

Atmospheric Concentration of Metals and Total Suspended Particulates in Rio de Janeiro

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■ Total suspended particulates (TSP) and metal concentrations were determined from August, 1975, to April, 1978, in two districts of Rio de Janeiro with different sources of airborne particulate matter. In both districts the TSP annual geometric means ranged around $100 \mu\text{g}/\text{m}^3$, well above the Brazilian standard of $80 \mu\text{g}/\text{m}^3$. High concentrations of V, Ni, Fe, Mn, Cr, and Zn were found in São Cristóvão, an industrial area, and NaCl accounted for 21% of TSP in Copacabana, along the seashore. A seasonal variation was observed for concentrations of TSP and most metals mainly for São Cristóvão, with peaks from May to August. Significant correlations between TSP and metal concentrations indicate that this seasonality was caused by common meteorological conditions. The apartment house garbage incineration ban did not produce any decrease in TSP concentration, although drops were observed for Cd and Cr contents. Variations in Pb concentrations are related to the amount of lead added to the gasoline consumed in the city.

Introduction

Rio de Janeiro, on the Atlantic coast, is the second largest city of Brazil, with seven million inhabitants distributed over 330 km^2 .

High levels of atmospheric pollution are present in Rio de Janeiro, originated from different sources such as traffic of motor vehicles employing gasoline and diesel engines, industries, building and road construction, stone quarries, garbage incineration, and sea spray.

Because of the socioeconomical problems of a developing country, controlling air pollution in Brazil is a very difficult task. A few groups, however, have been working to assess the present air pollution situation in the main cities of the country.

Total suspended particulate (TSP) measurements performed by FEEMA (1) in several districts of Rio de Janeiro showed very high values especially in Copacabana and São Cristóvão (Figure 1).

Despite its effect on visibility, human health, and soiling materials, very little has been done to determine the chemical composition of this particulate matter. Concentrations of several elements in spot sampling points throughout the city determined by Hotchandani (2) presented extremely high results, especially for Pb ($5 \mu\text{g}/\text{m}^3$) and S ($9 \mu\text{g}/\text{m}^3$) in Bonsucesso district ($\sim 8 \text{ km}$ north of São Cristóvão). It is known, however, that lead concentrations can vary greatly with elevation and/or with distance from the road (3, 4).

In this study concentrations of TSP and eleven metals (Pb, Cu, Cd, Cr, Mn, Ni, Fe, K, V, Zn, and Na) were determined weekly from August, 1975, to April, 1978, in Copacabana and São Cristóvão. Copacabana, a residential area along the seashore, is very influenced by sea spray and garbage incineration, and São Cristóvão, behind a mountain range, is a highly industrialized and commercial area. Both are affected by heavy traffic of motor vehicles. Since the samples were continuously collected for 1-week periods, on the top of buildings in open

spaces, these results are representative of large areas around the sampling stations and of a small size range of particulates which are carried up by air movements. The levels of atmospheric pollution are compared for the two different regions in Rio de Janeiro and other areas in the world as well. The seasonal variation of TSP and each metal concentration are also analyzed according to our previous knowledge of the conditions of atmospheric dispersion in Rio de Janeiro (5). The relative contributions of different emission sources of particulates are also discussed on the basis of the concentrations of some elements chosen as tracers: Na for ocean spray, V for industrial activities (since no space heating is necessary in Rio de Janeiro), and Pb for automobile exhaust (6, 7). Cd was chosen for apartment-house incinerators on the basis of an analysis of samples collected at the incinerator outlets.

In April, 1977, apartment-house garbage incineration was forbidden by law in the city of Rio de Janeiro. The effect of this policy on improving the air quality is evaluated on the basis of the annual mean concentration of TSP and trace metals before and after this event.

Methods and Materials

Samples of total suspended particulates were continuously collected from August, 1975, to April, 1978, in two sites in the urban area of Rio de Janeiro.

The samplers (8) maintained a constant flow rate of $27 \text{ m}^3/\text{h}$ during the 1-week sampling period, and Gelman glass fiber filters were used for most of the samples. A few were collected on Delbag microsorban-type filters to allow the determination of the sodium content in the particulate matter. The samplers were designed to collect particles smaller than $30 \mu\text{m}$.

The two sampling sites, 15 km apart, were separated by a mountain range: site 1, in Copacabana, 40 m above the ground and $\sim 100 \text{ m}$ from the ocean; site 2, in São Cristóvão, 10 m above the ground and $\sim 200 \text{ m}$ from the city's busiest highway.

