PARTICULATE MATTER (PM$_{10}$ AND PM$_{2.5}$) FROM DIFFERENT AREAS OF PUERTO RICO

Adriana Gioda, Ulda Peréz, Zenaida Rosa and Braulio D. Jimenez-Velez*

Center For Environmental and Toxicological Research, University of Puerto Rico, Medical Sciences Campus, Biochemistry Department, School of Medicine, PO Box 365067, San Juan, PR, 00936-5067

SUMMARY

Fine (PM$_{2.5}$) and coarse (PM$_{10}$) particles were characterized in different sites of Puerto Rico during 2000 to 2003. The sites were established in urban areas (Guaynabo, Salinas and Vieques) and in a reference site (Fajardo) at the east coast. Particulate matter (PM) samples were collected in Teflon and quartz filters then weighed and processed. PM mass concentrations in Teflon filter were determined gravimetrically and estimated for quartz. Samples were digested for metal analyses with appropriate field blanks. Seven to eight metals (Cd, Co, Cu, Fe, Ni, Pb, V and Zn) plus arsenic (As) were analyzed in each sample by Atomic Absorption Spectroscopy. Average PM$_{10}$ levels were around 25 µg m$^{-3}$ in all sites being, lower than the limits established by USEPA (50 µg m$^{-3}$). The annual average level of PM$_{2.5}$ in Guaynabo was 11.6 µg m$^{-3}$ versus 8.5 µg m$^{-3}$ in Fajardo. Most of the metals were present at higher levels in the urban sites (Guaynabo, Vieques and Salinas) than at the reference site (Fajardo). All species analyzed in PM$_{2.5}$, except Fe, were significantly higher at Guaynabo when compared to Fajardo. Ni and V exhibited the highest metal concentrations (Ni = 17 ng m$^{-3}$ and V = 40 ng m$^{-3}$) in Guaynabo. Fe showed stronger relationships between PM at each site suggesting their release from similar sources at that particular location, probably due to Sahara dust.

KEYWORDS: heavy metal, arsenic, air pollution, Sahara dust, respiratory uptake.

INTRODUCTION

Airborne particulate matter is one of the most important constituents of atmospheric pollution. Consequently, exposure to airborne particles is a common event. The effects on health caused by particulate matter depend mainly on particle size, but also a number of factors such as their content of toxic substances, their solubility in biological fluids, total human exposure, and others [1, 2]. Particulate matter is associated with epidemiological studies which has shown an increased mortality, morbidity, decreased lung function [1,3], asthma, bronchitis and lung cancer [4] and is pertinent to the development of chronic diseases as pneumoconiosis and emphysema [4].

Recent studies carried out in vitro or in vivo using animal models, showed strong correlation between metal content from particulate matter and pulmonary toxicity [5,6]. Trace metals distributed widely throughout the lung on particles could catalyze the formation of oxidants within the lung, which in turn produce tissue damage [7,8]. Laboratory studies show that some metals (Mn, Cd, Cu, Pb and Zn) are initiators or promoters of carcinogenic activity in animals [9]. Pollutant metals may accumulate in the fatty tissues of the body and in the circulatory system, affecting the central nervous system and internal organs [9].

This is the first integrated study developed in Puerto Rico to evaluate levels of PM$_{10}$ and PM$_{2.5}$ and their composition. Previous studies determined the concentration and characteristic of particulate matter in only one city (Ponce) in the south of the Puerto Rico Island [10-12].

The objective of this paper is to integrate all available data on particulate matter in Puerto Rico and expand the knowledge of the size distribution of particles contaminated with heavy metals.

