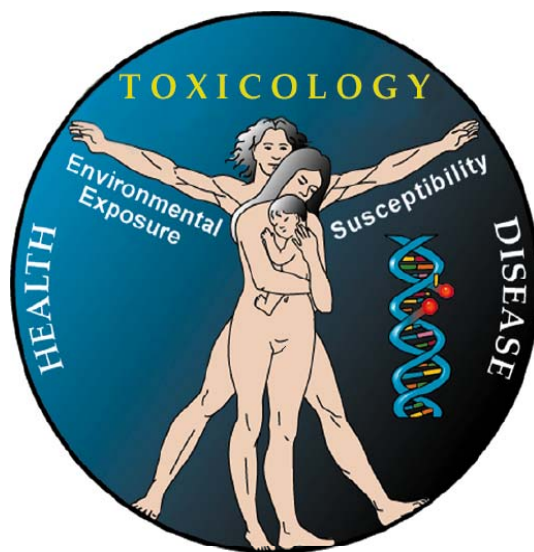


Center For Environmental and Toxicological Research
University of Puerto Rico
Medical Sciences Campus
School of Medicine



FINAL REPORT

December, 2003

Evaluating heavy metal concentrations in airborne PM₁₀ from the Jobos Bay National Estuary, at Salinas, Puerto Rico.

Through

Cooperative agreement between the University of Puerto Rico (Center for Environmental and Toxicological Research) and the Department of Environmental and Natural Resources, of Puerto Rico

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Table of Content

Introduction,.....1

Materials and Methods

Sampling,.....1

Analyses,..... 4
1.Digestion Procedure..... 4

Results and Discussion:..... 4

References:.....14

List of Figures

Figure 1. Geographical representation of sampling sites	2
Figure 2. Monthly distribution of particulate matter (PM ₁₀) in atmospheric from Salinas and Fajardo air during 2002-03.....	5
Figure 3. Fe concentration in PM ₁₀ in Salinas (solid line) and Fajardo	6
Figure 4. Total Ozone Mapping Spectrometer images of the Caribbean region during the period March 8-11, 2003.....	7
Figure 5. V and Ni concentrations in PM ₁₀ collected at Salinas and Fajardo during 02.....	9
Figure 6. As and Pb concentrations in PM ₁₀ from Salinas and Fajardo	10
Figure 7. The Cu and Cd concentration in PM ₁₀ in Salinas and Fajardo during 2002.	11
Figure 8. Correlation between trace element concentrations from Salinas and Fajardo.....	12

Introduction

The Jobos Bay Estuary is surrounded by industrial developments to the East and to the West, these energy driven activities as well as new developments that are expected to come, will continue to impact the Jobos Bay System (Jobos Bay, Puerto Rico National Estuarine Research Reserve System). The impact of the industrial influence on the Bay estuary needs to be evaluated in order to incorporate these findings to help elaborate and harmonize with the estuaries existent and or future management plan (Management Plan for the Jobos Bay, 2000). Among the relatively new industrial developments established in the vicinity of the Jobos estuary is a a 454 Mw/hr coal power plant which is located immediately to the West of Jobos Bay. This plant is currently in operation and approximately 433,000 tons of ashes have been estimated to generated as waste per year from this activity. The possible sources of any environmental impact to the system will arrive by two main avenues, water and air. It is well established that particulate matter particularly that of smaller size may contain toxic constituents (Darwin et al. 2000). Due to the lack of air quality information prevailing in the area of Salinas and its possible contributions, input and effects to the marine estuary, a study was conducted by the Center for Environmental and Toxicological Research from the University of Puerto Rico to look at the chemical constituents in airborne particulate matter PM₁₀ from the region. The results of this study are presented and summarized in this report.

Coal-fired power plants emit numerous toxic chemicals, such as **mercury, dioxins, arsenic, radionuclides** (J. P. McBride et al., 1978), **cadmium and lead**, that are known to persist in the environment and **bioaccumulate in the food chain** (Coal Combustion, Public Health and the Environment Clear the Air; Last update: May 8, 2001). We have analyzed the concentrations of various trace elements in the airborne PM₁₀ particulate matter from the Salinas area. The trace elements analyzed in airborne particulate matter were As, Pb, Cu, Fe, Ni, V and Cd. This report summarizes the data obtained from one year of sampling at the Salinas site and compares the results from air samples obtained concurrently from a reference site (Fajardo) located in the North east portion of the island (figure 1).

Materials and Methods:

Sampling

The Center for Environmental and Toxicological Research began sampling the air in Salinas (sector el Coqui) in August 2002 (figure 1) and in Fajardo (reference site). The air sampler is a Partisol Plus Model 2025 sequential PM-10 air monitor that collects airborne particles on a 47 mm Teflon filter. A reference site was also established in the northeast tip of the island at the Fajardo Lighthouse (Las Cabezas de San Juan). The samples were collected on a weekly base. The air samplers operate simultaneously at a flow rate of 16.7 L/min for 72 hours sampling period. Blank samples were placed at both stations every month. Unused clean filters, field and laboratory blanks were included in the analyses to determine possible background contamination, as a quality control measure.

