Concentrations of Ni and V, other heavy metals, arsenic, elemental and organic carbon in atmospheric fine particles (PM$_{2.5}$) from Puerto Rico

David Acevedo Figueroa$^a$, Carlos J Rodríguez-Sierra$^{a,b}$ and Braulio D Jiménez-Velez$^a$

$^a$Center for Environmental and Toxicological Research, Department of Biochemistry, University of Puerto Rico, Medical Sciences Campus, San Juan, Puerto Rico
$^b$Department of Environmental Health, Medical Sciences Campus, University of Puerto Rico, San Juan, Puerto Rico

Fine atmospheric particulate PM$_{2.5}$ (particles with diameters of $<2.5$ μm) were sampled in an urban industrialized area – Guaynabo, Puerto Rico (Figure 1) – and in a reference less polluted site – Fajardo, Puerto Rico – and analyzed for trace metals, and inorganic and organic elemental carbon. PM$_{2.5}$ samples were collected from November 2000 to September 2001 using an Andersen Instruments RAAS2.5-400 for periods of 72 h. Metals analyzed were arsenic (As), cadmium (Cd), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) by atomic absorption. Levels of elemental and organic carbon (EC/OC) were also determined. All metals analyzed, except for Fe, were significantly higher in PM$_{2.5}$ from Guaynabo when compared to Fajardo. Average levels of PM$_{2.5}$ in Guaynabo were 11.6 versus 8.5 μg/m$^3$ in Fajardo. Average levels of EC were 1.5 and $<0.14$ μg/m$^3$; and OC levels were 2.2 and $<1$ μg/m$^3$ for Guaynabo and Fajardo, respectively. Levels of Ni (17 ng/m$^3$) and V (40 ng/m$^3$) determined in PM$_{2.5}$ from the Guaynabo area were high when compared to other cities, and these metals could be responsible for respiratory problems reported in the area. Multivariate analyses showed strong relationships in Guaynabo between Ni and V, PM$_{2.5}$ and Fe and As and Cu and Pb. In Fajardo, the strongest associations were obtained between PM$_{2.5}$ and Fe, Cd and V and Ni and Pb and Cu, these last three elements exhibiting an inverse relationship.


Key words: arsenic; atmospheric pollution; heavy metals; particulate matter; PM2.5; trace elements

Introduction

Particulate air pollutants have been associated with increased respiratory, cardiovascular and cancer mortality and morbidity, and with other health problems (Dockery et al., 1993; Reichhardt, 1995). The fine fraction of the atmospheric particulate matter is of great concern because it is predominantly deposited in the alveolar region of the lung where absorption efficiency is higher and the overall removal of particles is relatively inefficient (Hlavay et al., 1992; Lippmann et al., 1980). Only about 20% of particles deposited in the alveolar region are cleared in the first day, and the remaining portion is cleared very slowly (Rozman and Klassen, 1996). The fine fraction includes particles with aerodynamic diameters of $<2.5$ μm, and is referred to as PM$_{2.5}$. PM$_{2.5}$ has shown a closer association with human adverse health effects than either particles $<10$ μm (PM$_{10}$) or total suspended particles (TSP) (Reichhardt, 1995). In addition,
several studies suggest an association between motorized traffic-related air pollution and diminished pulmonary function and/or increased respiratory symptoms in children (Kim et al., 2004; Weiland et al., 1994).

PM$_{2.5}$ is mainly produced by particles emitted directly into the atmosphere and particles formed in the air from the chemical transformation of gaseous pollutants (secondary particles) (Kim et al., 2005). The principal types of directly emitted particles are soil related, elemental/organic carbon (EC/OC) and other particles from the combustion of fossil fuels and biomass materials. However, PM$_{2.5}$ has a low level of soil particle components, and the main anthropogenic source is a product of the combustion of fossil fuels (Ohlström et al., 2000). Principal sources of PM$_{2.5}$ include combustion of coal, oil, gasoline, diesel or wood, atmospheric transformation products of NO$_x$, SO$_2$ and organic compounds, natural and anthropogenic (WHO, 2000).

It is well known that fine particles have high concentrations of many potentially toxic trace metals, such as cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn), that can be incorporated into the body through inhalation (Singh et al., 2002). The metal content on fine particles has been suggested as causative agents associated with adverse respiratory health effects (Dreher et al., 1997; Ghio et al., 1996). Most of the toxic metals in the air are in the form of fine particles, with a size distribution equivalent to that of aerosols (1.0 µm or less in diameter). It is suggested that these metals can produce lung tissue damage by catalyzing oxidant formation (Fang et al., 1999) and promoting the release of inflammatory mediators and cytotoxicity (Frampton et al., 1999). Recent epidemiological studies have linked low DNA repair activity with lung cancer (Paz-Elizur et al., 2003), showing that there is a component of the population with a higher cancer risk. The studies showed that this population may have a genetic predisposition to lung damage and is more susceptible to metal exposure from airborne particulates.