MATERIAL AND METHODS

Sampling

Air samples were obtained from Salinas, Vieques, Guaynabo and Fajardo (reference site). Salinas is a small town in the southern coast where the Aguirre Thermoelectric Plant is located. Vieques is an island where a marine is placed. Guaynabo is a city in the metropolitan area with urban and industrial activities. Fajardo was chosen as the reference site, because it is located in an ecological reserve at the east coast with no human activities upwind from the station. Air samples (PM$_{10}$) were obtained from Salinas during August 2002 to May 2003, Vieques during June to
December 2001 and April 2002 and Fajardo from June 2001 to May 2003. The PM$_{2.5}$ samples were collected in Guaynabo and Fajardo beginning in November 2000 and lasting in September 2001. Air samples were collected using a Partisol Plus Model 2025 sequential PM$_{10}$ air monitor that collects airborne particles on a 47 mm Teflon filter. All samples were collected on a weekly basis at a flow rate of 16.7 L min$^{-1}$ for 72 hours period. PM$_{2.5}$ was collected on quartz filters using the Fine Particulate Chemical Speciation Air Sampler (RAAS 2.5-400) from Andersen Instruments Inc. The flow meter (FM) units were set to intake air at 17 L min$^{-1}$ (FM 1 and 4), 4.1 L min$^{-1}$ (FM 2 and 5) and 3.5 L min$^{-1}$ (FM 3 and 6).

Each Teflon filter was placed and stored flat on a clean Petri dish during and after conditioning, weighing and storage. Pre-sampling and post-sampling weigh of filters were performed in an electronic microbalance (M-220D, Denver Instruments, Denver, CO, USA) with a sensitivity of five decimal points. All filters (either with or without mass) were stably weighed until a constant weight was achieved, following the USEPA methodology [13].

Reagents and solutions

HNO$_3$ Trace Metal Grade (Fisher Scientific, Pittsburg, PA), stock standard solution 1000 mg L$^{-1}$ (Mixed standard Perkin Elmer) and QCI 700 and 701 Ultracheck Metals Samples (Ultra Scientific, North Kingston, RI) were used. The modifiers used were Pd (Perkin Elmer AA modifier solution 10 g L$^{-1}$), Mg (Perkin Elmer AA modifier solution 10 g L$^{-1}$) and NH$_4$ (Perkin Elmer AA modifier solution 10% NH$_4$H$_2$PO$_4$). All solutions were prepared fresh on a daily-basis.

Analyses

Teflon filter samples (PM$_{10}$) collected were analyzed individually. For PM$_{2.5}$, a composite sample (around 4-8 quartz filters per composite) combined filters from either FM 2 or FM 5 of each month. The digestion process was performed by adding nitric acid with ultra pure water. Extraction was conducted on a hot plate, heated and refluxed at 90$^\circ$C $\pm$ 5$^\circ$C for 2 hrs. Acidified extracts were stored in polypropylene nalgene bottles until used for analysis [14, 15].

Metals were analyzed by Atomic Absorption (AA) using a Perkin-Elmer AA Spectrometer Model AAnalyst 800 (Norwalk, CT, USA). USEPA [16] methods 7060A, 7131A, 7201, 7211, 7381, 7421, 7521, 7911 and 7951 were used for the following elements: As, Cd, Co, Cu, Fe, Pb, Ni, V and Zn, respectively.

Quality Control and Statistical Analyses

Field blank filters were obtained during each sampling period at each site and consisted of exposure to all field process except air filtering. Unused filters, field and laboratory blanks were included in the analyses to determine possible background contamination, as a quality control measure. The accuracy of the method employed was evaluated using spike blanks of known metal concentration and a standard reference material (Urban Particulate Matter SRM 1648, National Institute of Standards and Technology (NIST), Gaithersburg, MD). The recovery efficiency was calculated on the base of the heavy metal concentration reported for the SRM [14,15]. The blanks were processed simultaneously and were handled in an identical manner as the samples. The average heavy metal and arsenic values in the blanks were subtracted from the levels obtained in each samples.

Statistical analyses were performed using the computerized software program “GraphPad Prism” version 4.0a. The t-test analyses were performed to establish statistical differences between the means of particulate matter, metal and arsenic concentrations from sites at the 95% confidence interval. Linear regressions were performed between trace elements and particulate matter analyzed per site in order to elucidate possible relationships among them.