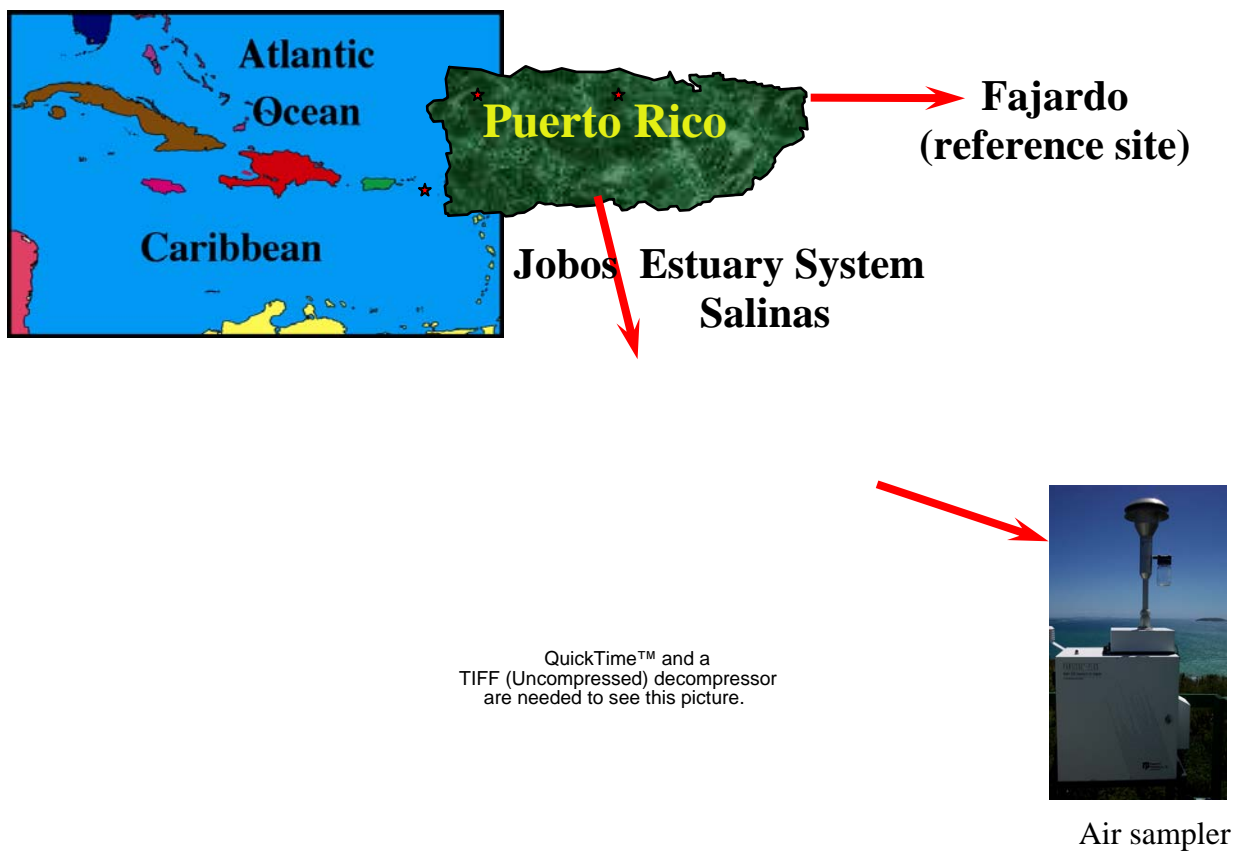


Figure 1. Geographical representation of sampling sites. Jobos Estuary system on the south coast of the island (Salinas) and the reference site (Fajardo) at the far east side of the island.

Each filter was placed and stored flat on a clean Petri dish during and after conditioning, weighting and storage. Pre-sampling and post-sampling weighting of filters were performed in an electronic microbalance with a sensitivity of six decimal points. The balance was calibrated at every weighting measurement. The unexposed and exposed filters were preconditioned under controlled temperature of $20-23\text{ }^{\circ}\text{C} \pm 2$ and relative humidity of $30-40\% \pm 5$ for 24 hrs before being weighed and analyzed. The filters were conditioned in an electric desiccator before and after collection. After humidity equilibrium, the filters were re-weighed in order to calculate the amount of PM_{10} mass on

the filter. All filters (either with samples or without sample) were weighed until a constant weight is achieved, following the USEPA methodology. Handling of filters in the laboratory includes the removal under yellow lights to prevent any photodegradation. A total of 81 filters have been obtained until May from Fajardo and Salinas (42 samples from Salinas and 39 from Fajardo) 81 field blanks were also collected. Of these 30 filters from Salinas and 29 from Fajardo were analyzed for trace metal analyses. The sampling dates of filters used for analyses and amounts of particulate matter obtained at each location is shown on Table 1.

Table 1. Sample identification for PM₁₀ particulate matter from Salinas and Fajardo.

Salinas Sample Id	Date	Weight (mg)	Fajardo Sample Id	Weight (mg)
1033408	9-12 Aug 02	2.58	1033435	2.61
1033428	14-17 Aug 02	1.65	1033448	1.64
1033437	21-24 Aug 02	1.79	2004852	0.94
2004853	4-7 Sept 02	0.97	2004875	4.13
2004857	11-14 Sept 02	4.49	2004882	4.36
2004874	25-28 Sept 02	4.30	2005658	1.41
2005668	3-6 Oct 02	3.50	2005662	0.94
2005672	16-19 Oct 02	1.01	2005693	3.07
2005677	27-30 Oct 02	3.10	2005860	1.86
2005891	9-12 Nov 02	1.33	2005874	1.13
2005895	23-26 Nov 02	1.75	2005877	0.94
2005897	30Nov-2Dec 02	1.02	2005890	1.39
2017205	7-10 Dec 02	0.89	2017214	0.83
2017217	14-17 Dec 02	0.84	2017221	2.36
2017234	21-24 Dec 02	1.12	2017922	1.73
2006903	4-7/Jan/2003	1.36	2006912	1.9
2017246	11-14/Jan/2003	1.54	2006922	2.05
2006905	25-28/Jan 2003	0.75	2006930	1.29
2006948	8-11/Feb/2003	1.08	2006949	1.72
2017913	15-18/Feb/03	1.36	2017950	1.52
2017927	22-25/Feb/03	2.03	2017933	0.96
2017948	8-11/Mar/03	1.22	2017951	1.82
2019967	15-18/Mar/03	2.19	2019960	1.69
2019969	22-25/mar/03	1.10	2019983	1.83
2019991	5-8/April/03	2.26	2019987	1.3
2019995	19-22/April/03	1.22	2019989	1.87
2019997	26-29/April/03	1.97	2019999	1.42
2037302	3-6/May/03	1.60	2037318	2.1
2037305	6-9/May/03	2.10	2037325	2.29
2037316	24-27/May/03	2.35	2037318	2.1

Analyses

1. Digestion Procedure

Filters collected were analyzed individually. Each filter was extracted by adding nitric acid and ultra pure water in a reaction vessel. Extraction was conducted on a hot plate, heated and refluxed at $90^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 2 hrs. Background contamination, was assessed by monitoring field blanks. These blanks were processed simultaneously with field samples, blank filters, spiked blanks and laboratory blanks. All samples and blanks were handled in an identical manner, and included in each individual batch digestion. The accuracy of the methods employed was evaluated using spike blanks of known metal concentration and standard reference material (Urban Particulate Matter SRM (1648), National Institute of Standards and Technology (NIST), Gaithersburg, MD; 1998), in order to calculate the recovery efficiencies. A total of 59 filters were digested and analyzed during a year, which includes the period of August 02 to May 03.

