Elementary Composition of $PM_{2.5}$ present in urban areas of Baja California, Mexico

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Abstract. The patterns of atmospheric dispersion in the state of Baja California are influenced by factors such as the proximity to the coastal zones, Santa Ana winds and climate in the state, characterized as dry and extreme with low annual precipitation. The objective of this study is the characterization of the elemental chemical composition of $PM_{2.5}$ generated in different residential zones located in urban areas of the state of Baja California, using a low volume (Mini-Vol sampler). The samples were collected in Teflon filters during 2005. PIXE was used for the multielemental analysis. S and Fe were abundant in all the study sites, whereas P and V were the least abundant. High enrichment factors (EF) of Cr, Ni, S and Zn indicate anthropogenic source contributions (processes of gasoline and diesel engine) and a low EF values Si, Ti, Ca, Cl and K, which indicate natural source contribution. The results showed that emissions generated by gasoline and diesel combustion influenced the air quality of the study sites.

Keywords: Baja California, Mini-Vol, $PM_{2.5}$.

INTRODUCTION

The contamination by fine particulate matter smaller than 2.5µm ($PM_{2.5}$) is of interest due to its negative effects in the human health and the environment. Therefore, it is considered as an important parameter in the evaluation of air quality.

Epidemiological studies link the particulate concentration in the atmosphere and adverse effects in human health, mainly due to $PM_{2.5}$ (fine particles) [1, 2]. They refer that the mortality risk related to particles smaller than 2.5 µm almost double the risk related to particulate matter smaller than 10 µm [3]. The $PM_{2.5}$ composition is an important factor in the determination of the degree of impact on the human health, as well as its solubility and dispersion in the atmosphere.

Epidemiological studies reported a relationship between heavy metal concentration and the increment of lung and cardiopulmonary diseases in exposed people to atmospheric pollutants [4, 5].

The morphologic and chemical characterizations of particulate matter $PM_{2.5}$ are suitable tools in the identification of the pollutant source: natural or anthropogenic. Its morphology can be affected by factors such as the process of formation of the particles, in addition to the physical and chemical properties of the superficial layers of the particles.

The size and composition of the particles are influenced by source, atmospheric processes; chemical and photochemical condensation, evaporation, coagulation, reactions, meteorological factors, and topography of the study area and properties of the particulate matter, such as density, shape, and hygroscopicity [2, 6].

The particles generated by natural sources can be created by emissions of the ground, volcanic eruptions, marine origin, biomass, spores, microorganisms, microfossils and viruses. Particles of anthropogenic origin may be generated through several combustion processes (domestic, industrial), agricultural and industrial activities, forest fires, photochemical reactions of the primary pollutant agents in the atmosphere, such as sulfur oxides (SO_X) and nitrogen oxides (NO_X).

Additionally, $PM_{2.5}$ can be formed by elements such as Na, Mg, Al, Si, or K [7], or constituted by chemical or mineral compounds such as metallic oxides, sulfates, nitrates, silicates, calcium carbonates, as well as particles with high carbon contents. Several authors indicate that these compounds represent around 60-70% of total PM_{10} mass [8, 9].

The objective of this study was the characterization of the elemental chemical composition of $PM_{2.5}$ in different residential zones located in urban areas of the state, using a low volume (Mini-Vol) equipment.

METHODOLOGY

The study areas are located in the state of Baja California, Mexico. The state is located in the northwest of the country, occupying the north portion of the peninsula of the same name; it is integrated by five municipalities. The predominant climates are dry and extreme with rains in winter.

An aspect of interest about the California (USA) and Baja California region is the phenomena called Santa Ana, characterized by winds towards the Southeast, that are originated in the desert regions during October and March with high temperature and wind intensities up to 80 km/h with a low humidity [10].

Six sites were selected for the study, all of them located at urban areas in Baja California. In Ensenada, Tecate and Playas de Rosarito, a site was selected in each city. In Tijuana, three sites were selected (Las Cumbres, M. Matamoros, El Pipila). Most of the sites are adjacent to commercial zones, with vehicular traffic and partially paved, with the exception of the site denominated El Pipila. The location and altitude of the sampling sites are shown in Table 1.

TABLE 1. Geographical localization

Study area	Latitude	Longitude	Altitude m asl
Ensenada	31º 52´	116º 36´	33
Rosarito	32º 22´	117º 03´	46
Tecate	32º 33´	116º 37´	606
Tijuana:			
Las Cumbres	32º 28´	116º 58´	176
El Pipila	32º 29´	116º 52´	196
M. Matamoros	32º 29´	117º 05´	200

Samples of $PM_{2.5}$ were collected using a Mini-Vol portable equipment (5 L/min.). The particles were collected on ringed Teflon (PTFE) filters, approved by EPA for $PM_{2.5}$monitoring. The filters were weighted and identified, and handled under stable conditions of temperature and humidity before and after the sampling.

The sampling was carried out for 24 h periods during five days of the week, all month, in April, May, June, July, and August 2005, collecting a total sixty samples. It is important to mention that the sampling was performed even under conditions with high percentage of humidity or drizzle, such April 18, 22, 26 and 28, and May 05. Also, under Santa Ana conditions (July 13).