RESULTS AND DISCUSSION

Particulate Matter

Average annual concentrations of PM$_{10}$ and PM$_{2.5}$ from 2000 to 2003 at different sites in Puerto Rico are shown in Figure 1. Average annual concentration of PM$_{2.5}$ in Guaynabo was 11.6 µg m$^{-3}$ and Fajardo 8.5 µg m$^{-3}$. The levels found for PM$_{10}$ in Fajardo (2001-2003) was 25.5 µg m$^{-3}$ ($n = 83$; standard error $\pm 1.2$), while Vieques (2001-2002) and Salinas (2002-2003) were 23.6 µg m$^{-3}$ ($n = 44$; standard error $\pm 3.4$) and 22.9 µg m$^{-3}$ ($n = 43$; standard error $\pm 3.8$), respectively. The greatest difference in PM annual concentration between sites was observed for PM$_{2.5}$ (P value 0.0013). Differences between urban and reference sites were not as marked for PM$_{10}$. PM$_{10}$ concentrations at Guaynabo were obtained from the Environmental Quality Board. The sampling period was from April to July 2001. The PM$_{10}$ average concentration at Guaynabo was 41.4 µg m$^{-3}$ ($n = 97$; standard error $\pm 1.9$) with a maximum of 106.2 µg m$^{-3}$ (during a Sahara event on July 3, 2001).
Metallic Elements

Annual mean concentrations of heavy metals in PM2.5 and PM10 for all sampling sites in Puerto Rico are presented in Table 1.

In the PM10 fraction, Fe was the most enriched element at all sites, followed by V, Cu and Ni. In the PM2.5 fraction, Fe also was in the highest concentration followed by V, Zn and Ni. In previous studies, Fe was also one of the most enriched metals in TSP in Puerto Rico [10]. The means showed the concentration follows this order in TSP Fe>Pb>Cu>Zn=V. In another study developed in Ponce city [12] a size distribution of heavy metals showed Fe, Zn and Pb were the most enriched elements in particles size of 7µm and 2.0-3.3µm. These results, although not directly comparable to ours, showed different metal distribution.

Most of the metals in PM10 (As, Co, Fe, Pb and V) presented slightly higher levels in Vieques than in Fajardo (2001-2002). In Salinas all metals presented higher concentrations than in Fajardo (2002-2003). The metal concentrations in Salinas were 1.2 to 3.4 fold higher than Fajardo (2001-2003) and Vieques (2001-2002). These results are in agreement of what is expected since Salinas is more of an urban site when compared to Vieques or Fajardo. This must be related to local inputs of PM from industrial sources in that region. The average PM2.5 concentration of all heavy metals analyzed, with the exception of Fe, were significantly higher (3.6 to 28) in Guaynabo than in Fajardo. Guaynabo is an urban and industrialized area with several sources of trace metal output.

Comparison with other places in the world and standard limits

Particulate matter concentrations determined throughout these studies were below the range established by USEPA [17]. While the average PM10 concentrations were half the standard value (50 µg m-3 - annual arithmetic mean, [17]) the PM2.5 concentrations were close to the limit (15 µg m-3 - annual arithmetic mean, [17]). A total of 58 events (18%) of particulate matter collections were greater than the standard (15 µg m-3) were registered in Guaynabo and 26 events (8.5%) in Fajardo. With respect to the PM10 concentration obtained at both site (Salinas and Fajardo), only two events during the year exceeded the USEPA PM10 annual standard of 50 µg m-3. In Vieques and Fajardo (2001-2002) only one event in both sites exceeded the standard. These events were traced to the dates of Sahara events (discussed below). Monthly mean levels of PM2.5 in Guaynabo ranged between 7.6 and 14.3 µg m3 and in Fajardo between 6.4 and 12.0 µg m3. Monthly means of PM10 varied from 20.3 to 37.8 µg m3 in Fajardo, 13.2 to 39.2 µg m3 in Salinas and 10.8 to 33.5 µm g in Vieques. Annual means of PM10 in the US ranged from 18 to 47 µg m3 and for PM2.5, 11 to 30 µg m3 [19]. In other cities in Greece and Turkey the average PM10 levels reached up to 200 µg m3 and around 50 µg m3 for PM2.5 [18-20]. In a remote site in Italy the average concentration of PM10 was 55 µg m3 and 48 µg m3 for PM2.5.[21]. When compared to other cities, PM2.5 and PM10 concentrations in Puerto Rico were relatively lower.