2. Measurements

Atomic absorption spectroscopy technique was employed for measurements of heavy metals. USEPA methods 7060A, 7131A, 7421 and 7740 was used for the following heavy metals analyzed: As, Cd, Cu, Fe, Pb, Ni and V.

Results and Discussion:

The distribution profile of the amount of PM_{10} material obtained at both sites is illustrated monthly in Figure 2. The average amount of PM_{10} during the summer is around $30\mu\text{g}/\text{m}^3$ reaching a peak in September and then decreasing afterwards. While studying PM_{10} it is important to consider events of dust storms and volcanic eruptions since these are possible sources of fine particles (Armienta et al. 2002). The earth probe indicating Total Ozone Mapping Spectrometer (TOMs) aerosol index obtained from satellite imaging shows a significant aerosol storm event during the month of September particularly within the dates of our collection period. This storm event with the aerosol cloud over Puerto Rico is shown within the figure Notice the amount of PM_{10} at both locations (Fajardo and Salinas) indicate a substantial increase in particulate matter. It is also interesting to observe that during April there is also a slight increase in particulate matter, however, the analysis of TOMs satellite imaging reveals a dust storm during this date that affects the south coast of the island (see figure2). The average annual PM_{10} concentration for Fajardo was $20.73\mu\text{g}/\text{m}^3$ and $22.93\mu\text{g}/\text{m}^3$ for Salinas. The amount of PM_{10} observed at both sites were very similar and no significant difference was detected between sites. Both sites were below the EPA national ambient air quality standard for PM_{10} is $50\mu\text{g}/\text{m}^3$ (annual average).

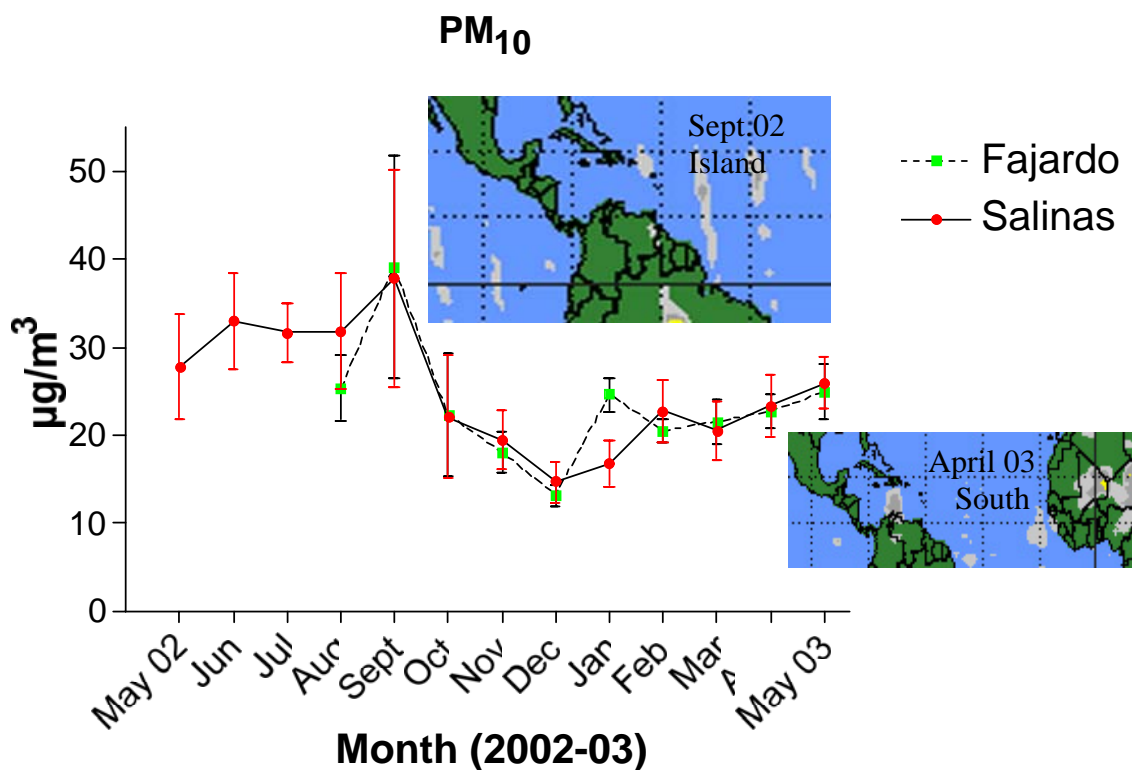


Figure 2. Monthly distribution of particulate matter (PM₁₀) in atmospheric from Salinas and Fajardo air during 2002-03. Each point on graph represents the average amount of PM₁₀ in µg/m³ obtained from three filters (n=3). The error bars illustrate the standard error of the mean. Aerosol from Sahara dust storms are shown over Puerto Rico and to the south during two periods that correlate with higher levels of PM₁₀.

Although no significant differences were observed on the average annual amount of PM₁₀ per site, significant differences were observed among metal concentrations. The best results that illustrate differences between sites throughout the island are obtained comparing concentrations of trace elements by unit mass. All our results are expressed and analyzed using this comparison.

Concurrent with the increase in airborne particulate matter PM₁₀ in September there is also a corresponding increase in Fe concentration (±30 mg/g), peaking at both sites (Figure 3) in September. This finding is in agreement with what has been previously reported. High levels of Fe associated with the Sahara desert dust storm enriching marine environments with Fe and concomitant blooming of red tide (Jason et al. 2001).

The Fe concentration in air was always slightly higher in Salinas than in the reference site, peaking in March. This high Fe concentration in Salinas during this month required a detailed examination of the data particularly during the specific dates corresponding to this dramatic increase. Initial thoughts drove us to evaluate the specific inputs of atmospheric particles from sources such as Sahara dust storms and volcanic activity.