The samples were digested in a $\text{HNO}_3\text{--HClO}_4$ mixture and analyzed by atomic absorption spectroscopy for the 11 elements of interest (8). Most samples were analyzed three times.

For some metals, such as K, V, Cr, and Ni, the results presented poor reproducibility; the pair of results closer to each other were taken to calculate the average.

Just before the apartment-house garbage incinerators were shut down in Rio de Janeiro, two samples were collected at the incinerator outlets of a residential and a commercial building. High-volume samplers and Gelman glass fiber filters were used. The volume of air sampled was not determined so that the results for metal concentrations were calculated in $\mu\text{g}/\text{g}$ of particulates.

Results and Discussion

Levels of Metals and TSP in Rio de Janeiro. The TSP and metal concentrations followed a log normal distribution. The geometric means and standard deviations for the 2-yr

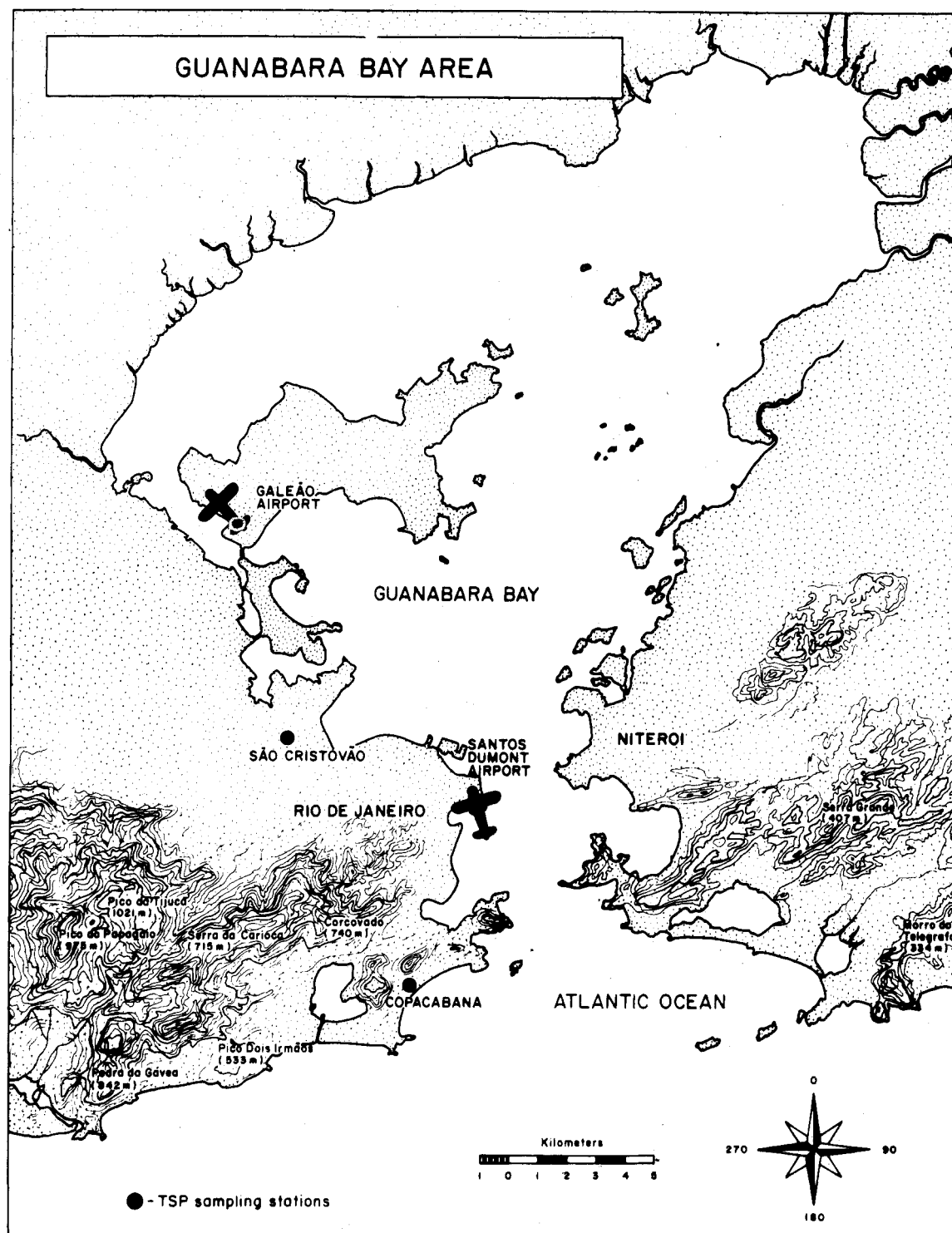


Figure 1. Map of Guanabara Bay Area.