The samples were analyzed with PIXE, using a 2.2 MeV proton beam produced by the Pelletron accelerator at IFUNAM. The protocols, including the irradiation chamber and detection system efficiency measurement with MicroMatter (Deer Harbor, WA, USA) thin film standards, are better described elsewhere [11, 12]. To check analytical accuracy, a second set of thin film standards was irradiated, resulting in a maximum error of 0.8 %.

RESULTS AND DISCUSSION

The concentration of elements detected during the 2005 sampling campaign, in spring and summer, are listed in Table 2. The presence of fourteen elements in the analyzed samples was detected: Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Ni, and Zn. The elements with the highest abundance were the S and Fe, while those with the lowest contents were P and V. The predominant metallic components in Ensenada, Playas de Rosarito and Las Cumbres (Tijuana) were Fe, Cr, Mn and Cu; in M. Matamoros and El Pipila (Tijuana) Fe, Cr, Zn and Cu. According to other researchers, Fe is one of the most abundant elements in the earth crust [2, 4, 8, 13].

The average levels of $PM_{2.5}$ during spring and summer showed variations for the sites located in Las Cumbres, Playas de Rosarito and Tecate. For these areas, S and K levels were higher in summer than in spring samples. Furthermore, Playas de Rosarito and Las Cumbres showed an increase in the levels of Ca, Mn, and Cu in summer; these differences can be due to factors such as dry season, and transport by wind.

Based on the elemental concentration measured in each study area, an effect of $PM_{2.5}$ "washing" can be observed during and after a drizzle event, as it happened in spring for the Las Cumbres, M. Matamoros and Playas de Rosarito areas, where a reduction in the levels of particulate matter was found in these sites.

Moreover, the meteorological conditions, including wind during the sampling (July 13) in Playas de Rosarito, had an effect on the following day, showing a reduction in the levels of V, Zn, Ti, K, Ca, Si, S, Mn and Fe.

The Enrichment Factor (EF) for each detected element was calculated using Fe as reference and reported values of the elements in the earth [15].

Based on the EF values of Cr, Ni, S and Zn (above 1) in the study areas, a contribution of anthropogenic origin was identified. S, Ni and Zn levels are related to emissions of gasoline and diesel combustion processes

and sulfides, while Cr is associated with industrial sources.

The EF of Cl was enriched by anthropogenic sources for M. Matamoros, El Pipila, Ensenada an Tecate. This element is associated with emissions of motor vehicles [15]. The EF for Mn showed a contribution of anthropogenic type in the areas of Ensenada, Tecate and M. Matamoros.

CONCLUSIONS

The multielemental analysis of particulate matter is one of the essential stages in the recognition of $PM_{2.5}$. Additionally, the meteorological variables and the local environmental conditions are factors to be considered in the distribution and dispersion of the pollutant agents. In the case of Baja California, the precipitation and winds in this zone conditioned the residence time dispersion of $PM_{2.5}$ in the atmosphere, as was rain observed during and after the rain or wind event. According to the EF values it is concluded that air quality in the study areas is influenced mainly by sources of $PM_{2.5}$ of anthropogenic origin, associated with processes of combustion of diesel and gasoline. The low values of EF showed also contributions from natural sources, such as of marine origin (areas near the coast) and resuspension of dust.

Finally, it is possible to state that a nondestructive analysis represents an advantage, allowing a further evaluation of collected samples using other complementary methods, such as Scanning Electron Microscopy (SEM) or Atomic Force Microscopy (AFM).

ACKNOWLEDGMENTS

TABLE 2. Mean concentration (ng/m³)

Element	Ensenada	Playas de Rosarito		Tecate		Tijuana			
						Las Cumbres		M. Matamoros	El Pipila
S	1051.41[1]	637.71[1]	2115.47[2]	2330.45[1]	2349.14[b]	668.42[1]	1987.21	1421.76[1]	3549.87[2]
Fe	451.68	451.68	562.44	791.00	834.52	461.75	440.17	771.02	789.72
K	29.00	87.47	262.41	364.45	443.06	139.95	186.60	332.38	465.04
Ca	53.73	186.47	360.30	437.74	356.31	102.72	169.09	589.44	1183.62
Cr	141.43	125.61	140.44	120.66	117.12	163.19	157.26	113.74	125.61
Si	553.59	154.17	147.16	1009.08	1643.27	420.45	77.08	679.73	953.02
Mn	34.32	49.57	52.11	63.55	37.23	45.75	63.55	49.57	52.11
Cu	31.84	34.57	40.33	37.45	26.18	37.45	54.73	69.14	72.02
Ni	22.92	31.25	20.84	8.33	31.60	4.17	35.42	43.75	22.92
Zn	14.99	7.49	Nd	75.45	49.69	11.24	28.10	97.41	67.44
V	Nd	Nd	13.32	31.71	Nd	18.01	14.92	4.97	17.26
Ti	23.94	Nd	18.62	29.27	110.60	Nd	Nd	Nd	30.60
Cl	409.76	Nd	Nd	19.58	304.33	Nd	Nd	363.06	130.31
P	Nd	Nd	Nd	Nd	242.60	Nd	Nd	Nd	Nd

[1] Spring;
[2] Summer
Nd: Not detected

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