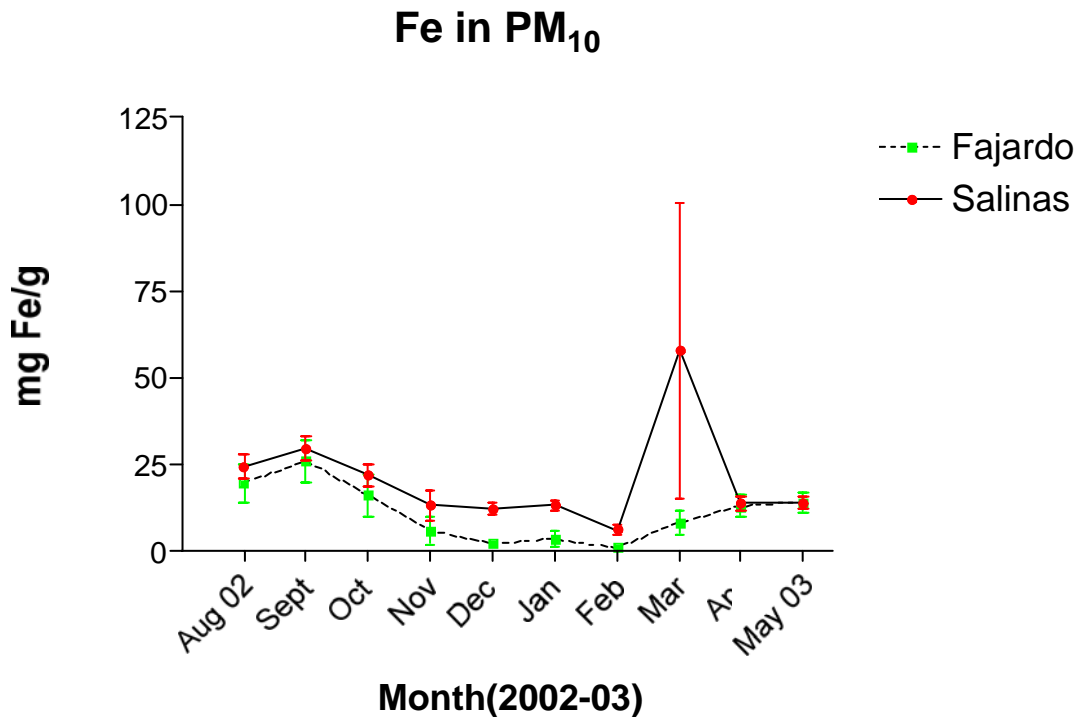


Figure 3. Fe concentration in PM₁₀ in Salinas (solid line) and Fajardo (dashed line) during 2002. Each point represents the average amount of Fe in $\mu\text{g/g}$ of PM₁₀ obtained from three filters. The error bars represent the standard error of the mean for each month.

However, this Fe increase was not correlated with dust storms or volcanic activity, during these dates (figure 4). Volcanic ashes have been reported to contain high levels of Cu, Zn, and V (Smichowski et al 2003). In addition, it was not correlated with the appearance of other elements during the same date of March 8-11, 2003. Higher levels of V were observed but at different dates during the month.

The levels of Fe in air samples were 4 fold higher than the levels normally detected during dust storms (142 vs 30 mg/g). Consequently, we conclude, that this increase in Fe concentration in air, was due to endemic inputs from other sources in the immediate region. This Fe value is the highest recorded for the entire study period at either of the sites, and represents 1.5% of the total particulate mass (PM₁₀) at that time in that station.

All of the trace elements examined during the study period (August 02 - May 03), exhibited higher averaged concentrations at the Salinas site when compared to levels at the reference site of Fajardo (see Table 2 and Figures 5-7). Concentrations for all heavy metals analyzed were higher in Salinas and values ranged from 1.6-3 folds greater than in the reference site, Fajardo. Of all of the heavy metals analyzed, the greatest differences were observed in As and Cd exhibiting 3 and 2 fold higher annual concentrations in