period (April, 1976, to March, 1978) are presented in Table I for the two regions studied in the city of Rio de Janeiro: Copacabana and São Cristóvão. Provided for comparison are concentrations of the same elements found elsewhere: New York (7); Tel Aviv (9); the South Pole (10), an unpolluted area; and the North Atlantic (11), where pollution originates from remote sources.

Trace-metal levels of anthropogenic origin like Pb, Cu, V, Ni, and Cd are higher in New York than in Rio de Janeiro. On the other hand, Rio presents very high levels of Na, K, Fe, and Mn mainly from natural sources (sea spray and soil particulates). A large contribution of these sources and a high content of organic matter may explain the higher values of TSP found in Rio relative to New York.

Although the levels of TSP are similar in both regions, in Rio de Janeiro, the São Cristóvão district is more affected by industrial sources of pollutants, resulting in higher levels of most metals analyzed: V and Ni from oil burning in industrial boilers and furnaces; Fe, Mn, Cr, Cd, Cu, and Zn from metallurgical and electroplating industries.

The similar lead contents for the two districts show that the traffic of automobiles has an equivalent contribution to the total suspended particulate matter in both areas.

Copacabana presents a sodium content 4 times higher than São Cristóvão, resulting from sea spray.

If one assumes that all the Na in the samples is present as NaCl (valid for Copacabana where the sampling station was located 100 m from the seashore), it accounts for 21% of the

Table I. Metal and TSP Concentrations (ng/m³) in Rio de Janeiro Compared to Other Regions

metals	Rio de Janeiro ^a		New York	Tel-Aviv	North Atlantic (range)	South Pole
	Copacabana	S. Cristovão				
Pb	499 ± 1.8	518 ± 1.7	1074	370	0.1–64	0.63
Cu	18.0 ± 1.4	24.9 ± 1.5	43.9		0.12–10	0.0008
V	11.7 ± 1.7	30.6 ± 1.4	38.8	50	0.06–14	0.0015
Ni	7.6 ± 1.6	15.9 ± 1.5	35.2	70		
K	1028 ± 1.7	1504 ± 1.6	99			0.3
Fe	1231 ± 1.6	2467 ± 1.5	1012	2830	3.4–220	0.84
Mn	23.1 ± 1.7	54.8 ± 1.5	19.7	220	0.05–5.4	0.01
Cd	1.8 ± 2.0	3.1 ± 1.6	4.1	40	0.003–0.6	
Cr	14.3 ± 2.2	21.6 ± 1.8	8.5		0.07–1.1	0.005
Zn	145 ± 1.6	298 ± 1.7	293		0.3–27	0.03
Na	8541 ± 1.4	2160 ± 1.5	813			7.2
TSP	(104 ± 1.4) × 10 ³	(103 ± 1.5) × 10 ³	52.5 × 10 ³	260 × 10 ³		

^a Geometric mean and standard deviation.

Table II. Trace Metal Concentrations (μg/g) in Particulate Matter Emitted by Incinerators Compared with Atmospheric Concentrations

metal	Incinerators		atmosphere (range)
	residential building	commercial building	
Pb	411	1362	1007–12434
Cu	127	759	72.8–275
K	8462	6016	1526–23524
Ni	12.3	50.9	26.1–109
V	6.8	65.9	14.3–235
Fe	599	2569	4211–15410
Mn	37.9	146	42.8–488
Cd	319	58.4	1.9–44.1
Zn	2566	2769	517–4320
Cr	33.7	2578	11.2–1027

particulate matter in Copacabana and 5% in São Cristovão. Other ions such as Mg²⁺, SO₄²⁻, etc., were neglected since their concentrations in seawater are 1 order of magnitude lower than Na⁺ and Cl⁻ (12).

Garbage Incineration and the Concentrations of Trace Metals and TSP. Table II presents the results obtained for two samples collected directly at the incinerator outlets of a residential building burning food waste, packaging materials, etc., and a commercial building burning mainly paper, fabrics, and news print. The results are given in μg/g of particulate matter since the volume of air filtered was not measured. For the commercial building Cu, Cd, and Cr were found in concentrations much higher than those observed in the atmosphere in the same region. Cd content was extremely high for the residential building, resulting from burning of plastic containers.

