

CUBATAO AEROSOL SOURCE APPORTIONMENT STUDY

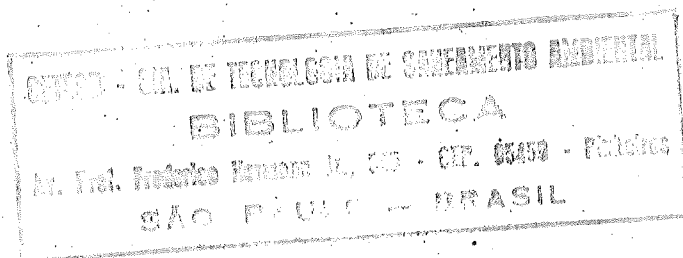
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ABSTRACT

Source contributions to fine, coarse, and total suspended particulate material in Cubatao and Vila Parisi, Brazil, were quantified by chemical mass balance receptor modeling methods. Over 250 ambient and source samples were collected in October, 1984, and analyzed by such methods as X-ray fluorescence and ion chromatography. Chemical mass balance calculations apportioned the largest source impacts to phosphate fertilizer processing sources. The results were consistent with source characteristics and meteorology.

The methods used are described and the chemical compositions of the ambient and source aerosols are presented. Source contributions at Vila Parisi are also presented and discussed.



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## INTRODUCTION

Cubatão is a heavily industrialized area located approximately forty kilometers southeast of São Paulo, Brazil. More than twenty major plants operate within a forty square kilometer area surrounding the city of Cubatão and the village of Vila Parisi. Included within this small area are petrochemical operations, an iron and steel mill, an oil refinery, gypsum and cement plants, and numerous fertilizer manufacturing plants.

The Cubatão industrial area lies on a coastal basin at the base of a major range of mountains that rise to over 800 meters to the northwest of the city. The airshed is further surrounded by mountains on the northeast and southwest with an opening to the southeast towards the coastal resort area of Santos, about ten kilometers from Cubatão. The major geographical features, as well as the locations of major plants, are illustrated in Figure 1.

The airshed's meteorology is influenced by these geographical features which cause a consistent diurnal land-sea breeze pattern with superimposed valley drainage and trade wind patterns. The winds are predominantly from the north during the night and from the south during the day with an average speed of 1.5 meters per second.

Suspended particulate levels, which are highest during winter months (May through August), frequently exceed a warning level of  $625 \mu\text{g}/\text{m}^3$ , and approximately once a year exceed an emergency level of  $875 \mu\text{g}/\text{m}^3$ .

Development of a cost-effective control strategy for the Cubatão airshed requires an accurate, quantitative understanding of source contributions to ambient particulate levels. Previous attempts to quantify source impacts focused primarily on emission inventory estimates but have been relatively ineffective due to large uncertainties in absolute emission rates and the potential for large meteorological influences.

The objective of this study was to quantify source impacts with chemical mass balance (CMB) receptor oriented source apportionment methods.<sup>1-3</sup>

## EXPERIMENTAL

### Source Impact Assessment

Source impacts were quantified with an effective-variance least squares CMB regression analysis routine.<sup>4, 5</sup> Source contributions were calculated by fitting selected source profiles to ambient chemical patterns with the least squares regression analysis. The

most probable combination of sources were selected in an iterative manner on the basis of goodness-of-fit criteria such as reduced chi square, percent of mass explained, and calculated to measured chemical mass ratios. This method requires only the relative chemical composition of a source's emissions and the chemical composition of ambient particles at a receptor sampling site.

#### Ambient Sample Collection

Day and night ambient sampling was conducted for a twenty-eight day period in October, 1984, at the downtown Cubatao and Vila Parisi monitoring sites (Figure 1). This day and night sampling schedule was selected to take advantage of the expected variability in source impacts due to strong diurnal land-sea wind patterns. Daytime samples were collected with an average start time of 10:00 AM and an average duration of nine hours, while nighttime samples were collected with an average start time of about 7:00 PM and an average duration of fifteen hours.