| TABLE 1 - Average arsenic and heavy metal levels (mean ± SE) found in particulate matter from Fajardo, Guaynabo, Salinas and Vieques in Puerto Rico (2000 – 2003). |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
|                                 | As (ng m-3) | Cd (ng m-3) | Co (ng m-3) | Cu (ng m-3) | Fe (µg m-3) | Ni (ng m-3) | Pb (ng m-3) | V (ng m-3) |
| Fajardo - PM10 (2001-2002)     | 0.23(±0.1)  | 0.023(±0.01) | 0.14(±0.04) | 1.87(±0.06) | 0.27(±0.09) | 0.78(±0.1)  | 0.72(±0.2)  | 1.87(±0.2)  |
| (n = 28)                        |       |        |        |        |          |           |           |           |
| Vieques - PM10 (2001-2002)     | 0.29(±0.03) | 0.020(±0.004) | 0.16(±0.04) | 1.00(±0.1)  | 0.33(±0.11) | 0.68(±0.2)  | 0.90(±0.1)  | 2.50(±0.3)  |
| (n = 44)                        |       |        |        |        |          |           |           |           |
| Fold difference                 |       |        |        |        |          |           |           |           |
| Vieques/Fajardo                | 1.2   | 0.9   | 1.1   | 0.5   | 1.2   | 0.9   | 1.2   | 1.3   |
| Fold difference                 |       |        |        |        |          |           |           |           |
| Fajardo - PM10 (2002-2003)     | 0.13(±0.01) | 0.028(±0.003) | -     | 1.5(±0.2)  | 0.36(±0.08) | 1.70(±0.1)  | 0.86(±0.08) | 1.60(±0.2)  |
| (n = 29)                        |       |        |        |        |          |           |           |           |
| Salinas - PM10 (2002-2003)     | 0.34*(±0.03) | 0.058*(±0.005) | -     | 2.50*(±0.1) | 0.55(±0.09) | 2.30(±0.2)  | 1.40*(±0.1) | 2.50(±0.3)  |
| (n = 50)                        |       |        |        |        |          |           |           |           |
| Fold difference                 |       |        |        |        |          |           |           |           |
| Salinas/Fajardo                | 2.6   | 2.0   | -     | 1.7   | 1.5   | 1.3   | 1.6   | 1.6   |
| Fold difference                 |       |        |        |        |          |           |           |           |
| Fajardo - PM2.5 (2000-2001)    | 0.09(±0.03) | 0.015(±0.004) | -     | 0.7(±0.1)  | 0.10*(±0.32) | 1.9(±0.6)  | 0.57(±0.06) | 1.4(±0.2)  | 3.0(±1)    |
| (n = 158)                       |       |        |        |        |          |           |           |           |           |
| Guaynabo - PM2.5 (2000-2001)   | 0.39*(±0.02) | 0.055*(±0.007) | -     | 5.5*(±0.6) | 0.09(±12) | 17.0*(±2) | 3.0*(±0.5) | 40.0*(±3) | 12.0*     |
| (n = 158)                       |       |        |        |        |          |           |           |           |           |
| Fold difference                 |       |        |        |        |          |           |           |           |
| Guaynabo/Fajardo               | 4.3   | 3.6   | -     | 7.8   | 0.9   | 8.9   | 5.2   | 28.6 | 4.0       |

(-) not analyzed
(*)Significantly different at P<0.05 level
None of the metals (Cd, Co, Pb, V and Zn) exceeded the limit suggested by national [17] and international [22, 23] organization. These agencies do not have guideline values for Fe and Cu.

In general, most airborne trace metals in Puerto Rico are below the average limit values reported for collected urban particulates [23]. However, Ni and V present in PM$_{2.5}$ hence the highest concentrations among all metals analyzed and also higher than other urban locations [24-26]. These high levels of Ni and V in inhalable particles have been suggested to be associated with pulmonary toxicity [27-29] and can be responsible or contribute to the development of respiratory diseases in Puerto Rico.