Sahara dust in the Caribbean during March 08-11 2003

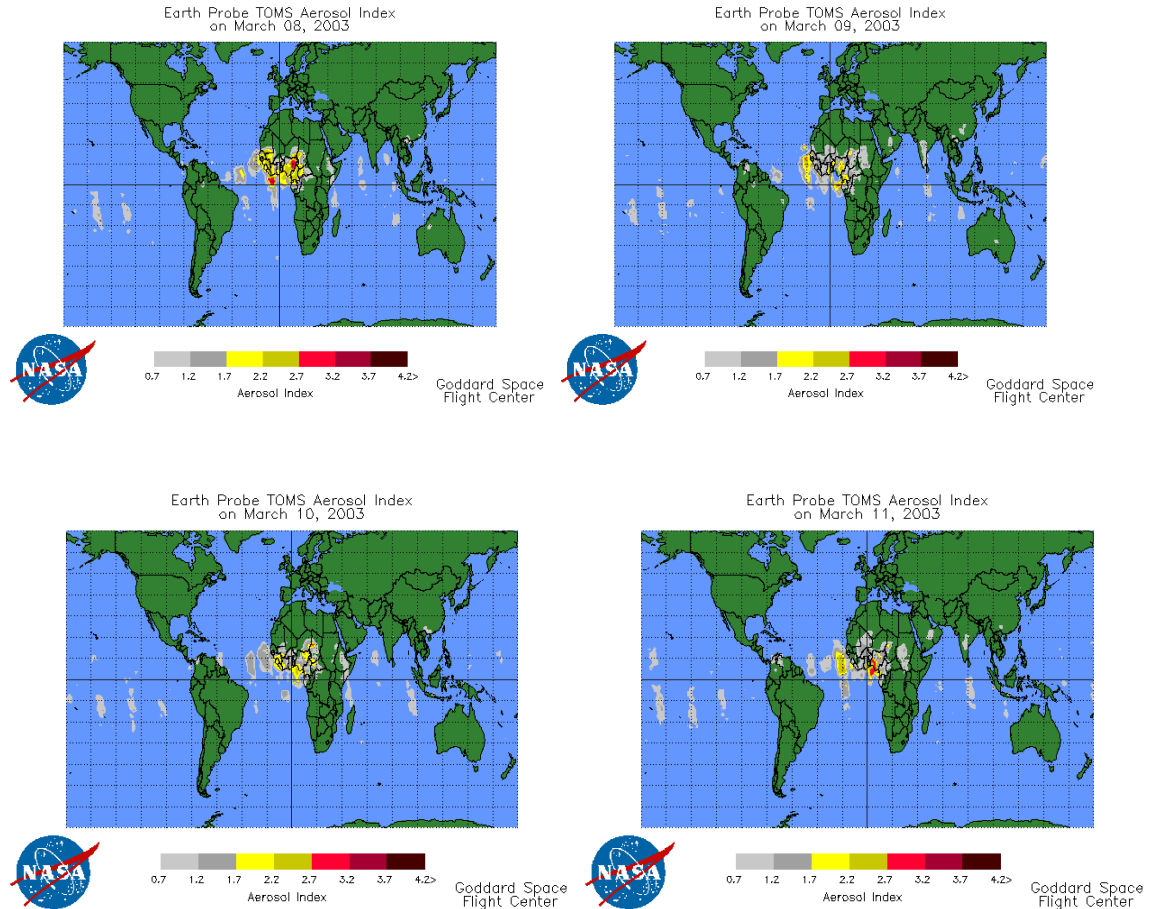


Figure 4. Total Ozone Mapping Spectrometer images of the Caribbean region during the period March 8-11, 2003. No Sahara dust storms in the Caribbean region during these dates are noticeable.

Table 2. Annual average concentration of trace elements in Salinas and in Fajardo during August 02 to May 2003.

Site	PM ₁₀ ($\mu\text{g}/\text{m}^3$)	As ($\mu\text{g}/\text{g}$)	Cd ($\mu\text{g}/\text{g}$)	Cu ($\mu\text{g}/\text{g}$)	Fe (mg/g)	Ni ($\mu\text{g}/\text{g}$)	Pb ($\mu\text{g}/\text{g}$)	V ($\mu\text{g}/\text{g}$)
Salinas	22.93	15.83	2.54	112.46	20.45	113.28	60.42	108.06
Fajardo	20.73	5.20	1.24	64.79	10.82	69.75	36.32	61.29
Fold Diff	0	3	2	1.7	1.8	1.6	1.7	1.8

Salinas. The consistent elevated levels of trace elements for this site indicates the contribution of anthropogenic sources in the atmospheric environment of Salinas.

Concentrations of V and Ni throughout the year exhibited similar patterns among themselves, particularly in Salinas (figure 5). Notice that the highest concentrations of these metals are obtained during the months of January and March (Ni) and March for (Fe and V). The maximum releases of V and Ni were found to occur on 22-25 of March 2003. No dust storms were found to pass through the island during these months. The annual average concentration for Ni at Salinas was about twice as high as that at the reference site (113 vs 69 $\mu\text{g/g}$), Average Ni concentrations as high as 225 $\mu\text{g/g}$ were detected during these months. These two elements were found to peak during the same dates in this period suggesting concurrent releases from various activities or releases from similar origin. In fact there seems to be a linear correlation between atmospheric concentrations of these elements $r=0.47$ (Figure 8).

The most striking differences in metal concentration between sites were observed between the following trace elements As, Pb, Cu and Cd (figures 6-7). As and Pb are closely correlated in Salinas and Fajardo at concentrations lower than 12 $\mu\text{g/g}$ As (figure 8). This correlation, which we have found in particulate matter from other areas in the island, is considered as the background levels in air throughout Puerto Rico. This background consists in part of marine aerosols forming over the Atlantic Ocean (Parungo et al. 1986). The highest As concentration in Fajardo throughout the year was 11.8 $\mu\text{g/g}$. However, higher concentrations (38.86 $\mu\text{g/g}$) were encountered in Salinas (figure 6). At these higher As concentrations there is no correlation or relationship between As and Pb. This suggests that at background levels (lower than 12 $\mu\text{g/g}$ of As) both As and Pb come from similar sources. The higher concentrations of As and Pb released at Salinas are due to endemic anthropogenic sources. The annual average concentration of As and Pb in the reference site is 5.2 and 36.3 $\mu\text{g/g}$ respectively, while in Salinas it is 15.8 (3 fold higher) and 60.4 $\mu\text{g/g}$ (1.7 folds). Surges of Pb releases are observed 3-4 times a year. These surges (Aug, Dec and Feb) reflect releases higher than 100 $\mu\text{g/g}$ in particulate matter. The highest average concentration of Pb in air was obtained during the month of December while As ranged from December to April 2003. The As and Pb concentrations in Salinas varied greatly within the month and this variability was considerably greater than that found in Fajardo.

Both Cu and Cd are generally increasing during the year at the Salinas site until March. Thereafter the levels begin to decrease. In Fajardo levels slightly increase until February at which time they really take off and remain elevated during March and April. To evaluate these apparent relationships we also performed a linear regression between Cu and Cd at both site. The highest concentrations of Cu were obtained in March 22-25 2003, which appear the same dates as high Ni, V, As releases in Salinas atmosphere.

Correlations between metals were evaluated at both sites (figure 8). Multiple linear regressions were performed on all of the trace elements analyzed for all metals and only four elements showed correlations (Cu vs Cd and As vs Pb). A very strong correlation was found between As and Pb as stated previously but this relationship was obtained at