Each ambient monitoring site included a wind speed and direction anemometer, high-volume and low-volume TSP samplers, and two dichotomous samplers. The high-volume TSP samplers collected particles on glass fiber filters for mass and carbon measurements. The low-volume TSP samplers collected particles less than approximately 30  $\mu\text{m}$  on teflon filters for analysis of inorganic species. Each virtual impactor dichotomous sampler had an inlet particle size cut point of 15  $\mu\text{m}$  and a fine particle cut point of 2.5  $\mu\text{m}$ . At each site, one dichotomous sampler collected particles on quartz fiber filters for carbon analysis while the other sampler collected particles on teflon filters for analysis of inorganic species.

#### Source Sample Collection

Samples of emissions from major source categories based on emission inventories were collected during the same period as ambient samples. Estimated average emission rates for the major industrial source categories are listed in Table 1 along with an indication of the type of sample collected for chemical characterization. Samples representing 95% of the industrial emissions were collected and characterized using a size-segregating dilution sampler for high temperature emissions,<sup>6</sup> a non-diluting collimating sampler for low temperature emissions,<sup>7</sup> and bulk dust grab samples for process fugitive dust or low priority stack emissions.

Passive fugitive emissions such as road dust were collected with a special dust-vacuuuming sampler;<sup>7</sup> grab samples were collected to represent other passive fugitive emissions such as material handling and wind-blown dust from storage facilities. Bulk dust samples were resuspended in a laboratory dust chamber and the resulting aerosol sampled using a standard dichotomous sampler with a 15  $\mu\text{m}$  inlet.

## Sample Analysis

Net deposit mass was determined for valid high-volume TSP, low-volume TSP, and teflon fine and coarse dichotomous filters using an electrobalance and a torsion balance. Nearly 250 of the ambient and source samples collected on teflon filters were analyzed for thirty-four elements by X-ray fluorescence (XRF) analysis. A small selected subset of these samples were analyzed by ion chromatography (IC) for eight ions, inductively coupled argon plasma (ICAP) for twenty-eight elements, a pyrolytic method for elemental and organic carbon (OC/EC), and a wet chemical method for ammonium.

## RESULTS AND DISCUSSION

### Ambient Aerosol Characteristics

High-volume TSP levels observed during October, 1984, ranged from  $7 \mu\text{g}/\text{m}^3$  to  $890 \mu\text{g}/\text{m}^3$ . Highest levels were recorded at the Vila Parisi site during the night, with four samples above  $700 \mu\text{g}/\text{m}^3$  and a monthly average of  $328 \mu\text{g}/\text{m}^3$ . In contrast, only one of the day-time samples at Vila Parisi exceeded  $400 \mu\text{g}/\text{m}^3$ , and the monthly average was  $211 \mu\text{g}/\text{m}^3$ . Night and day concentrations at the Cubatao monitoring site were substantially lower, with high-volume TSP monthly averages of 103 and  $82 \mu\text{g}/\text{m}^3$ , respectively.

Average compositions for selected elements are compared in Table 2 for fine and coarse particle samples collected both during the night and day at the Vila Parisi site. Average mass levels were higher at night for both size fractions. The fine fraction mass concentrations increased at night by a factor of 1.7, while the coarse fraction increased by a factor of 1.2. Elemental concentrations generally increased at night but not by these same factors, indicating differences between day and night source impacts. Of particular note is the six-fold difference between day and night fine particle silicon concentrations.

### Source Aerosol Characteristics

Fine, coarse, and total particle profiles for thirty-three sources were developed for CMB calculations. These included a sinter plant, basic oxygen furnace, lime kiln, diammonium phosphate plant, superphosphate plant, superphosphate granulation, ammonium nitrate prill tower, oil boiler, coke cooler, carbon black reactor, cement ball mill, catalytic cracker, sodium tripolyphosphate plant, steel desulfuration, soil and road dust, phosphate rock, gypsum, blast furnace slag, sinter ore, green coke, carbon black, galvanizing, secondary sulfate, secondary organic carbon, and marine aerosol.