The atmospheric lifetime of PM$_{2.5}$ is in the order of days to weeks and it has been shown to travel hundreds to thousands of kilometers (Raes et al., 2000). These characteristics can result in prolonged exposure, promoting or aggravating health problems. Fine particles are also largely water soluble and hygroscopic, with the exception of carbon and some organic compounds, which makes them bioavailable (WHO, 2000).

Previous studies performed in Puerto Rico have shown that the population of urban Guaynabo had more types and cases of cancer than any other regions of the island, also suffering from respira-
tory health problems, such as asthma, particularly affecting children and elderly people (US NCEH, 1997). Reyes et al. (2000) demonstrated that TSP and PM$_{10}$ organic extracts from the Guaynabo site were more toxic than in the reference site of Fajardo. However, PM$_{2.5}$ particles were not evaluated in the previous study, and their effects need to be addressed.

Little research has been conducted in Puerto Rico to characterize and study the chemical and toxicological composition of airborne PM$_{2.5}$ throughout the island. Recently, the Puerto Rico Environmental Quality Board established a monitoring program for PM$_{2.5}$ in several locations throughout the island. However, regular analyses of the chemical composition of samples are not included as a parameter in the monitoring program. The purpose of this study is to evaluate and compare the concentrations of PM$_{2.5}$, its levels of EC/OC, and a series of toxic metals, such as As, Cd, Cu, Fe, Ni, Pb, V and Zn, from two sites in Puerto Rico during a 12-month period. Differences in variables between these two sites are compared and evaluated. These are the first reported values of metals in PM$_{2.5}$ from Puerto Rico.

**Materials and methods**

**Sampling**

The procedures used in this research were based on the Quality Assurance Guidance Document 2.12 (USEPA, 1998). The instrument used for sampling was the Fine Particulate Chemical Speciation Air Sampler (RAAS 2.5-400) from Andersen Instruments Inc. RAAS2.5-400 (Franklin, MA, USA), which satisfies the monitoring requirements promulgated in the new PM$_{2.5}$ National Ambient Air Quality Standards (USEPA, 1997). The instrument is a filter-based gravimetric sampler with six filter modules to capture specific PM$_{2.5}$ particles to be used for speciation analysis and identification of those particles. The advantages of this sampler are multiple filters, the capability to produce 24-h samples, and a PM$_{2.5}$ cut-point (www.thermo.com/air). The flow meters (FM) were set to intake air at flows of 17 L/min (FM 1 and 4), 4.1 L/min (FM 2 and 5) and 3.5 L/min (FM 3 and 6). The RAAS 2.5-400 monitors and records the ambient manifold and enclosure temperatures, barometric and pump vacuum pressures, humidity, flow rates, and volumes of each individual channel of the instrument.

PM$_{2.5}$ Teflon filters were placed in channels 1, 3, 4 and 6, while quartz filters were placed in channels 2 and 5. Teflon filters were used to determine PM$_{2.5}$ levels by weight difference in a five decimal place balance (M-220D, Denver Instruments, Denver, CO, USA). Quartz filters were used to determine heavy metal (FM 2 and FM 5) concentration as well as the EC/OC (FM 5). The sampling period began in November 2000 and lasted until September 2001. Each filter contained the material collected in a 72-h period. Sampling periods were set to begin and end at midnight. Containers with the Guaynabo and Fajardo samples were placed inside a cooler and kept at 4°C. Filters were transported to the laboratory and the conditioning process was initiated immediately. Maintenance of instruments was performed on a regular basis (every four weeks) in order to ensure the quality of data and to comply with EPA regulations (USEPA, 1998).

**PM$_{2.5}$ and metal measurements**

Teflon filters for PM$_{2.5}$ were weighed and conditioned at a temperature of 20–23±2°C and a humidity level of 40–45±5% (USEPA, 1998). Filters were stored in Petri dishes and kept in desiccators until the conditioning process was achieved. Filters were weighed every day, and provided three similar consecutive measurements until a standard deviation of 0.00002 g was achieved.

**Metals**

The heavy metal analyses were performed on the Quartz filters from either FM 2 or FM 5 channels. A monthly composite sample (four to eight filters per composite) from either FM 2 or FM 5 was digested on a hot plate. Acidified extracts were filtered through a Whatman 41 filter paper, previously rinsed with 1% HNO$_3$. Metals were analyzed by atomic absorption (AA) using a Perkin-Elmer AA Spectrometer Model A Analyst 800. USEPA (1986–1996) methods 7060A, 7131A, 7211, 7381, 7421, 7521, 7911 and 7951 were used.
for the following heavy metals analysed: As, Cd, Cu, Fe, Pb, Ni, V and Zn, respectively.

