.320
	2.841	1.821	13.623	1.255	2.134	0.146	0.000	0.054	2.051	0.325	0.608
	0.879	3.085	1.462	0.957	1.115	0.063	0.023	0.042	1.346	0.136	0.222
	0.199	0.007	4.196	1.467	1.204	0.507	0.118	0.119	0.271	0.276	0.018
	0.000	5.636	2.877	1.655	0.522	0.493	0.112	0.012	0.273	0.201	0.000
	0.628	2.715	1.988	0.586	0.591	0.032	0.031	0.043	0.830	0.198	0.208
A-II	0.000	0.450	0.320	0.422	0.383	0.063	0.017	0.034	0.243	0.100	0.130
	0.089	0.557	0.270	0.228	0.330	0.049	0.017	0.000	0.303	0.307	0.149
	0.749	0.703	0.394	0.427	0.655	0.047	0.031	0.036	0.756	0.010	0.010
	0.422	2.819	0.434	1.121	0.624	0.086	0.011	0.000	0.671	0.220	0.112
	0.047	1.762	0.399	0.363	0.376	0.037	0.019	0.035	0.346	0.109	0.091
	0.053	2.178	0.319	0.437	0.302	0.020	0.019	0.046	0.270	0.257	0.171
	0.000	0.450	0.320	0.422	0.383	0.063	0.017	0.034	0.243	0.100	0.130

3.2. Morphological Analysis

3.2.1. Scanning Electron Microscopy (SEM)

It is possible to carry out a morphological analysis using the contact technique and supported by SEM. Figure 2 shows a series of micrographs that show the particles with are agglomerates made up of spherical-shaped nanoparticles (Figure 2a). All these are attributed to carbon and other rough multi-porous spherical nanoparticles and homogeneous spheroids (Figure 2b), considered as clay material of different sizes and shapes as isolated agglomerates. The latter generally identifies a steady presence of carbon and oxygen, and the other elements in a homogeneous manner within the different analyzed areas.

It showed the constancy of different size-and-shape cluster nanoparticles, in certain areas the cluster is clearly shaped (Figure 2c), and in other areas it is in formation process. Also, average-sized nanoparticles of 200 nm can be observed (Figure 2d).