The major chemical characteristics of eight of the more significant sources are presented in Table 3.

## Source Impacts

Impacts for thirty sources were resolved and quantified in this study. All of these sources, however, were not resolved on each filter due to inadequate detection limits, interferences, etc. The average source impacts for the most important source categories are summarized and illustrated in Figures 2 and 3 for the fine and coarse particles collected in the day and night at Vila Parisi. The sources are grouped into the following categories:

- Road and Soil Dust
- Iron and Steel - sinter plant, basic oxygen furnace, desulfuration, sinter ore handling
- Phosphate Fertilizer - diammonium phosphate, superphosphate, superphosphate granulation
- Phosphate Rock - handling
- Calcium Sources - lime kiln, gypsum kiln, gypsum handling, cement ball mill
- Carbonaceous Sources - carbon black reactor, carbon black handling, coke kiln, coke cooler, coke handling, oil boiler, secondary organic carbon
- Sulfate - secondary sulfate, ammonium sulfate plant, sulfur handling
- Other - marine aerosol, galvanizing, transportation

The sources in the iron and steel category were combined in these summary pie charts because of their location within a common plant facility in addition to their relatively small impacts.

The profiles for the superphosphate and diammonium phosphate plants were both strongly dominated by silicon in both size fractions. A notable difference between the two was the large amount of fluoride in the superphosphate profile, whereas none was detected in the DAP plant emissions. For these two sources, silicon and fluoride would exert the most fitting pressure during CMB calculations. However, fluoride was measured on only a few ambient samples, so the sources were not always resolvable. Thus, they are combined along with superphosphate granulation in a common phosphate fertilizer group.

The profiles of the calcium sources were dominated by calcium and were not readily resolvable from each other.

The carbonaceous source category is composed of sources whose emissions are dominated by carbon species. These sources were

generally not resolved or quantified because carbon species were measured on only a few ambient samples. As a result, the average contribution determined for this source category is expected to be low, which probably accounts for much of the unexplained mass. This limitation was more pronounced in the samples collected at the downtown Cubatao monitoring site due to the presence of most of the carbonaceous sources in this area (i.e., coke kilns and coolers, coke handling, catalytic cracking).

The sulfate category is a combination of secondary sulfate, ammonium sulfate, and particulate sulfur handling emissions. In the absence of ambient IC data, these sources were not resolvable from each other. In most cases, excess sulfur was explained as a combination of these three sources.

During the day, the largest source of coarse particles was road and soil dust which accounted for 41.2% of the coarse particle mass. This source, however, accounted for only 21.5% of the nighttime coarse particle mass and 7.8% and 3.0% of the day and night fine particle mass, respectively. The fine to coarse ratio of the absolute contribution of this source both during the day and night was consistent with the low fine to coarse particle ratio observed for resuspended soil and road dust. Furthermore, the soil and road dust impacts were higher during the day than during the night by a factor of about two in both size fractions, consistent with higher traffic activity during the daytime period.

The next largest source of daytime coarse particles was the calcium source category. It accounted for 11.6% of the daytime coarse particle mass but only 8.6% of the coarse particle mass during the night. Phosphate rock and phosphate fertilizer source contributions to nighttime coarse particles, on the other hand, were both about twice as high as the calcium source. The phosphate rock impacts, like the road dust impacts, were larger in the coarse particle size fraction as expected from this source's small fine to coarse particle ratio. The CMB-calculated phosphate fertilizer source impacts were also consistent with fine to coarse particle ratios measured at the source. In this case, the fine fraction impacts were greater than the coarse fraction impacts. The phosphate rock and phosphate fertilizer source impacts were both about three and a half times greater at night than during the day.

The iron and steel impacts were higher during the day than during the night but accounted for only between 0.6% of the nighttime fine particle mass and 9% of the daytime coarse particle mass.