All metal concentrations were corrected using the field blank and calculated on the basis of PM$_{2.5}$ mass collected and normalized by the volume of air passed through the filters during the sampling period. Metal concentrations were estimated by multiplying the concentrations of PM$_{2.5}$ (obtained from the four Teflon filters weighed during the same sampling period) by the air volume passed through the quartz filters. The calculated mass was added for all filters included in the composite. Concentrations of heavy metals in the samples were corrected by the levels found in field blanks. For statistical purposes, a zero value was assigned to a sample when a negative value was obtained. This assignment only occurred in Fajardo, where samples contained the lowest metal concentrations. However, when levels were below the quantification limits, but higher than the field blank, a rough concentration estimate was calculated and used as an approximated value for statistical purposes.

**Elemental and organic carbon**

Samples from the FM 5 channel were used to analyze EC/OC. A filter from the beginning, middle and end of each month from each sampling site was sent to Sunset Laboratory (Oregon, USA) for EC and OC content. The EC/OC ratio was analysed according to NIOSH 5040 method (NIOSH, 1999). OC sample levels were corrected by the average amount found in field blanks. Field blanks did not show any contamination for EC, therefore the EC levels were not corrected by field blank values. An average value for each month was calculated.

**Quality control and statistical analyses**

Field blank filters (Teflon and quartz) were obtained during each sampling period at each site. A total of 81 field blanks were collected in Guaynabo and 79 in Fajardo during the sampling period. Each sample was handled with powder-free gloves. Preparatory blanks, field blanks, spike blanks and standard reference material (SRM) 1648 (NIST, 1998) were digested in each batch. Field blanks were also sent to Sunset Laboratory for EC/OC analyses. The averaged heavy metal values in the Guaynabo and Fajardo field blanks were subtracted to levels obtained in Guaynabo and Fajardo samples, respectively. Similarly, the total averaged OC mass obtained in field blanks was subtracted from the mass obtained in Guaynabo and Fajardo samples. The EC concentrations were not corrected since the amounts found in field blanks were below the uncertainty value of the analysis (uncertainty value was 0.21 µg/cm$^2$).

On average, recoveries from spike blanks fluctuated from 82% for As to 104% for Pb, while recoveries for the SRM 1648 ranged from 61% for Fe to 88% for Ni. Spike blank recoveries were reasonably accurate, therefore, no substantial loss occurred in the sample preparation process.

Statistical analyses were performed using the computerized software program Statistical Program for Social Sciences, version 10.0 (SPSS 10.0). The $t$-test analyses were performed to establish statistical differences between the metal concentrations from the Guaynabo and Fajardo sites, at the 95% confidence interval. Multivariate analyses were performed between metal species analyzed per site in order to elucidate possible relationships among them. Factor and cluster analyses were carried out in Guaynabo on the trace element concentrations for As, Cd, Cu, Fe, Ni, Pb and V, as well as for PM$_{2.5}$ concentrations. The factor and cluster analyses were carried out for Cd, Cu, Fe, Ni, Pb and V levels in Fajardo, and PM$_{2.5}$ concentrations were also added to these variables. A factor analysis was performed for the correlation matrix of the variables analyzed, using principal component analysis as the extraction method of factors. The rotation method of VARIMAX with Kaiser normalization was used (Mardia et al., 1979; Srivastava and Muni, 2002). Dendograms were performed with the agglomerative, the group average linkage and the hierarchy process from the squared Euclidean distance matrices. Distances, where the clusters combined, were rescaled in dendograms. Dendograms performed with levels expressed in terms of volume and mass formed mostly the same grouping of variables. The hierarchical technique (with the agglomerative process) was performed on the cluster analysis. The approach of averaged linkage between groups was selected to avoid the scaling problem. Standardization coding of the variables was performed in order to have means of zero and variances of one (Manly,
1986). This is expressed by the following equation:

\[
\text{Standardized (normalized) value} = \frac{([\text{Me}] - \text{Ave}_{\text{Me}})}{\text{Std. Dev.}}
\]

where \([\text{Me}] - \text{Ave}_{\text{Me}}\) is the metal concentration minus the average metal level, and Std. Dev. is the standard deviation of metal concentration.