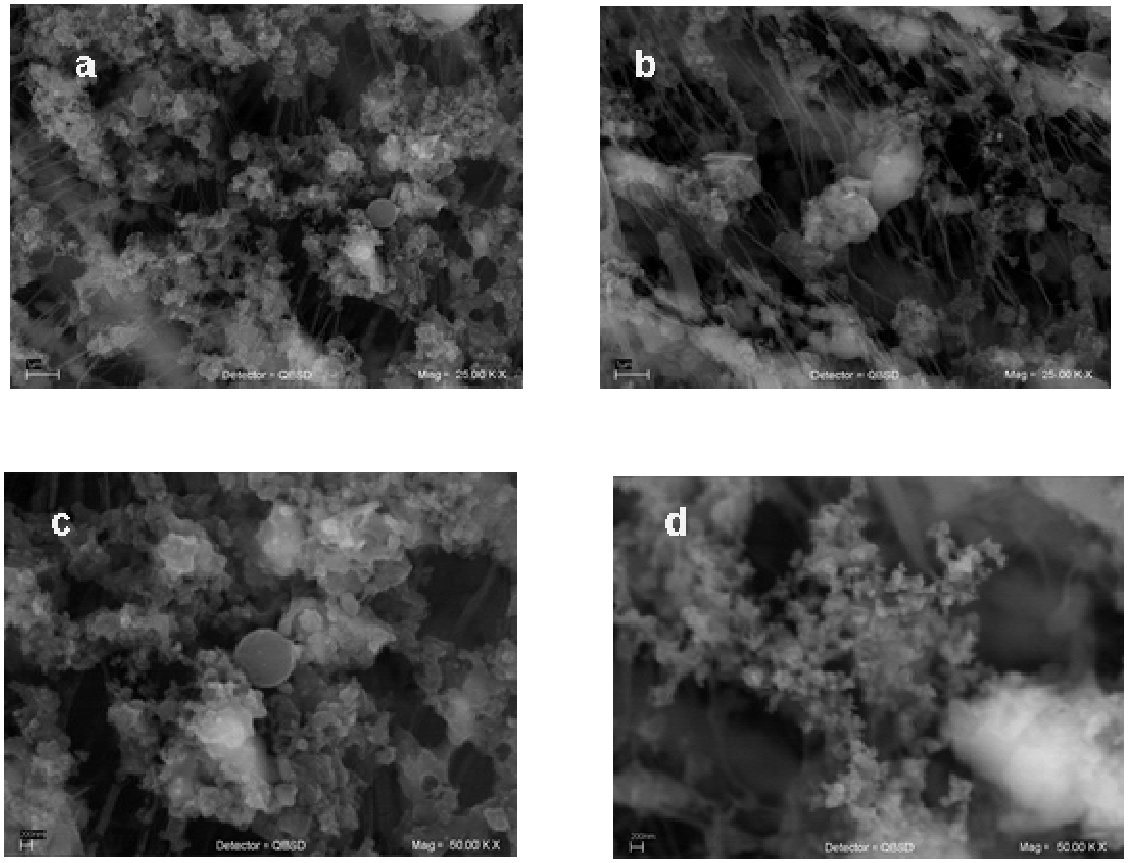

Figure 2: SEM Micrographs nanoparticles; (a) spherical-shaped, (b) multi-porous spherical and spheroids, (c) clusters and (d) disintegraten

3.2.2. Atomic Force Microscope (AFM)

The application of the Atomic Force Microscopy technique is relatively new in the process of particulate material characterization. It is possible to observe the cluster granular formation at nanometers level; to visualize the shape of such cluster-forming particles in two and three dimensions; and to evaluate the average diameter through an image treatment for limiting grain borders, thus observing the cluster-forming nanoparticles. In Figure 3 a series of micrographs are presented, these micrographs make it possible to observe the state of the agglomerates, its conformation by nanoparticles, between intervals of 30 nm to 75 nm as general average, with different degree of compacting. Such compacting, due to same conditions of transportation and/or formation, in a humid climate tends to form agglomerates where there is a predominance of unity principally where water acts as an agglomerate agent. The borders of nanoparticles can be clearly observed, and under variable climate conditions, temperature, humidity and velocity of wind, could disintegrate (Figure 3a and b), material generated by soil erosion and or generated in or by unstable or anthropogenic sources. Agglomerates with a higher degree of compaction, cementation or adhesion are similarly present. The borders of union of nanoparticles a probable product of material generated during the thermic process that has promoted the fusion of components to conform compact agglomerate can not be clearly observed. Figure 3c and 3d, clearly shows a set of compacted agglomerates and those considered joined by light forces of attraction.