The average unexplained mass was highest in the daytime fine fraction, 37%, but averaged only 19% in the nighttime coarse fraction, and less than 1% in the nighttime fine fraction. The high unexplained

mass in the daytime fine particle fraction was due primarily to the inability to apportion the contribution of sources whose profiles are dominated by carbonaceous species when these species are not measured in the ambient sample. This was particularly a problem for the daytime fine fraction because carbonaceous species were measured on only one of the seven filters included in the average. The unexplained mass on the one sample for which carbonaceous species were measured, however, was only 16% when carbon species were included in the CMB fit but was 34% when the carbon species were removed from the fit, which is consistent with the observed average.

The CMB results differ considerably from the emission inventory shown in Table 1. The iron and steel category (iron ore handling, iron ore sinter plants, basic oxygen furnaces) accounted for 64% of the emission inventory, while the phosphate fertilizer industry (phosphate fertilizer processes, phosphate rock handling) accounted for 17% of the emission inventory. This is in contrast to the CMB-calculated impacts where the phosphate fertilizer industry accounted for up to 80% of the mass, while the iron and steel industry exhibited a maximum impact of 9%.

These CMB results, however, are consistent with the typical meteorology during the twenty-eight days of the study. The daytime average wind speed was 2.4 m/sec. and from the south to southwest 90% of the time, putting most of the major sources downwind of the receptor during the day. The fertilizer plants, for example, were upwind of the Vila Parisi monitoring site only 6% of the time during the day while the iron and steel sources were upwind only 1% of the time. In contrast, the fertilizer plants were directly upwind 40% of the time at night when the average wind speed was only 1.3 m/sec., and the iron and steel sources were upwind 7% of the time. These meteorological features are consistent both with the CMB-calculated relative day and night source impacts as well as the ratio of calculated fertilizer to iron and steel source impacts.

#### CONCLUSIONS

The general conclusions of the study are summarized below:

- Highest particulate levels occurred during the night at the Vila Parisi monitoring site.
- During periods of high particulate levels at Vila Parisi, the fine particle chemistry was characterized by high levels of Si and fluoride.
- The source category with the largest contributions to all particulate sizes during periods of high suspended particulate levels was the phosphate fertilizer group, composed of phosphate rock, superphosphate, diammonium phosphate, and their granulators. The impact from these sources accounted for as much as 80% of the particulate mass at Vila Parisi.

- Iron-rich emissions from the iron and steel plant were of lesser importance, accounting for less than 10% of the particulate mass at Vila Parisi and downtown Cubatao.
- The relative impacts of the fertilizer sources and iron and steel mill sources were strongly influenced by the wind direction and frequency patterns which put the Vila Parisi monitoring site downwind of the steel mill less than 5% of the time during the entire twenty-eight day study period.
- The average particulate levels at the downtown Cubatao site were less than half of those recorded at Vila Parisi.
- Road dust was the largest single explained source of coarse and total particulate at the downtown Cubatao site, accounting for 43% of the daytime TSP and 28% of the nighttime TSP.

Source control strategy during periods of excessive particulate levels should focus primarily on the phosphate fertilizer industry. If high particulate levels are noted during the day, special controls should be implemented during the night since this is typically the period of highest levels. This control strategy will be effective when meteorological conditions are similar to those observed during this study, but not as effective during extended periods of air stagnation. The source contributions during stagnation regimes were not determined in this study because of their lack of occurrence. The iron and steel mill may represent a larger portion of the problem during air stagnation conditions.