## Results and discussion

### PM\(_{2.5}\) and heavy metals

The PM\(_{2.5}\) concentrations were consistently higher during the summer months (May–July) at both sites studied (Figure 2). The highest level was detected at the Guaynabo site (14.3 \(\mu g/m^3\)) during July 2001 and at the Fajardo site (12.0 \(\mu g/m^3\)) during June. These high concentrations coincide with reports of frequent Sahara dust storms arriving from Africa during the summer months and impacting the Caribbean region (Colarco et al., 2003; Graham and Duce, 1979; Prospero et al., 1986). When averaged throughout the year, the annual mean of PM\(_{2.5}\) concentration at the Guaynabo site was significantly \((P<0.0001)\) higher than the annual mean of Fajardo. PM\(_{2.5}\) from the Guaynabo site (11.6 \(\mu g/m^3\) \(\pm\) 0.6) exhibited 27 \(\pm\) 2\% more PM\(_{2.5}\) material than the Fajardo site (8.5 \(\mu g/m^3\) \(\pm\) 0.5). This additional fraction is attributed to onsite contributions due to industrial activity. Adverse health effects have been reported to occur during long-term exposure of PM\(_{2.5}\) levels of 10 \(\mu g/m^3\), which are slightly lower than those found in Guaynabo (WHO, 2000). However, the PM\(_{2.5}\) concentrations in Guaynabo were not as high as in other countries around the world, such as China, Brazil, and Italy. Table 1 has been prepared for purposes of comparisons.

The PM\(_{2.5}\) concentration is important for evaluating health risks (Dockery et al., 1993; Reichhardt, 1995); however, the chemical composition of such particles is just as important. The average concentration of all heavy metals analyzed in this study, with the exception of Fe, was several fold higher in Guaynabo (the industrialized urban site) than in Fajardo (Table 2). A \(t\)-test of paired mean comparison showed that the annual average for all metals, except Fe, was significantly higher in Guaynabo \((P<0.05)\). The highest concentration of metals in airborne particulate matter was found for V, Ni and Cu, which showed a 29, 9 and 8-fold increase, respectively. The mass of three heavy metals (V, Ni and Fe) was detected at the mg/g level. As and Pb were 4- to 5-fold higher in Guaynabo compared to Fajardo, indicating that they originate from local sources. The highest Pb concentrations in Guaynabo were found during winter, while the highest As concentrations were encountered during summer (Figure 3). A comparison with other studies performed on the composition of PM\(_{2.5}\) in various regions of the world (Table 1) indicates that the concentration of the heavy metals found in Fajardo (reference site) are generally lower than those found in other areas of the world. This supports the use and selection of Fajardo as a reference site. Concentrations of Pb, Cd, Zn, V, and As in Guaynabo, while significantly higher than in Fajardo, were lower than the suggested guideline levels by the national (EPA) and international (EEA, WHO) regulations.
### Table 1. Heavy metals, arsenic and EC/OC levels found in PM$_{2.5}$ from different regions of the world.