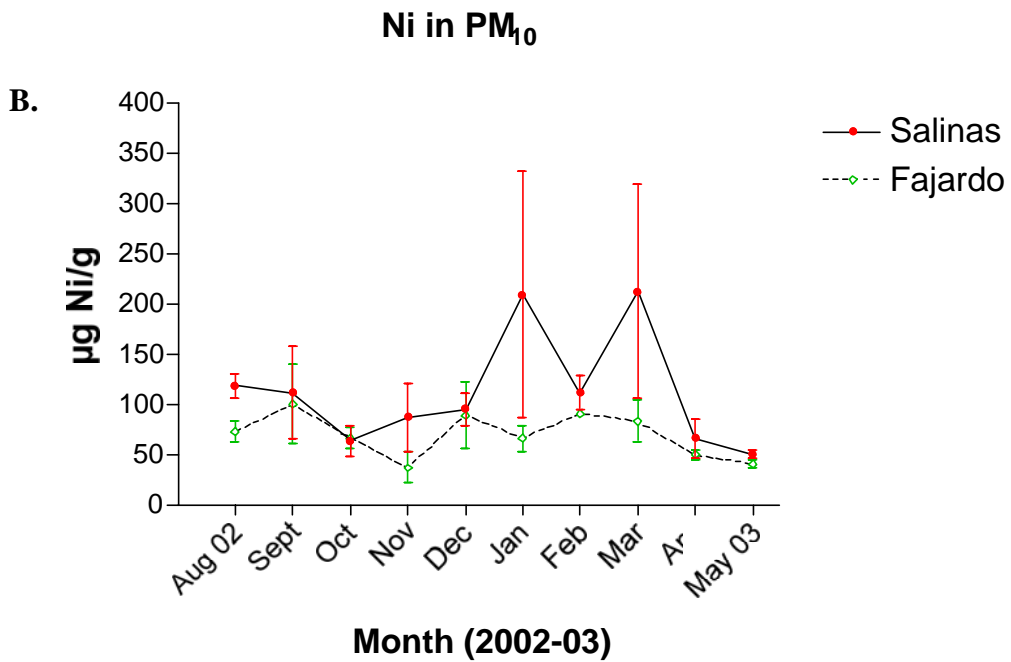
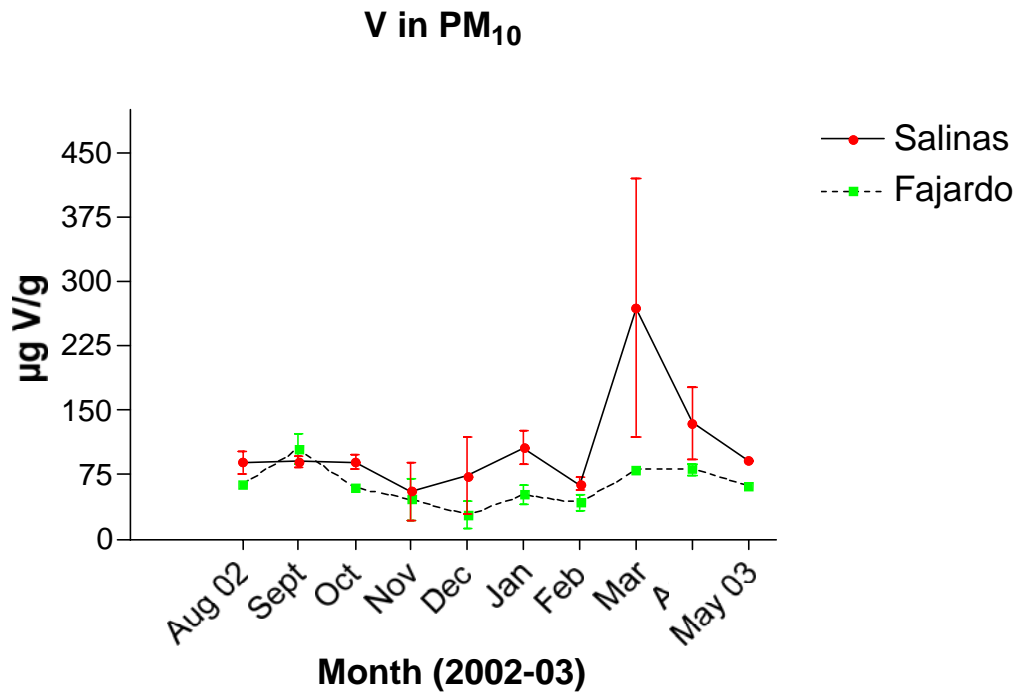
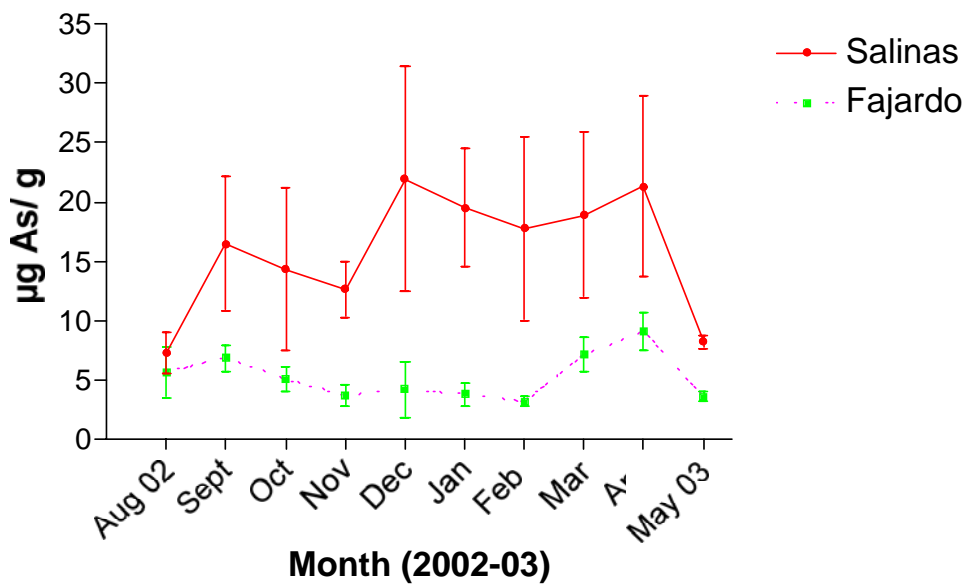


Figure 5. V and Ni concentrations in PM₁₀ collected at Salinas (solid line) and Fajardo (dashed line) during 2002-03. Each point represents the average amount of V (A) or Ni (B) in µg/g of PM₁₀ obtained from three filters collected at each site (n=3). The error bars represent the standard error of the mean for each month.