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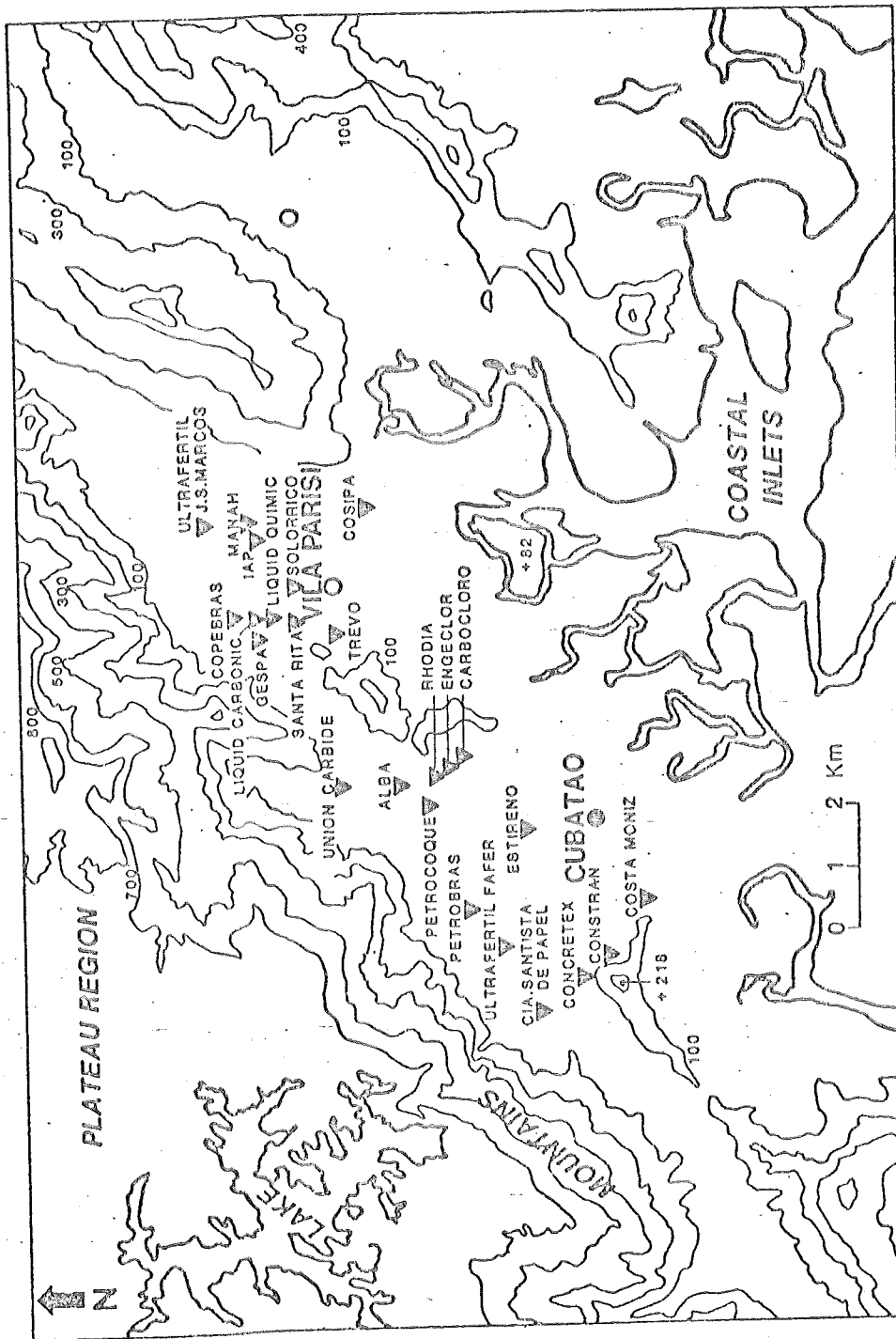


Figure 1. Map of the Cubatao airshed showing geographical features, location of the residential areas of Cubatao and Vila Parisi, and major industrial point sources.