<table>
<thead>
<tr>
<th>References</th>
<th>Site</th>
<th>PM$_{2.5}$</th>
<th>EC</th>
<th>OC</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fang et al. (1999)</td>
<td>THU (suburban), Taiwan</td>
<td>25.9</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>22</td>
<td>1300</td>
<td>na</td>
<td>54</td>
<td>na</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>HKIT (rural), Taiwan</td>
<td>25.7</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>22</td>
<td>330</td>
<td>na</td>
<td>19</td>
<td>na</td>
<td>85</td>
</tr>
<tr>
<td>Singh et al. (2002)</td>
<td>Downey (urban), Los Angeles</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>13</td>
<td>296</td>
<td>4.4</td>
<td>11</td>
<td>5.2</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Riverside (inland), Los Angeles</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>4</td>
<td>170</td>
<td>1.9</td>
<td>4.1</td>
<td>4.1</td>
<td>13</td>
</tr>
<tr>
<td>Hien et al. (2001)$^a$</td>
<td>Ho Chi Minh, Viet Nam</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>2.5</td>
<td>na</td>
<td>2</td>
<td>261</td>
<td>na</td>
<td>79</td>
<td>7.8</td>
<td>245</td>
</tr>
<tr>
<td>Castanho et al. (2001)</td>
<td>Sao Paulo (winter), Brazil</td>
<td>30.2</td>
<td>7.6</td>
<td>15.8</td>
<td>na</td>
<td>na</td>
<td>19</td>
<td>532</td>
<td>3.9</td>
<td>42</td>
<td>11.7</td>
<td>126</td>
</tr>
<tr>
<td>Wei et al. (1999)</td>
<td>Downey (urban), Los Angeles</td>
<td>15.0</td>
<td>4.1</td>
<td>5.3</td>
<td>na</td>
<td>na</td>
<td>5</td>
<td>179</td>
<td>3.1</td>
<td>23</td>
<td>8.9</td>
<td>51</td>
</tr>
<tr>
<td>Marczan et al. (2001)</td>
<td>Four cities, China</td>
<td>92</td>
<td>na</td>
<td>na</td>
<td>31</td>
<td>na</td>
<td>29</td>
<td>na</td>
<td>na</td>
<td>341</td>
<td>0.10</td>
<td>420</td>
</tr>
<tr>
<td>Chan et al. (1999)</td>
<td>Milan, Italy</td>
<td>55</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>18</td>
<td>190</td>
<td>6.5</td>
<td>138</td>
<td>138</td>
<td>9</td>
</tr>
<tr>
<td>Querol et al. (2001)</td>
<td>Castello, Spain</td>
<td>20</td>
<td>na</td>
<td>na</td>
<td>8.5</td>
<td>0.5</td>
<td>10</td>
<td>250</td>
<td>3.0</td>
<td>288</td>
<td>6</td>
<td>178</td>
</tr>
<tr>
<td>Wang et al. (2002)$^a$</td>
<td>Nanjing, China</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>22</td>
<td>17</td>
<td>4.5</td>
<td>13</td>
<td>2</td>
<td>73</td>
</tr>
<tr>
<td>Diociaiuti et al. (2001)</td>
<td>Rome, Italy</td>
<td>31</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>1.6</td>
<td>na</td>
<td>322</td>
<td>1</td>
<td>124</td>
<td>3</td>
<td>34</td>
</tr>
<tr>
<td>Puxbaum et al. (2004)</td>
<td>Urban – Austria</td>
<td>21.5</td>
<td>3.3</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ho et al. (2002)</td>
<td>Background – Austria</td>
<td>17.5</td>
<td>1.8</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Traffic – China</td>
<td>50.9</td>
<td>5.8</td>
<td>9.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Industrial – China</td>
<td>57.4</td>
<td>5.0</td>
<td>10.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rural – China</td>
<td>42.3</td>
<td>1.4</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avino et al. (2001)</td>
<td>Urban – Italy</td>
<td>12.10</td>
<td>8.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Robinson et al. (2002)</td>
<td>Urban – US</td>
<td>11 (w)</td>
<td>0.4 (w)</td>
<td>4.7 (w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 (s)</td>
<td>0.8 (s)</td>
<td>7.9 (s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This article</td>
<td>Guaynabo, Puerto Rico</td>
<td>11.6</td>
<td>1.5</td>
<td>2.2</td>
<td>0.39</td>
<td>0.055</td>
<td>5.5</td>
<td>93</td>
<td>17</td>
<td>3.0</td>
<td>40.0</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>Fajardo, Puerto Rico</td>
<td>8.5</td>
<td>&lt;0.14</td>
<td>&lt;1.0</td>
<td>0.09</td>
<td>0.015</td>
<td>0.7</td>
<td>103</td>
<td>1.9</td>
<td>0.57</td>
<td>1.4</td>
<td>3.0</td>
</tr>
<tr>
<td>WHO Standard (2000)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>USEPA Standard (1990)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Water soluble elements.

Particulate material analyzed was <2 μm. na = not analyzed. Metal concentrations are given in ng/m$^3$. PM$_{2.5}$ and EC/OC are in μg/m$^3$. 

Characterization of PM$_{2.5}$ in Puerto Rico

DA Figueroa et al.
organizations (Table 1). However, these agencies do not have guideline values for Fe or Cu. Ni and As are known carcinogens (WHO, 2000), hence, their concentrations in air as well as in other media should be viewed carefully. Metal levels in PM$_{2.5}$ from Guaynabo, particularly Ni and V, were

![Levels of Lead (Pb) in PM$_{2.5}$ at Guaynabo and in Puerto Rico](image1)

![Levels of Arsenic (As) in PM$_{2.5}$ at Guaynabo and Fajardo](image2)

**Figure 3.** Pb and As annual distribution profiles at Guaynabo and Fajardo, showing their annual concentration peaks.
significantly higher than in the reference site (Figure 4). However, lower levels were detected in April due to meteorological conditions with high rainfalls during this period. The average concentrations were in fact several fold higher than in other places around the world (Table 1). Ni and V are metals of high abundance in residual oil fly ash, which is a combustion by-product of oil used as a fuel source (Swaine, 1980; WHO, 2000). These trace elements are frequently used as fingerprint markers for petroleum derived hydrocarbons (Laden et al., 2000; Thurston and Spengler, 1985). The Ni/V ratio for oil combustion has been reported to be around 3 (Pacyna and Pacyna, 2001), while that of gas and diesel ranges from 0.3 to 0.5 (Rodríguez-Navarro and Sebastian, 1996). The annual ratio Ni/V for Fajardo was calculated at 0.7, while that of Guaynabo is 2.3. These results indicate that the main source of Ni and V at Guaynabo comes from fossil fuel combustion, while that of Fajardo comes from traffic, boating and recreational activities in the adjacent area. These metals exist in these particles in an easy soluble form, which makes them bioavailable (Dreher et al., 1997). In addition, Ni and V have been identified as causative agents of acute lung injury in animals (Dreher et al., 1997). Their toxicity is discussed herein.