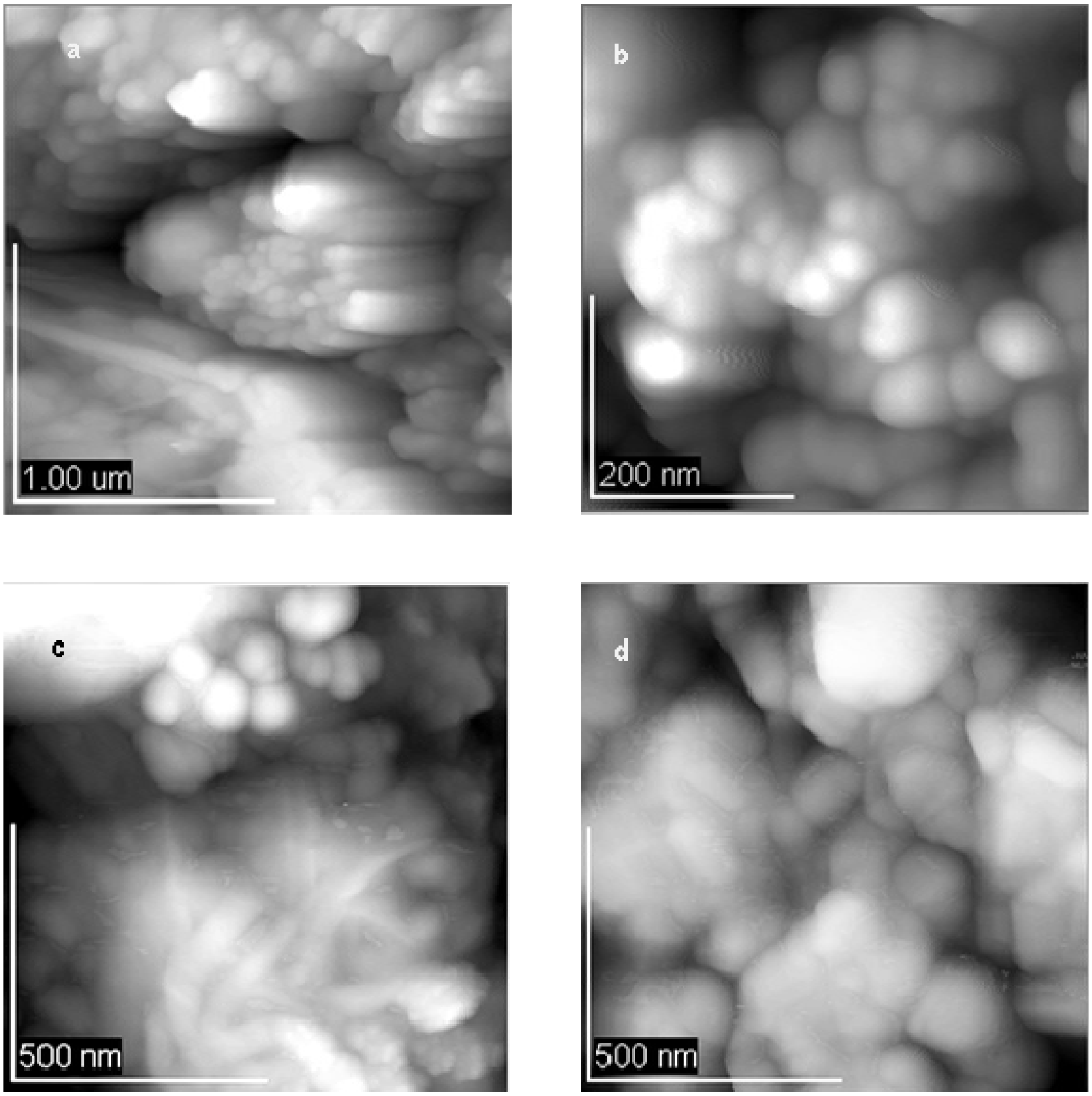

Figure 3: AFM Micrographs Particles; (a, b) Agglomerates of Nanoparticles Intervals Sizes of 30 nm to 75 nm, (c, d) Agglomerates with a Higher Degree of Compaction

Finally, in the series of AFM micrographs (Figure 4), present a sequence of agglomerate material, where the border of the nanoparticles is lightly noticeable, (Figures 4a and b), we can observe the presence of nanoparticles with sizes under 30 nm. An analysis of the aspects of the agglomerates is constantly present in the series of sampling material in a 7 day period.