A. As in PM₁₀ from Salinas and Fajardo



B. Pb in PM₁₀

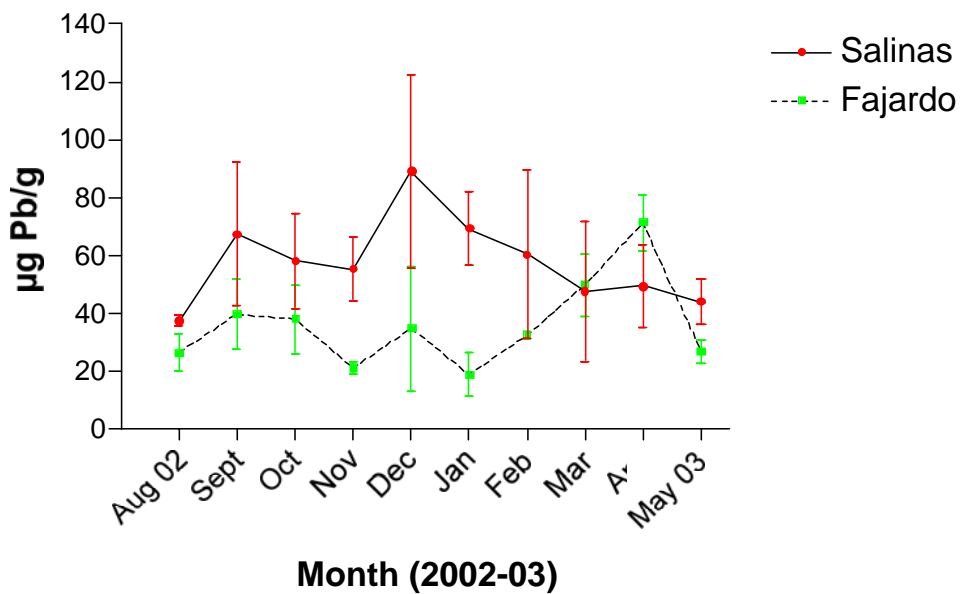


Figure 6. As and Pb concentrations in PM₁₀ from Salinas (solid line) and Fajardo (dashed line) during Aug 02 to May 2003. Each point represents the average amount of As (A) or Pb (B) in µg/g for 3 filters (n=3).

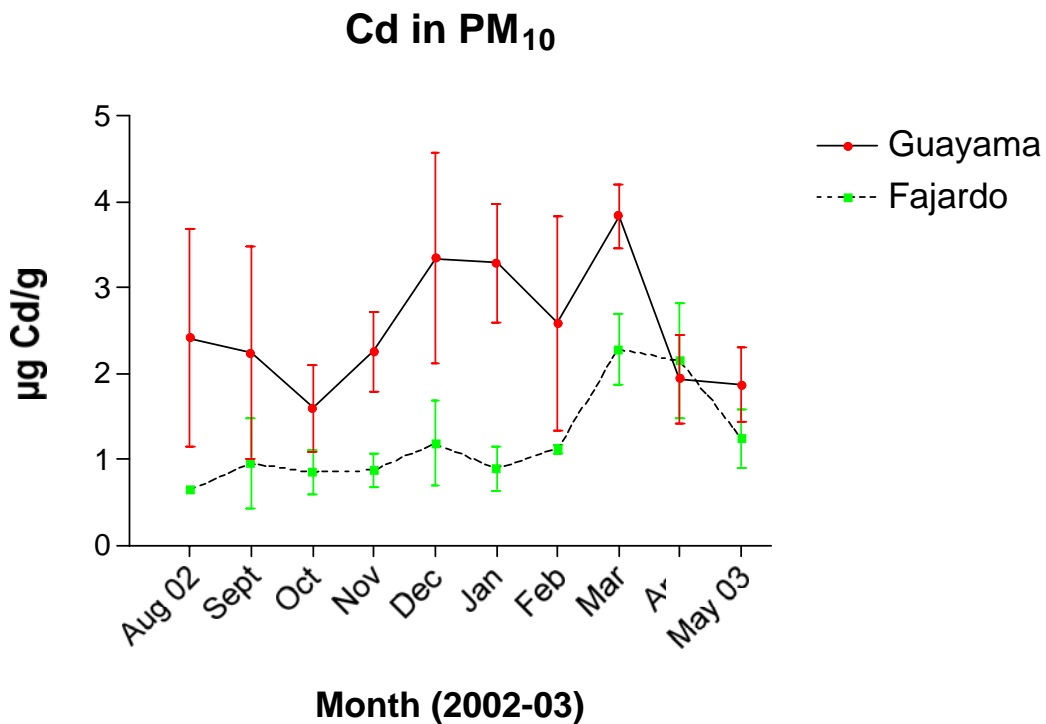
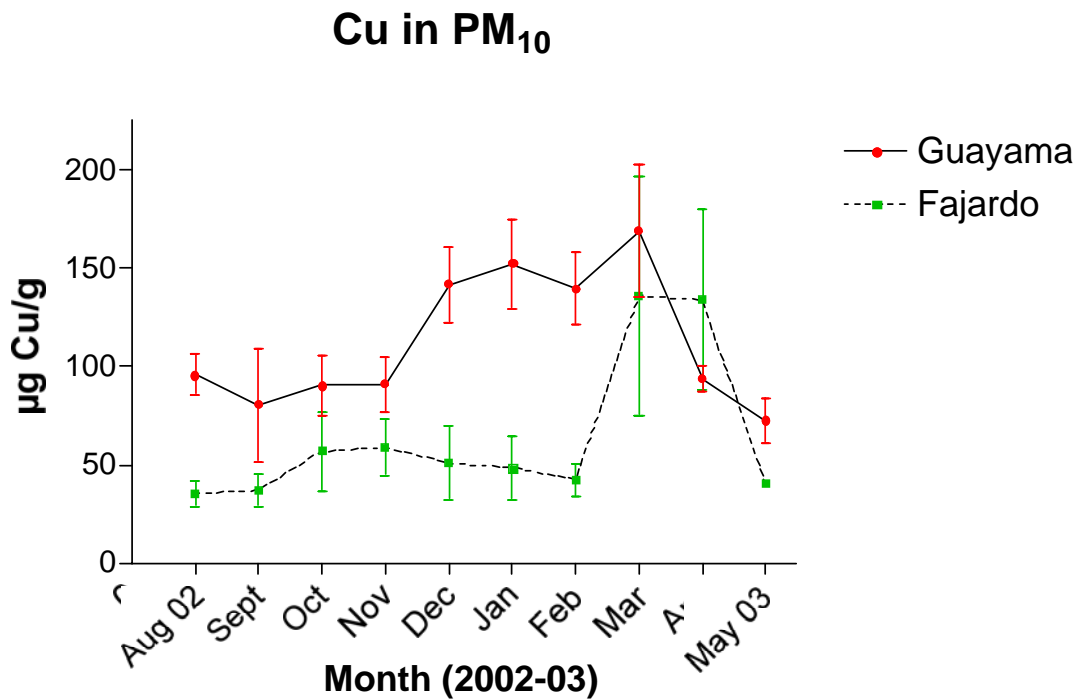


Figure 7. The Cu and Cd concentration in PM₁₀ in Salinas (solid line) and Fajardo (dashed line) during 2002. Each point represents the average amount of Cu (A) and Cd (B) in µg/g of PM₁₀ obtained from three filters at each site (n=3). The error bars represent the standard error of the mean for each month.