**Toxicological effects of metals**

Although there is no consistent evidence for the carcinogenicity of arsenic compounds in animals (WHO, 2000), there is sufficient evidence to indicate that inorganic arsenic compounds are skin and lung carcinogens in humans (WHO, 2000). Inorganic arsenic seems to affect DNA repair mechanisms (Rossman, 1981). Teratogenic effects in the hamster, rat and mouse were detected at high exposure levels (WHO, 2000). Chronic exposure to arsenic causes neurotoxic effects in human (Lagerkvist and Zetterlund, 1994). Increased mortality from cardiovascular diseases has been observed in epidemiological studies of smelter workers exposed to high levels of airborne arsenic (WHO, 2000). In addition, spontaneous abortions and lower mean birth weights have been registered in smelter workers and among subjects living in the vicinity of the smelter (WHO, 2000). We estimate an uptake of

---

**Figure 4.** Levels of Ni and V found in PM$_{2.5}$ from Guaynabo and Fajardo, Puerto Rico. Data is expressed in $\mu$g/m$^3$. 

---

Characterization of PM$_{2.5}$ in Puerto Rico
DA Figueroa et al.
3.9 ng/day of As in the Guaynabo area, while only 0.9 ng/day uptake at the reference site. This represents a 4-fold increase in the levels of As in Guaynabo compared to our reference site (Table 2).

Nickel compounds induce respiratory tract irritation, chemical pneumonia, emphysema, varying degrees of hyperplasia in pulmonary cells, and fibrosis (pneumoconiosis) in animals by inhalation (WHO, 2000). Ottolenghi et al. (1974) described a significant increase in the number of lung tumors in rats following inhalation exposure to nickel sub-sulfide for about two years. Nickel carbonyl inhalation in rats has produced lung tumors in one of three reported experiments compared to none in corresponding control groups (WHO, 2000). Acute inhalation exposure to nickel carbonyl has also caused lung damage, mucosal irritation, and asthma in workers exposed to inorganic nickel compounds (WHO, 2000). There is no epidemiological information on nickel uptake from the environment or relations with cancer incidence in the general population. However, nickel refinery workers exposed through inhalation to various nickel compounds have a higher risk of lung cancer and nasal cavity cancers than the non-occupationally exposed population (ICNCM, 1990; WHO, 2000). Some studies show a correlation between nickel workers and incidence of laryngeal, kidney, prostate or bone cancer (ICNCM, 1990). There is no need to emphasize the significance and need to learn more about the relevant environmental exposure concentrations of nickel, which would exert a health effect on the exposed community. We have estimated a conservative intake of 170 ng/day of Ni using the annual mean Ni concentration from Guaynabo. This is about ten times higher than the uptake at Fajardo. We assumed a breathing rate of 20 m$^3$/day and 50% uptake in a 70-kg person.

Vanadium compounds present different toxicities which are related to the balance of the vanadium compound. The toxicity of vanadium is intermediate in the case of respiratory exposure (Vouk, 1979). Acute exposure to vanadium (tens of mg/m$^3$) is responsible for systemic effects in animals. Damage to the liver, kidneys, gonads, haematological, cardiovascular and nervous systems have been reported (Vouk, 1979). In addition, systemic effects at very low levels of exposure have also been reported (WHO, 2000). Carter et al. (1997) showed that metals in airborne particles can induce the secretion of inflammatory cytokines in respiratory airway cells. These findings demonstrate that exposure to this metal may be associated with respiratory illness problems. Positive correlations were obtained between V concentrations in urban air and mortality from bronchitis, pneumonia, cancer and heart disease (Stocks, 1960). Vanadium intake from PM$_{2.5}$ at Guaynabo has been estimated at 400 ng/day (assuming 50% absorption through the lungs). This estimate is 30-fold higher than the estimated intake at the reference site (Table 2). Both Ni and V are found at relatively high concentrations at the Guaynabo site, which links them again with the industrialized activity at this urban site.