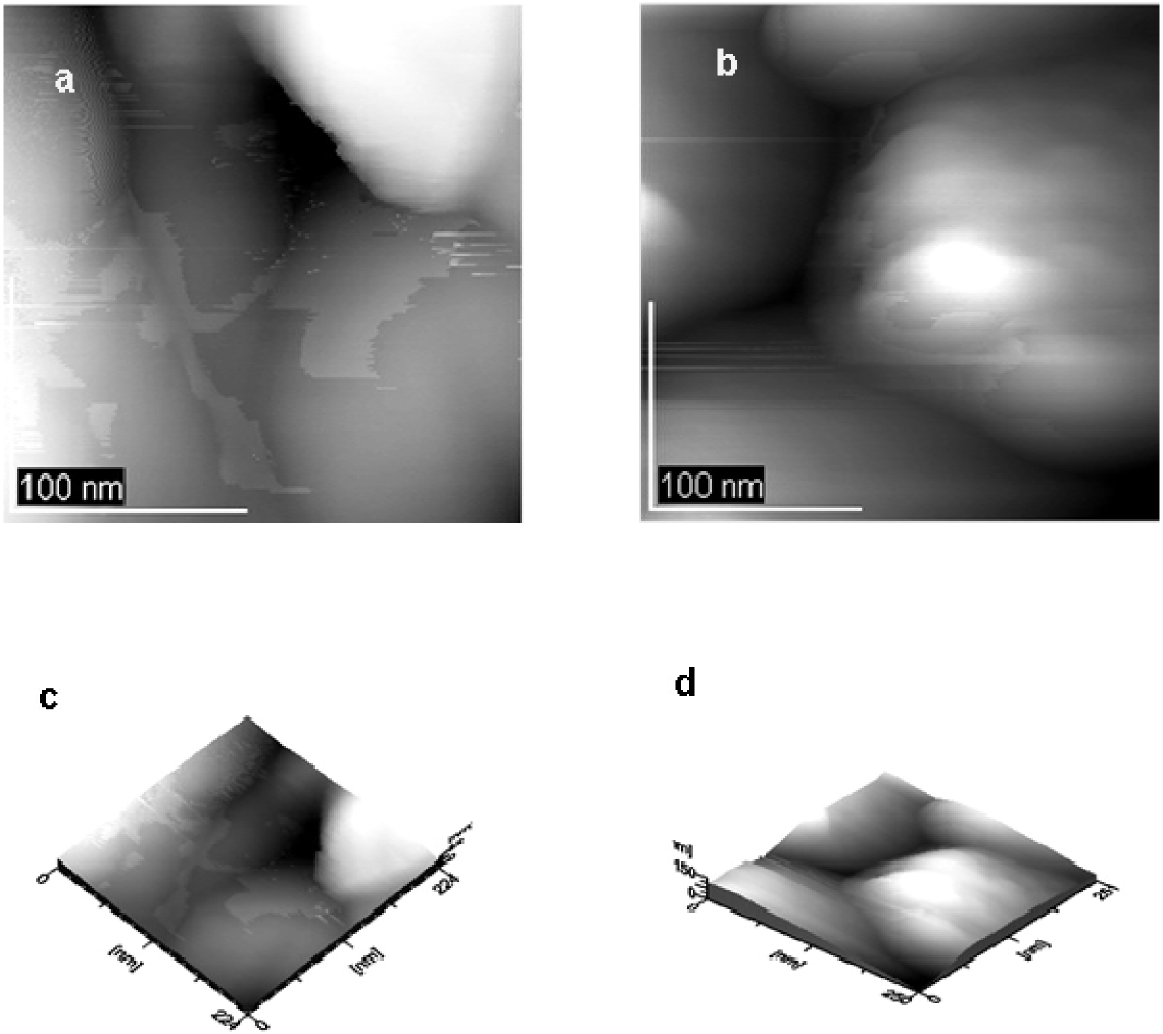

Figure 4: AFM Micrographs; (a, b) border of the nanoparticles, sizes under 30 nm. (c, d) third dimension Analysis

Through an image treatment, it is possible to visualize the analyzed zone in third dimension, turn the image and observe the aspect that presents different angles allow us to see the conformation of the agglomerate. In Figure 4c and e, we can notice a pair of micrographics turn to an angle of 90^0. We can observe the degree of compaction of the nanoparticles and to some extent predict the conformation of the agglomerate analyzing its sections. By analyzing its sections through an alternate microelemental chemical analysis of the different trajectory zones, we can estimate the possible sources of nanocontaminants and possibly, in a qualitative manner, the degree of disintegration of the agglomerate in terms of the visualization of cementation or adhesion of the nanoparticles.

4. Conclusions

According to the results, the particulate material sampling is made of a micro-elemental composition where the elements are provided by: those of natural origin from soil erosion that due to climate conditions of the area were transported in forest fires, and those by mobile sources and fire caused by men. Concerning the reported quantity in a micro-elemental analysis, observed that in the study area A-1 the values reported in $\mu g/m^3$ are higher than the reported for the A-II site. Bases on these results, micro-elements related with biomass burning, mineral origin and soil as K, CI, Si and Fe presented higher values compared to elements related to vehicle traffic (Zn, Cu, V). To this respect, the latter diminished during the state of alarm, where recommendations to avoid driving through the streets of the city were made by the municipal authorities.

The A-II site presented similar behavior. The results concerning its morphology applying SEM/EDX and AFM let us estimate that the sampling material is made of particles in a size interval from 30 nm to 75 nm, resulting in a form of cumulus or agglomerates. Likewise, it is possible to observe by AFM two types of agglomerates; those that present a light compaction and that clearly show the different borders of the nanoparticles and the agglomerate with a high degree of cementing and / or adherence has a tendency to be generated as a product of a thermic effect, either natural, during the natural geological process or mainly fires caused by the burning of residues.

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