Respiration uptake

Human exposure to airborne contaminants can be estimated by air quality monitoring. Daily respiratory uptake (DRU) of heavy metals in ambient air can be estimated from the equation: DRU$_i$ = CiAR, where Ci is the concentration of the “i” inhaled metal, R is the daily inhalation rate (m$^3$ day$^{-1}$) and A is the absorption rate of this metal after inhalation of the “i” inhaled metal, R is the daily inhalation rate (m$^3$ day$^{-1}$) and A is the absorption rate of this metal after inhalation [30]. There are different values for these three variables used by different authors. We calculated the DRU of heavy metals by multiplying the concentration of metals in the bioaccessible metal fraction from PM$_{2.5}$. They found DRU values for urban and industrial sites for the following metals: Cd (3.4-5.9 ng day$^{-1}$), Cu (1290-652 ng day$^{-1}$), Ni (56-65 ng day$^{-1}$), Pb (3.8-4.5 ng day$^{-1}$) and Zn (574-1513 ng day$^{-1}$). In spite of different methodologies adopted to estimate DRU, our results show lower levels of metals absorbed daily, except for Ni and Pb when compared with the results obtained by Voutsas and Samara [30]. However Pb was lower than that reported by Zhang et al [32] and Ikeda et al. [33]. When compared to the daily intake suggested by WHO, our estimated values were lower. There is no procedure or standard limit established for DRU, which will provide an accurate exposure estimates for the airborne pollutants. Our data establishes that Ni and V are highly absorbed in the Guaynabo area in Puerto Rico and that they are significantly higher than other regimes reported throughout other cities of the world.

Sources

Dust from Sahara and Sofriere Hill volcano has a strong impact on the airborne environment in Puerto Rico. However, the volcano impact is not very frequent and depends on the intensity of the eruption. Frequent dust outbreaks from the Sahara affect the island especially during summer months although big events have been also detected in winter. According to NASA’s Earth Probe TOMS (Total Ozone Mapping Spectrometer) (http://toms.gsfc.nasa.gov/aerosols/aerosols.html) most of the episodes occurred from June to September.

### Table 2 - Estimated metal mass concentration absorbed daily (DRU) and intake in various areas of Puerto Rico and estimated daily intake suggested by WHO.

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<td>PM$_{10}$ (µg day$^{-1}$)</td>
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<td>Fe</td>
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<td>3.15</td>
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<td>V</td>
<td>50.0</td>
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<td>Cu</td>
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<td>33.7</td>
<td>16.8</td>
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<td>Ni</td>
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<td>24.8</td>
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<td>Pb</td>
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<tr>
<td>Cd</td>
<td>1.16</td>
<td>0.58</td>
<td>0.51</td>
<td>0.26</td>
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<td>Co</td>
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<td>PM$_{2.5}$ (µg m$^{-3}$)</td>
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<td>229.0</td>
<td>486.0</td>
<td>243.0</td>
<td>472.0</td>
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The information of volcanic eruption obtained from (http://www.volcano.si.edu/gvp/reports/usgs/archive.cfm) indicated that only 1 or 2 events a year with duration of 1 or 2 days have reached PR during the last 5 years. Some metals as As, Cd and V come from volcanic activities [23], while Fe is associated to Sahara dust [34]. Approximately twenty millions tons of Sahara dust reaches the Caribbean annually [35]. Sahara and volcanic events influence the amount of PM and metal distribution and concentrations throughout the island environment. Figure 2 shows PM distribution per month in our sampling sites in Puerto Rico indicating the dates and number of events from Sahara and Montserrat storms. Notice that the increase in PM concentrations correlates with the increase in number of Sahara events during the summer months. This effect is noticed throughout the island and is also evident at the Fajardo (reference site). Although several Sahara events occurred in April and May, the PM levels were lower not reaching those in summer. This could also be influenced by the rainy period, which begins in late April-May.

The highest levels of PM$_{10}$ in Salinas and Fajardo (2002-2003) were obtained during September. The maximum concentration reached 30.2 µg m$^{-3}$ in Fajardo and 39.0 µg m$^{-3}$ in Salinas. Five Sahara events (9 days) occurred during this month and apparently they influenced the amount of PM$_{10}$ in air (Figure 2A). The same behavior in terms of concentrations was observed in both sites (Salinas and Fajardo) during this period (September 2002) that could corroborate the influence of Sahara events. Other months (November 2002 to February 2003) showed lower levels of PM$_{10}$ and no Sahara event occurred. Volcanic events seemed not to have strong influence in PM concentrations in Puerto Rico. Although in April to May 2003 two Sahara events occurred, the PM$_{10}$ concentration was lower than September 2002. This difference can be related to cloud size and intensity of particulate matter from Sahara and with time over the island. Moreover the rainy days are frequent during some months as March to May.