The annual geometric means of the atmospheric concentrations of TSP and trace metals were calculated for each year before and after the garbage incinerators were banned. The results are presented in Table III for the two districts studied.

A decrease in concentrations of Pb, Cd, and Cr from one year to the other is observed for Copacabana, where there was a higher density of apartment-house incinerators. There were 1695 incinerators in Copacabana vs. 235 in São Cristovão. The drops in Cd and Cr concentrations are explained on the basis of the measurements performed at the stacks of the incinerators (Table II). The decrease in Pb concentration in both

Table III. TSP and Metal Concentrations (Geometric Means in ng/m³) Before and After the Incinerator Ban

metal	Copacabana		São Cristovão	
	with incineration	without incineration	with incineration	without incineration
Pb	572	391	582	451
Cu	17.4	19.2	25.7	23.9
V	11.2	13.2	28.5	34.3
K	1043	1006	1666	1318
Ni	7.4	8.2	16.8	14.8
Fe	1191	1304	2533	2387
Mn	20.0	29.7	53.7	56.3
Cd	2.1	1.4	3.0	3.2
Na	8949	7513	1806	2493
Cr	18.4	8.6	29.5	15.3
Zn	154	134	315	285
TSP	97.6 × 10 ³	117 × 10 ³	101 × 10 ³	105 × 10 ³

districts is due to changes in the lead content of the gasoline, as will be shown later in this paper.

The average concentrations of TSP and the other trace elements (Cu, V, K, Ni, Fe, and Mn) did not decline substantially, and in Copacabana they were even higher for the year after incinerators were shut down. This shows either that this source did not contribute significantly to the particulate matter concentration in the atmosphere or that an increase in human activities made it impossible to observe the effect of the incinerator ban.

When TSP concentrations were normalized for constant meteorological conditions (5, 13), a slight decrease in TSP was observed for the first 6 months after the incinerators were banned. This trend however was overcome by an increase of TSP in the following semester leading to a high annual average.

Seasonal Variations of Trace-Metal Concentration. Figure 2 shows a regular seasonal variation of TSP both in São Cristovão and in Copacabana. Peaks of concentration occurred from May to August for both years. This variation proved to be inversely proportional to dispersion factor, defined as the product of the daily average surface wind speed and the mixing depth (5).

The 33 months covered in this study were divided into five periods, and the geometric means of TSP and metal concentrations for each period are presented in Figure 3 for Copacabana and São Cristovão.

The expected pattern with high concentrations for periods

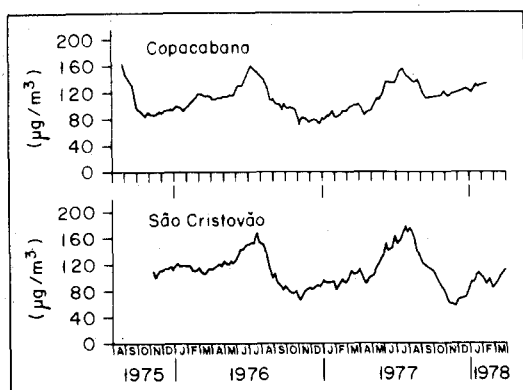


Figure 2. Total suspended particulates (TSP).

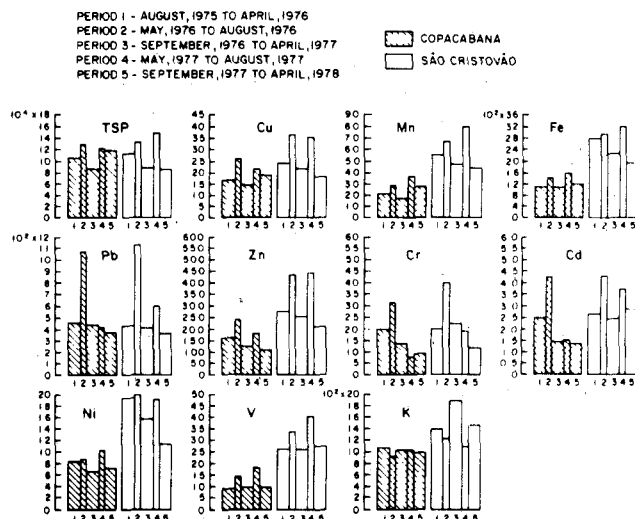


Figure 3. Seasonal variations of TSP and metal concentrations in two areas of Rio de Janeiro (ng/m^3).