Table 1

## CUBATAO AIRSHED INDUSTRIAL EMISSION INVENTORY AND SOURCES SAMPLED

Source Description	Average Emission (kg/day)	% of Total Inventory	Sampling Method*
Iron Ore Handling	59,435	37.7	G
Iron Ore Sinter Plants	37,417	23.7	D
Phosphate Fertilizer Processes	19,282	12.2	D, C, G
Coke Ovens, Kilns and Coolers	11,879	7.5	D, G
Lime Kilns, Gypsum and Cement Processes	11,133	7.1	D, C, G
Phosphate Rock Handling	6,658	4.2	G
Iron Tapping, Slag Pouring, Scarfing, etc.	2,680	1.7	-
Basic Oxygen Furnaces	2,295	1.5	C
Miscellaneous Industrial Combustion	1,330	0.8	-
Catalytic Cracker	976	0.6	G
NH <sub>4</sub> NO <sub>3</sub> Prill Tower	965	0.6	C
Boilers, Furnaces, etc.	488	0.3	D
Carbon Black Processes	312	0.2	D, G

\* D = Dilution Sampling

C = Collimating Sampling

G = Grab Sampling

Table 2

SUMMARY OF AVERAGE AMBIENT ELEMENTAL  
COMPOSITIONS AT THE VILA PARISI SITE DURING OCTOBER, 1984

	Daytime $\mu\text{g}/\text{m}^3$		Nighttime $\mu\text{g}/\text{m}^3$	
	Fine	Coarse	Fine	Coarse
Al	0.55	5.2	0.90	4.0
Si	2.6	12.7	15.0	14.1
P	0.30	1.5	1.1	4.9
S	3.3	2.9	3.6	4.9
Cl	0.97	1.9	3.0	3.2
K	0.36	1.1	0.33	1.4
Ca	0.71	13.3	1.8	16.0
Ti	0.02	0.39	0.05	0.49
V	0.01	0.04	0.04	0.08
Mn	0.04	0.35	0.05	0.24
Fe	0.75	7.8	0.90	6.5
Zn	0.07	0.07	0.01	0.01
Br	0.01	0.01	0.01	0.01
Pb	0.05	0.15	0.04	0.07
Mass	46.2	126	80.7	148

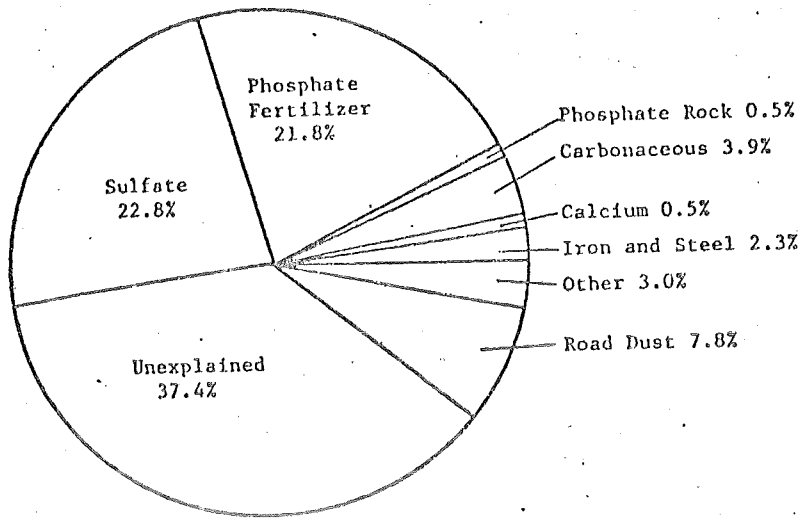
Table 3

MAJOR CHARACTERISTICS OF SOME CUBATAO SOURCES  
(% COMPOSITION)