Monthly PM$_{10}$ maxima were registered in Vieques in August 2001 (33.5 µg m$^{-3}$) and Fajardo in June 2001 (34.9 µg m$^{-3}$). As shown in Figure 2B, the number of Sahara dust events seem to have a direct relation associated increases in PM$_{10}$. When we compare June 2001 and July 2001 the relationship seems directly proportional to the number of Sahara events, but when we compare with April 2002, this relationship becomes weak, probably due to rainy days. The higher frequency of Sahara dust episodes registered during summer could lead to an increase in PM levels including at the reference site. The difference among concentrations in summer in both sites (June to August) is minimum and it could prove the influence of Sahara dust in PM$_{10}$ levels. Also, the volcanic activity does not have a direct effect on PM levels (since many of these events do not reach the island because the eruptions are not of significant magnitude and the prevailing winds at these times are not strong enough to drive the particles to the Northwest).

![Average PM$_{10}$ concentrations at Fajardo and Salinas (August 2002 to May 2003)](image1)

![Average PM$_{10}$ concentrations at Fajardo and Vieques (June 2001 to April 2002)](image2)

![Average PM$_{10}$ concentrations at Fajardo and Guaynabo (November 2000 to September 2001)](image3)

**FIGURE 2** - Monthly average PM concentrations (µg m$^{-3}$) in different sites in Puerto Rico and their relationship with Sahara Events (SE) and Montserrat Volcano Events (VE) during the sampling period. 2A) Average PM$_{10}$ concentrations at Fajardo and Salinas (August 2002 to May 2003); 2B) Average PM$_{10}$ concentrations at Fajardo and Vieques (June 2001 to April 2002); 2C) Average PM$_{2.5}$ concentrations at Fajardo and Guaynabo (November 2000 to September 2001).

In Guaynabo and Fajardo the maximum PM$_{2.5}$ levels were obtained during June 2001 where Fajardo reached (12.0 µg m$^{-3}$) and in Guaynabo (14.3 µg m$^{-3}$) in July 2001. Sahara events have shown to have more impact than volcanic activities in the concentrations of airborne particulate matter on the island (Figure 2C). The maximum PM levels were obtained during the summer and this fact is evidence that links Sahara events to increases of PM exposure on the island. Certainly Sahara events are more frequent than volcanic events making Sahara dust a stronger influence on air quality in Puerto Rico.
Sahara dust has been reported to be associated with respiratory illness in Caribbean countries. Since 1970 the amount of African dust that reaching the Caribbean islands has increased and the respiratory diseases have increased proportionally [34-36]. However, a recent report did not find any association between Sahara dust and increase in respiratory illness (Prospero, personal communications) in the Island of Barbados. In addition effects on Caribbean coral reefs have been reported [36,37] which links increase in dust deposition in shallow waters due to Sahara dust deposition. In Puerto Rico high incidence of asthma has been found, but it is not necessarily associated with Sahara events [38,39], although anecdotal information from physician and residents on the island indicate that respiratory diseases worsen during Sahara episodes. This phenomenon has to be investigated and needs to be studied more carefully in order to support or reject such hypothesis.

African dust is a major source of dissolved Fe in the tropical North Atlantic [36,40]. The Fe levels present similar behavior or profile as the PM levels. This evidence is corroborated by good correlation obtained from all sites between Fe and PM concentrations: Fajardo (PM$_{10}$: $r^2 = 0.5$, P value 0.06; $r^2 = 0.7$, P value 0.0048; PM$_{2.5}$: $r^2 = 0.8$, P<0.0001), Salinas ($r^2 = 0.5$, P value 0.0184), Vieques ($r^2 = 0.8$, P value 0.0028) and Guaynabo ($r^2 = 0.6$, P value 0.009).

