Published in final edited form as:

Toxicol Ind Health. 2006 March ; 22(2): 87–99.

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

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Abstract

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/m³ in Fajardo. Average levels of EC were 1.5 and <0.14 µg/m³; and OC levels were 2.2 and <1 µg/m³ for Guaynabo and Fajardo, respectively. Levels of Ni (17 ng/m³) and V (40 ng/m³) 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.

Keywords

arsenic; atmospheric pollution; heavy metals; particulate matter; PM_{2.5}; 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 $<2.5 \mu\text{m}$, and is referred to as $\text{PM}_{2.5}$. $\text{PM}_{2.5}$ has shown a closer association with human adverse health effects than either particles $<10 \mu\text{m}$ (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).

$\text{PM}_{2.5}$ 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, $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 ($1.0 \mu\text{m}$ 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 $\text{PM}_{2.5}$ 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 respiratory health problems, such as asthma, particularly affecting children

and elderly people (US NCEH, 1997). Reyes *et al.* (2000) demonstrated that TSP and PM₁₀ 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% HNO₃. 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 $\mu\text{g}/\text{cm}^2$).

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 matrixes. 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 hierarchic 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:

$$\text{Standardized (normalized) value} = ([Me] - Ave_{[Me]}) / Std. Dev.$$

where $([Me] - Ave_{[Me]})$ 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 $\mu\text{g}/\text{m}^3$) during July 2001 and at the Fajardo site (12.0 $\mu\text{g}/\text{m}^3$) 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 ($11.6 \mu\text{g}/\text{m}^3 \pm 0.6$) exhibited $27 \pm 2\%$ more PM_{2.5} material than the Fajardo site ($8.5 \mu\text{g}/\text{m}^3 \pm 0.5$). 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 $10 \mu\text{g}/\text{m}^3$, 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) 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 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 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 subsulfide 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 m³/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/m³) 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/m³ in November 2000 to 1.1 µg/m³ in February 2001. OC concentrations ranged from 3.8 µg/m³ in November 2000 to 1.4 µg/m³ 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/m³, respectively (Avino *et al.*, 2001); and in Vienna, the average levels were 3.3 and 4 µg/m³, respectively (Puxbaum *et al.*, 2004). Guaynabo's average level of EC was 1.5 and 2.2 µg/m³ for OC. 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/m³). Levels found in field blanks established MRL for OC (1 µg/m³). 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 levels 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 (excepted 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/m³ 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 were 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.

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Figure 1.
Geographical location of sampling stations: Guaynabo (urban) and Fajardo (reference site on the east coast), Puerto Rico.

Figure 2. Levels of PM_{2.5} from Guaynabo and Fajardo, Puerto Rico during a one year period (2000–2001) (Error bars=standard error of the mean; number=*N* value;)

Figure 3. Pb and As annual distribution profiles at Guaynabo and Fajardo, showing their annual concentration peaks

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

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

Table 1
Heavy metals, arsenic and EC/OC levels found in PM_{2.5} from different regions of the world.

References	Site	PM _{2.5}	EC	OC	As	Cd	Cu	Fe	Ni	Pb	V	Zn
Fang <i>et al</i> (1999)	THU (suburban), Taiwan	25.9	na	na	na	na	22	1300	na	54	na	121
Singh <i>et al</i> (2002)	HKIT (rural), Taiwan	25.7	na	na	na	na	22	330	na	19	na	85
	Downey (urban), Los Angeles	na	na	na	na	na	13	296	4.4	11	5.2	35
	Riverside (inland), Los Angeles	na	na	na	na	na	4	170	1.9	4.1	4.1	13
Hien <i>et al</i> (2001) ^a	Ho Chi Minh, Viet Nam	na	na	na	2.5	na	2	261	na	79	7.8	245
Castanho <i>et al</i> (2001)	Sao Paulo (winter), Brazil	30.2	7.6	15.8	na	na	19	532	3.9	42	11.7	126
	Sao Paulo (summer), Brazil	15.0	4.1	5.3	na	na	5	179	3.1	23	8.9	51
Wei <i>et al</i> (1999)	Four cities, China	92	na	na	31	na	29	na	na	341	na	420
Marcazan <i>et al</i> (2001)	Milan, Italy	55	na	na	na	na	18	190	6.5	138	9	110
Chan <i>et al</i> (1999)	Brisbane, Australia	7.3	1.81	na	na	na	na	50	na	51	na	27
Queroi <i>et al</i> (2001)	Castello, Spain	20	na	na	8.5	0.5	10	250	3.0	288	6	178
Wang <i>et al</i> (2002) ^a	Nanjing, China	na	na	na	na	na	22	17	4.5	13	2	73
Diociaiuti <i>et al</i> (2001)	Rome, Italy	31	na	na	na	1.6	na	322	1	124	3	34
Puxbaum <i>et al</i> (2004)	Urban - Austria	21.5	3.3	4.0								
Ho <i>et al</i> (2002)	Background - Austria	17.5	1.8	3.1								
	Traffic - China	50.9	5.8	9.4								
	Industrial - China	57.4	5.0	10.1								
	Rural - China	42.3	1.4	5.6								
	Urban - Italy		12.10	8.6								
Avino <i>et al</i> (2001)	Urban - US	11 (w)	0.4 (w)	4.7 (w)								
Robinson <i>et al</i> (2002)		24 (s)	0.8 (s)	7.9 (s)								
This article	Guaynabo, Puerto Rico	11.6	1.5	2.2	0.39	0.055	5.5	93	17	3.0	40.0	12.0
	Fajardo, Puerto Rico	8.5	<0.14	<1.0	0.09	0.015	0.7	103	1.9	0.57	1.4	3.0
WHO Standard (2000)						5 ng/m ³ annual				0.5 µg/m ³ annual	20 µg/m ³	
EEA Standard (2003)						0.05 µg/m ³ 24 h mean				1.5 µg/m ³ annual		50 µg/m ³ annual
										3.0 µg/m ³ 24 h mean		100 µg/m ³

References	Site	PM _{2.5}	EC	OC	As	Cd	Cu	Fe	Ni	Pb	V	Zn
USEPA Standard (1990)		1.5 µg/m ³ annual										24 h mean 24 h mean

Particulate material analyzed was <2 µm. na = not analyzed. Metal concentrations are given in ng/m³. PM_{2.5} and EC/OC are in µg/m³.