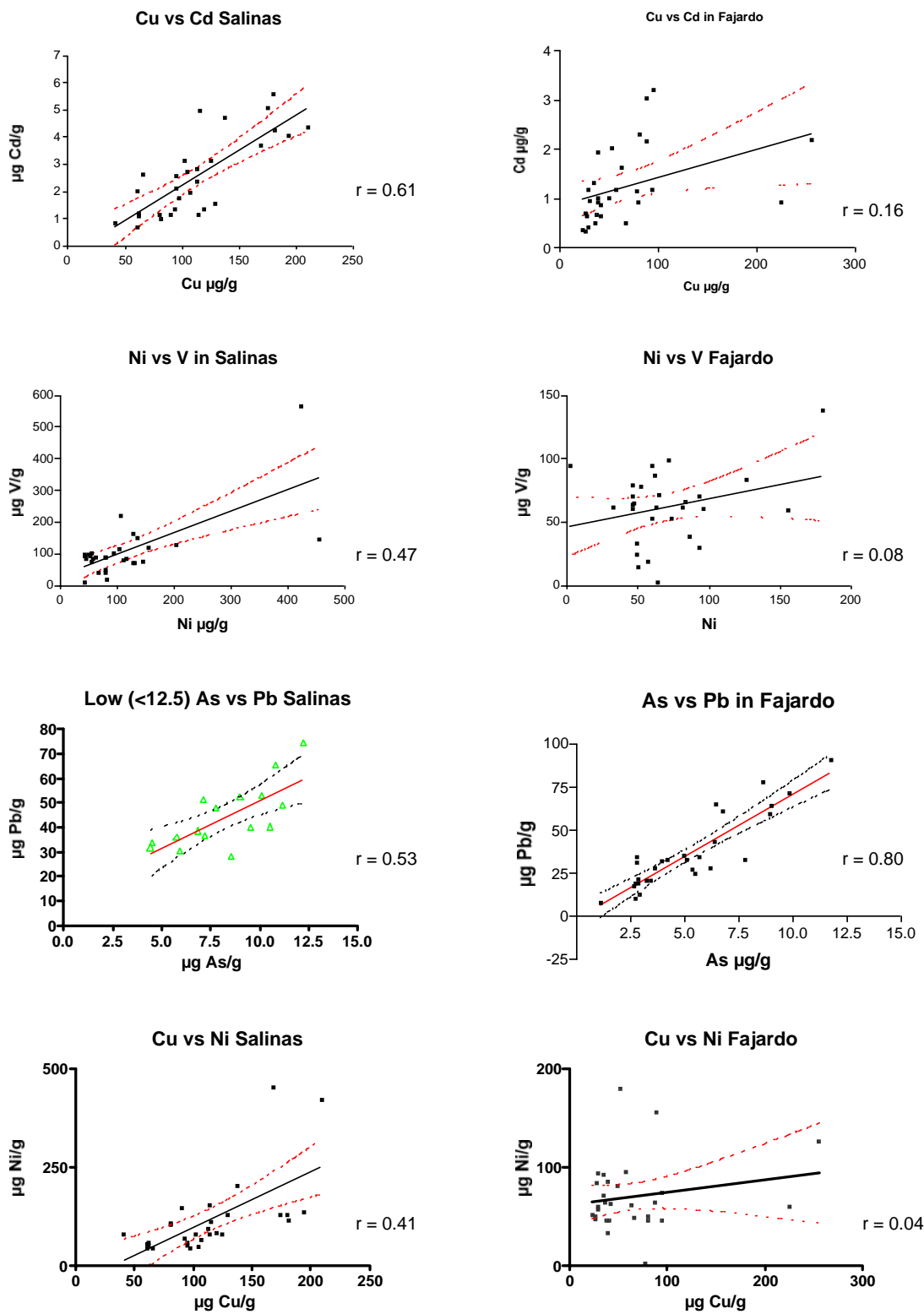


Figure 8. Correlation between concentrations of trace elements from Salinas and Fajardo. Correlation coefficients are shown on lower right for each graph (r = correlation coefficient)). Red lines correspond to the 95% confidence interval of the regression.

low As concentrations establishing basic characteristics of background of particulate matter PM₁₀ arriving to the island. The relationship between these two elements suggests that they originate from similar natural sources, probably from the mixture of marine and continental matter. This correlation, however, does not stand at higher As concentrations. Correlations between two other variables (Cu and Cd) show a relatively good relationship in Salinas (Figure 8) ($r=0.6$). The relationship between these two metals at the Fajardo site was much weaker ($r=0.15$). This indicates differences among the contributing sources at both sites. Indicating that these two metals mainly originate from a common source at the Salinas site.

This project allowed us to evaluate the PM₁₀ distribution throughout 2002-03 at Salinas and a reference site (Fajardo) in order to establish comparisons of heavy metal constituents. We have observed that the levels of most of the trace elements evaluated are consistently higher at the Salinas site. We have also been able to identify certain periods throughout the year in which considerable levels of heavy metals are released into the atmosphere of Salinas particularly Pb. It is critically important to continue this evaluation further in order to characterize further the release of heavy metals into the Salinas environment. Power plants are the number one industrial source of the air pollution responsible for ozone-smog, acid rain, global warming, deadly particulate matter, toxic mercury and a significant amount of toxic metals like beryllium, aluminum, **iron and nickel**. Other pollutants that are equally important which have not been analyzed for at these sites are radionuclide (Uranium, Thorium) and mercury. Under these conditions, there can be a loss of natural habitat and decline in the abundance of commercially and ecologically valuable fish, plants, mangrove and other aquatic life.

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