A certain influence of Sahara dust can be appreciated by the increase in Fe concentration with storm events (Figure 3). Viana et al. [41] reported levels of Fe in PM$_{10}$ ranging from 5 to 8 µg m$^{-3}$ during Sahara episodes and 0.4-0.6 µg m$^{-3}$ during non-African scenarios at the Canary Island. These values are a little higher than that we find in Puerto Rico (monthly average 0.7-1.5 µg m$^{-3}$) during the months that have Sahara events. However these levels represent the average obtained for these months and not for the episode itself. We also need to keep in mind that these differences could be attributed to the proximity of the sources. This slight difference is probably due to differences in size distribution among PM material. Fe content > 2% in PM is a reliable indicator of Sahara dust transport [42], which has been already demonstrated for Puerto Rico [14]. Our results show some correlation between Sahara episodes and % Fe (Figure 3). In the rainy period, March to May, the correlations are not so clear. Most of the Sahara events that reached the island showed high levels of Fe, higher than 2% in PM therefore corroborating the influence of this source. While normal levels of Fe during non-Sahara periods being lower than < 1%.

The literature shows that Fe is broadly considered as tracers characterizing soil erosion and dust in the absence of smelters and or steel industries [43]. Fe, predominantly in PM$_{10}$, comes from natural sources as resuspended airborne soil dust. In Puerto Rico, in spite of the relatively large density of industries, iron remains greatly associated to Sahara dust except in center of industrial activity such as near coal plants as the case in Salinas (Figure 3A). Iron also composes the major fraction of PM$_{2.5}$ (> 2%) collected during Sahara events.

Although volcanic ash is known to contain heavy metals such as Cd, Hg, V plus As its contribution was not evident in particulate collected during our study, however our work was not directed towards dressing this question.

Most of the metals found in the fine particles (PM$_{2.5}$) at the urban/industrial site (Guaynabo) are higher than the coarse fraction (PM$_{10}$) at the reference site of Fajardo and also in Vieques and Salinas. The high levels of trace elements (Ni, V, Pb and As) at the urban site originate from anthropogenic sources mainly from fuel combustion and automobile exhaust. This is consistent with what is reported in the literature, which states that metal concentrations (Cd, Cu, Pb, Ni, V and Zn) from anthropogenic sources predominate in small particles [23]. It was associated Cd and Zn with diesel and fuel products combustion. V is linked...
to combustion of fuel-oil that in turn, is one of the main fuels release from the furnace of refineries [43]. There is a refinery and two power plants in the Guaynabo site that have contributed to the output of As, Cd, Cu and Zn. High Ni and V concentrations as well as the amount of heavy traffic in the area (related with handling of goods from the commercial port).

CONCLUSIONS

Characterization of PM$_{2.5}$ and PM$_{10}$ was determined during the period of 2000 to 2003 at different sites in Puerto Rico. Average levels of PM$_{10}$ and PM$_{2.5}$ were below standard limit suggested by EPA (15 µg m$^{-3}$ and 50 µg m$^{-3}$, respectively). Also they were lower as compared to those of other cities in the US. Metals also presented low levels, except for Ni and V that were one of the highest of those reported in the literature for PM$_{2.5}$ trend. Associating Fe and PM levels with Sahara events was found and reported herein. However, this is relatively good for both PM$_{10}$ and PM$_{2.5}$ when expressed in Fe%. In all cases, the highest concentration of PM$_{10}$ and Fe were obtained during summer when Sahara events occurred. Anthropogenic sources contribute to the presence of Ni, Pb, Zn and V. Only Ni presented high levels of DRU when compared with literature data. Ni and V have been reported to exert toxic effects and are known to induce proinflammatory cytokines in animals and in human cell cultures. The effect and relationship of these elements to respiratory illness at the urban site should be evaluated and studied further. These data are one of the few available for Puerto Rico and should be available for comparison of future research of particulate matter and characteristic of air quality.

ACKNOWLEDGEMENTS

This work was supported by GM61838 NIGMS-RISE Program, SO6 GM08224 NIH-MBRS SCORE Program and NIH NCRR RCMI G12RR03051. The publication's contents are solely the responsibility of the authors and do not necessarily represent the official views of NCRR or NIH".

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Received: August 11, 2006 Accepted: September 29, 2006

CORRESPONDING AUTHOR

Braulio D. Jimenez-Velez
Center for Environmental and Toxicological Research
University of Puerto Rico
Medical Sciences Campus
Biochemistry Department
School of Medicine
PO Box 365067
San Juan 00936-5067
PUERTO RICO
Phone/Fax: +1 787 7538784
e-mail: bjimenez@rcm.upr.edu