	Vila Parisi Road Dust		Phosphate Rock		Lime Kiln		Superphosphate Fertilizer		Diammonium Phosphate		Sinter Plant		Basic Oxygen Furnace		Coke Cooler	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Al	10.2	8.0	2.5	2.1	1.1	0.77	0.57	1.5	1.1	3.6	2.2	5.6	0.38	0.21	0.17	0.17
Si	19.0	16.1	3.3	2.5	1.8	1.3	26.6	64.8	25.8	39.4	3.7	7.4	1.5	0.30	0.17	0.17
P	2.2	1.1	11.2	9.5	0.23	0.09	0.07	0.35	0.73	4.5	0.59	0.73	0.22	0.14	0.08	0.08
S	2.5	1.8	1.3	0.88	7.5	3.8	0.14	0.52	4.7	5.3	6.5	3.4	1.5	1.5	0.70	0.70
Cl	1.7	1.4	0.36	0.41	0.44	0.29	1.3	3.7	5.9	4.3	15.4	2.1	1.8	0.07	< 0.01	< 0.01
K	2.1	2.1	0.37	0.20	1.8	0.17	< 0.01	0.01	0.60	2.1	16.3	3.1	2.8	0.06	0.01	0.01
Ca	9.4	8.6	19.9	22.9	22.6	26.7	0.08	0.32	0.62	6.5	1.6	11.4	0.93	0.16	0.05	0.05
Li	0.37	0.41	1.1	0.84	0.03	0.04	< 0.01	0.02	0.02	0.20	0.11	0.33	0.38	0.01	< 0.01	< 0.01
V	0.02	0.02	0.14	0.10	0.01	0.01	< 0.01	< 0.01	0.04	0.04	0.02	0.06	0.09	0.10	0.05	0.05
Mn	0.19	0.17	0.33	0.19	0.24	0.20	< 0.01	< 0.01	0.02	0.15	0.28	1.1	2.1	0.01	< 0.01	< 0.01
Fe	3.0	4.1	7.6	4.2	1.9	1.6	0.03	0.04	0.93	3.6	4.2	24.0	50.1	0.33	0.21	0.21
Zn	0.09	0.06	0.09	0.05	0.01	0.01	< 0.01	< 0.01	0.10	0.09	0.05	0.02	0.06	0.01	< 0.01	< 0.01
Br	0.01	0.01	0.02	0.01	0.01	< 0.01	0.01	0.02	0.02	< 0.01	0.79	0.05	0.02	0.02	< 0.01	< 0.01
Pb	0.06	0.04	0.14	0.03	0.04	0.02	0.01	0.01	0.08	0.19	2.6	0.24	0.08	0.01	< 0.01	< 0.01
OC	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	3.3	1.3	1.3
EC	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	73.9	94.7	94.7
P	NA	NA	NA	NA	NA	NA	52.9	NA	< 0.01	NA	NA	NA	NA	NA	NA	NA
Fine to Coarse Ratio		0.06		0.11		0.33		4.0		4.5		2.0	-		0.39	

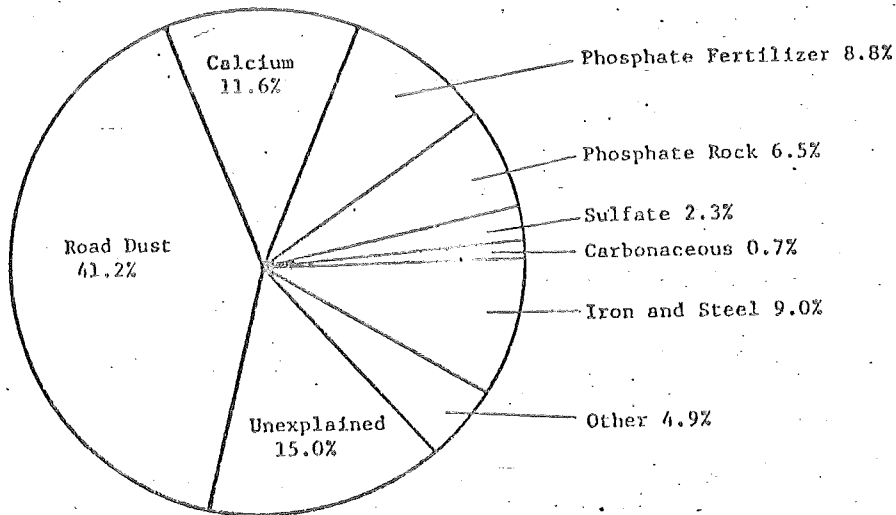
NA: Not analyzed.