The intake for As, Ni and V were within the range of that reported by WHO (2000) – As 20–200 ng/day, Ni 100–800 ng/day and V 1.5 µg/day. Although the levels of Ni and V were found to be relatively high in Guaynabo, they are comparable to the WHO (2000) report. However, one should consider the fact that the combined toxicity of metals is many times greater than the single metal (Shubert et al., 1978). Consequently, the need to analyze these individual constituents in ambient air is evident in order to incorporate such interactions in future epidemiological studies.

Elemental and organic carbon

Atmospheric carbonaceous species are one of the major contributors of aerosol particles in urban locations. They are emitted from many sources and contribute to approximately 20–50% of fine particles mass (Gray et al., 1986; Hamilton and Mansfield, 1991; Puxbaum and Wopenka, 1984). The two major components of carbonaceous species are organic carbon (OC) and elemental carbon (EC). Guaynabo levels of EC and OC are presented in Figure 5. EC concentrations fluctuated from 2.6 µg/m$^3$ in November 2000 to 1.1 µg/m$^3$ in February 2001. OC concentrations ranged from 3.8 µg/m$^3$ in November 2000 to 1.4 µg/m$^3$ in July 2001. Both EC and OC are highest during the winter period at both sites. During the same period in Rome, EC and OC concentrations varied from 12–8 and 10–6 µg/m$^3$, respectively (Avino et al., 2001); and in Vienna, the average levels were 3.3 and 4 µg/m$^3$, respectively (Puxbaum et al., 2004). Guaynabo’s average level of EC was 1.5 and 2.2 µg/m$^3$ for OC.
The concentrations of EC and OC were similar to those found at background areas in Austria. The levels of EC and OC were lower than those found at reference sites reported in the literature. The EC and OC levels in Guaynabo have a very similar trend (Figure 5), probably indicating common sources. The correlation of EC and OC is good ($r^2=0.685$ with a P-value of 0.0178), which clearly indicates a direct relationship between them. Fajardo levels of EC and OC were below the minimum-reporting limit (MRL). EC levels were below the MRL because of the uncertainty of the analysis (0.14 µg/m$^3$). Levels found in field blanks established MRL for OC (1 µg/m$^3$). OC/EC equals this ratio if higher than 2, and identifies the source as secondary. This is consistent with reports in other areas of the world (Ho et al., 2002). The EC/OC ratios present lower values during the summertime, during the stability period, probably because of the degradation of organic compounds in particles. This ratio close to 2 is an indication of a secondary source.

**Figure 5.** Levels of elemental and organic carbon (EC/OC) in PM$_{2.5}$ from Guaynabo, Puerto Rico. (Error bars = standard error, N=3; Fajardo levels for EC/OC were <0.14 and <1.0 µg/m$^3$, respectively. Therefore, they were not included.)

The concentrations of EC and OC were similar to those found at background areas in Austria. The levels of EC and OC found at our reference site were lower than those of any reference sites reported in the literature. The EC and OC levels in Guaynabo have a very similar trend (Figure 5), probably indicating common sources. The correlation of EC and OC is good ($r^2=0.685$ with a P-value of 0.0178), which clearly indicates a direct relationship between them. Fajardo levels of EC and OC were lower than the minimum-reporting limit (MRL). EC levels were below the MRL because of the uncertainty of the analysis (0.14 µg/m$^3$). Levels found in field blanks established MRL for OC (1 µg/m$^3$). OC/EC equals this ratio if higher than 2, and identifies the source as secondary. This is consistent with reports in other areas of the world (Ho et al., 2002). The EC/OC ratios present lower values during the summertime, during the stability period, probably because of the degradation of organic compounds in particles. This ratio close to 2 is an indication of a secondary source.

**Statistical and evaluation by factor and cluster analysis**

Three components were extracted for factor analysis and described approximately 90% of the variation of the original set of variables. Factor loadings of variables analyzed for the three components extracted for Guaynabo and Fajardo are shown in Table 3. Metal concentrations expressed in terms of volume of air sample, and metal levels in terms of PM$_{2.5}$ mass are shown in Table 3. The variables highly correlate with each other, with variances explained with a common factor for Guaynabo as follows: As, Cu and Pb (first factor); PM$_{2.5}$ levels correlating with Fe and negatively with Cd (second factor); and Ni and V highly correlated to each other (third factor). Metal groups correlated in Fajardo were: Ni and Pb, and a negative correlation of Cu (first factor); PM$_{2.5}$ correlating with Fe (second factor), and Cd and V with high loadings in the third factor.