^aWater soluble elements.

Table 2

Average heavy metal levels in PM_{2.5} from Guaynabo and Fajardo, Puerto Rico (November 2000 to September 2001) given in mass/m³ and mass/g of particles.

Site	As (ng/m ³)	Cd (ng/m ³)	Cu (ng/m ³)	Fe (ng/m ³)	Ni (ng/m ³)	Pb (ng/m ³)	V (ng/m ³)	Zn (ng/m ³)
Guay	0.39 ^b ±0.02	0.055 ^d ±0.007	5.5±0.6	93 ^d ±12	17 ^d ±2	3.0±0.5	40±3	12 ^a ±3
Faj	0.09±0.03	0.015±0.004	0.7±0.1	103±32	1.9±0.6	0.57±0.06	1.4±0.2	3 ^f ±1
Fold difference	4.3	3.7	7.9	0.9	8.9	5.3	28.5	4.0
	As ^c (µg/g)	Cd ^c (µg/g)	Cu ^c (µg/g)	Fe ^c (mg/g)	Ni ^c (mg/g)	Pb ^c (µg/g)	V ^c (mg/g)	Zn ^c (mg/g)
Guay	36 ^b ±2	5 ^d ±h	501±64	8.03 ^d ±0.77	1.5 ^e ±0.16	268±47	3.53±10.25	1.11±0.28 ^a
Faj	10±12	2.1±0.5	94±20	11.7±3.0	0.35±0.12	73±9	0.180±0.03	0.396±0.2 ^f
Fold difference	3.6	2.4	5.3	0.7	4.3	3.7	19.6	2.8

Uncertainty values are standard error with $N = 11$ months and are all field blank corrected.

^a Levels at six months were below the quantification limit (Zn = 50 µg/L), therefore average concentrations included levels that were roughly estimated.

^b Levels at nine months were below the quantification limit (As = 0.5 µg/L), therefore, average concentrations included levels that were roughly estimated.

^c Significantly different at $P < 0.05$ level.

^d Level obtained for one month was below the average value for field blanks (Cd = 0.069 and Fe = 63 in µg/L). A zero value was assigned to this month for statistical purposes.

^e Levels obtained for three months were below the average value for field blanks (Ni = 7 µg/L). Zero values were assigned to these months for statistical purposes.

^f Levels at six months were below the quantification limit (Zn = 50 µg/L), therefore averaged concentrations included levels that were rough estimates. In addition, levels obtained for the other five months were below the average value for field blanks (Zn = 23 µg/L). Zero values were assigned to these months for statistical purposes.

Table 3

Factor loadings of components extracted for Guaynabo and Fajardo, with metal levels expressed in terms of volume of air sampled and PM_{2.5} mass.

Variables	Guaynabo component factors			Variables	Fajardo component factors		
	1	2	3		1	2	3
PM _{2.5} (µg/m ³)	0.181	0.749	0.532	PM _{2.5} (µg/m ³)	0.220	0.959	-0.031
PM _{2.5} (µg/g)	-0.273	0.848	0.150	PM _{2.5} (µg/m ³)	-0.380	0.916	-0.197
As (µg/m ³)	0.769	0.545	0.093				
As (µg/g)	0.853	-0.168	-0.162				
Cd (µg/m ³)	0.430	-0.761	-0.088	Cd (ng/m ³)	-0.288	0.133	0.874
Cd (µg/g)	0.633	-0.621	0.208	Cd (µg/g)	-0.427	-0.143	0.817
Cu (µg/m ³)	0.912	-0.126	0.279	Cu (ng/m ³)	-0.919	-0.108	0.003
Cu (µg/g)	0.905	-0.085	-0.340	Cu (µg/g)	-0.703	-0.643	-0.091
Fe (µg/m ³)	0.063	0.862	0.234	Fe (ng/m ³)	0.101	0.968	-0.060
Fe (µg/g)	-0.003	0.771	-0.026	Fe (µg/g)	-0.166	0.931	-0.260
Ni (µg/m ³)	0.048	0.353	0.888	Ni (ng/m ³)	0.711	0.027	-0.566
Ni (µg/g)	-0.100	0.343	0.875	Ni (µg/g)	0.832	-0.134	-0.436
Pb (µg/m ³)	0.936	-0.100	-0.085	Pb (ng/m ³)	0.893	0.261	0.038
Pb (µg/g)	0.889	-0.105	-0.050	Pb (µg/g)	0.936	-0.154	0.120
V (µg/m ³)	0.077	0.121	0.960	V (ng/m ³)	0.281	-0.279	0.892
V (µg/g)	0.155	-0.252	0.910	V (µg/g)	0.287	-0.360	0.868

Extraction method: principal component analysis. Rotation method: VARIMAX with Kaiser normalization. The Guaynabo component show 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). In Fajardo, Ni and Pb and Cu negatively (first factor); PM_{2.5} levels correlating with Fe (second factor); and Cd and V highly correlated to each other (third factor).