FINE FRACTION



Number of Samples = 7  
 Average Mass = 63.2  $\mu\text{g}/\text{m}^3$   
 Average Chi-squared = 2.0

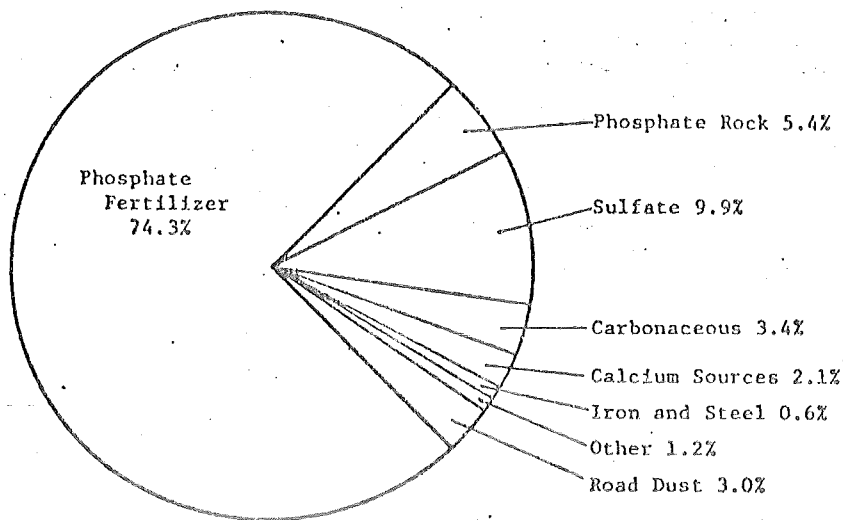
COARSE FRACTION



Number of Samples = 7  
 Average Mass = 142.2  $\mu\text{g}/\text{m}^3$   
 Average Chi-squared = 2.3

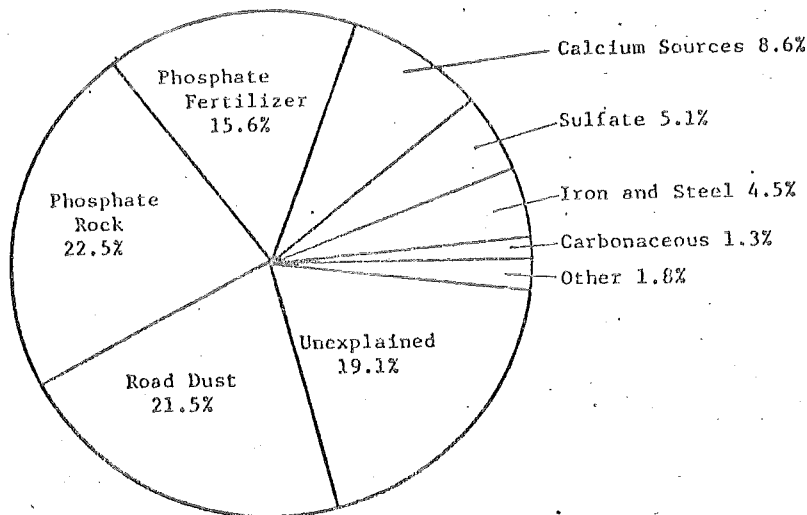
Figure 2. Average CMB results for daytime samples collected at the Vila Parisi Site.

FINE FRACTION



Number of Samples = 10  
 Average Mass = 100.9  $\mu\text{g}/\text{m}^3$   
 Average Chi-squared = 1.9

COARSE FRACTION



Number of Samples = 10  
 Average Mass = 179.9  $\mu\text{g}/\text{m}^3$   
 Average Chi-squared = 1.3

Figure 3. Average CMB results for nighttime samples collected at the Vila Parisi Site.

25/07/85

Nome:

Libertad:

Preço: Cr\$ 4,00

Data Tombe: 25/07/85