When factor analysis was performed with metal levels expressed in terms of mass, the groups formed in Fajardo did not vary. However, a slight variation in the Cd relationship was observed in Guaynabo. Cd factor loading decreased from $-0.761$ to $-0.621$ (Table 3) in factor 2 and increased from 0.430 to 0.633 in factor 1. Factor analysis was also performed without including PM$_{2.5}$ levels as a variable. Results showed that three correlated groups were primarily conserved. These groups were (As, Cu, Pb), (Ni, V) and (Fe) for Guaynabo. Cd correlated negatively with Fe when the levels were expressed in terms of volume and joined the group of (As, Cu, Pb) when expressed in terms of mass. In Fajardo, the groups of (Cd, V), (Ni, Pb, Cu negatively) and (Fe) were maintained with metals expressed in terms of volume of air sampled. However, in metal levels expressed in terms of PM$_{2.5}$ mass, Cu left the group of (Ni, Pb) and joined (Fe) with a negative correlation. The use of factor analysis shows that the relationship between metals change from site to site indicating differences between sites.

When cluster analysis was performed, a close relationship between (Ni, V) and (Cu, Pb) was found using these groupings for Guaynabo. The other group formed was PM$_{2.5}$ with Fe.

As joined the group formed by (Cu, Pb). Four principal groups, formed by dividing variables, were (Ni, V), (PM$_{2.5}$, Fe), (As, Cu, Pb) and (Cd). This pattern is consistent with that obtained using factor analysis.

The grouping of variables from Fajardo shows a strong relationship with (PM$_{2.5}$, Fe). The same pattern or principal groups were obtained using cluster analysis with factor analysis confirming the results. The cluster analysis supports the findings.
obtained with the factor analysis. Evident from the analyses is that Fe is closely related to PM$_{2.5}$ particulate matter and this association is independent of specific locations throughout the island. The differences in association between elements from both locations indicate that the sources of these elements depend on the site. Statistical analysis using both methodologies show that Ni and V levels in Guaynabo are correlated suggesting they come from a source of oil combustion.

### Conclusion

The urban (industrialized) location of Guaynabo is higher in PM$_{2.5}$, EC and OC levels, and metal levels (except Fe) than the reference site at Fajardo. Factor and cluster analysis grouped variables, indicating a common origin for sources of metal species. Three strong relationships were observed in Guaynabo forming the following groups (Ni, V), (PM$_{2.5}$, Fe) and (As, Cu, Pb). Cd, on the other hand, had a more variable behavior when the analysis was changed (factor analysis or cluster analysis) and performed with different numbers of variables or performed using different concentration units (ng/m$^3$ or µg/g). The predominant groups in Fajardo were formed by (PM$_{2.5}$, Fe), (Ni, Pb) and (Cd, V), and Cu, varied little, demonstrating no relationship with Ni and V or association with sources of oil combustion.

When levels where compared with other regions of the world, it was found that Fajardo samples had relatively low concentrations of Ni and V and other metals, supporting its selection as a reference site. However, Guaynabo had relatively high concentrations of Ni and V. These high concentration levels of Ni and V present in fine particles in the Guaynabo region are expected to be associated with soluble forms of these metals, making them more bioavailable through inhalation. The concentrations of Ni and V should be continuously monitored in Guaynabo, since they could represent a potential threat to public health in this area. These metals are thought to contribute to the incidence of cardiovascular, respiratory, and cancer morbidity and mortality health problems.

### References


Carter, J., Ghio, A. and Samet, J. *et al.* 1997: Cytokine production by human airway epithelial cells after exposure...


Chan, Y.C., Simpson, R.W. and McTainsh, G.H. et al. 1999: Source apportionment of PM_{2.5} and PM_{10} aerosols in Brisbane (Australia) by receptor modeling. *Atmospheric Environment* 33, 3251–68.


Diociaiuti, M., Balduzzi, M. and De Beraldis, B. et al. 2001: The two PM_{2.5} (Fine) and PM_{2.5...10} (Coarse) fractions: evidence of different biological activity. *Environmental Research* 98, 254–62.


Fang, G.C., Chang, C.N. and Wu, Y.S. et al. 1999: The characterization of chemical species in PM_{2.5} and PM_{10} aerosols in suburban and rural sites of central Taiwan. *The Science of the Total Environment* 234, 203–12.


Hien, P.D., Binh, N.T. and Truong, Y. et al. 2001: Comparative receptor modeling study of TSP, PM_{2.5} and PM_{2.5...10} in Ho Chi Minh City. *Atmospheric Environment* 35, 2669–78.


Stocks, P. 1960: On the relations between atmospheric pollution in urban and rural localities and mortality from cancer, bronchitis and pneumonia, with particular reference to 3,4-benzopyrene, beryllium, molybdenum, vanadium and arsenic. British Journal of Cancer 14, 397–418.