2 and 4 and lower values for periods 1, 3, and 5 was observed in São Cristóvão for TSP and most metals: V, Cd, Mn, Pb, Zn, and Cu. Other metals such as Fe and Ni presented concentrations in period 1 higher than expected.

In Copacabana, the variations were not so uniform. The standard pattern was observed only for V, Mn, Fe, and Zn. TSP and Cu presented high averages for period 5, which cannot be explained either by a sudden increase in human activities or by an abnormal prevalence of unfavorable dispersion conditions which would be reflected in higher levels of the other trace metals in this same period.

As it was said before, the sharp decrease in Cd and Cr concentration in Copacabana during periods 4 and 5 is probably due to the discontinuing of incineration. However, an equivalent decrease in Cr in São Cristóvão is also observed which must have been caused by interferences from electroplating, leather tanning, and pigment industries releasing Cr in this area (14, 15).

The potassium concentrations followed a unique pattern in both sites. It should be noted here that this element is very difficult to determine in the presence of high blank values of the glass fiber filters. The averages presented involve lower number of samples and may not be representative of the whole period. K is also associated with soil dust, construction, and other sources of large-size particulates which have a different behavior in the atmosphere compared with the small-size particulates associated with other elements such as Zn, Cd, Pb, V, Ni, etc.

The variation of Pb concentrations in the atmosphere are due to changes in the lead content of the gasoline since the

PERIOD 1 - AUGUST, 1975 TO APRIL, 1976
PERIOD 2 - MAY, 1976 TO AUGUST, 1976
PERIOD 3 - SEPTEMBER, 1976 TO APRIL, 1977
PERIOD 4 - MAY, 1977 TO AUGUST, 1977
PERIOD 5 - SEPTEMBER, 1977 TO ABRIL, 1978

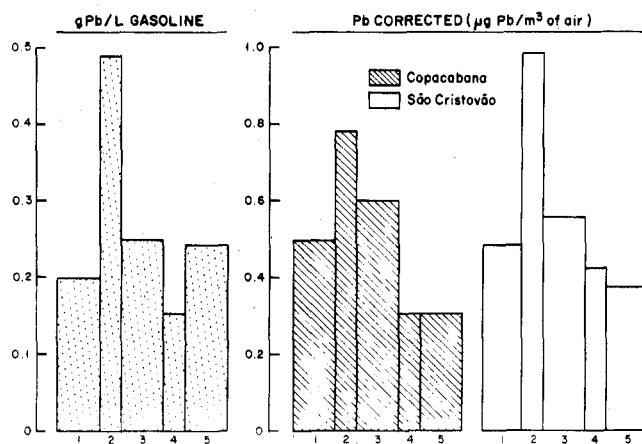


Figure 4. Lead content in the gasoline compared with "corrected" concentrations of lead in the atmosphere of Copacabana and São Cristóvão.

tetraethyllead added to the gasoline varies from batch to batch (16). Practically only the regular-type gasoline produced by Petrobrás was consumed in Rio de Janeiro during this period.

Figure 4 shows a close relationship between the average concentrations of Pb per liter of gasoline for the different seasons and the "corrected" concentrations of Pb (Pb_{cor}) in the atmosphere of Copacabana and São Cristóvão. According to Kleinman (13) the Pb_{cor} calculated as

$$\text{Pb}_{\text{cor } i} = (\text{Pb}_i)(\text{DF}_i)/(\overline{\text{DF}})$$

where $\text{Pb}_{\text{cor } i}$ = "corrected" Pb concentration, Pb_i = atmospheric concentration of Pb for week i , DF_i = average dispersion factor for week i , and $\overline{\text{DF}}$ = average dispersion factor for a 2-yr period, reflects the variations of emission intensities for constant atmospheric dispersion conditions.

Correlation Study. Tables IV and V present the correlation coefficients between each pair of parameters including metal concentrations, total suspended particulates (TSP), and dispersion factor (DF) for Copacabana and São Cristóvão.

The following points should be emphasized from these results. (1) With a few exceptions most metal concentrations correlate significantly with each other and with TSP, showing an inverse relationship with dispersion factor. (2) In Copacabana Na was found to be directly correlated to dispersion factor, indicating that the concentration of this metal grows under unstable atmospheric conditions probably due to sea activity. (3) No correlation was found between Na and the other metals, showing that it comes from an independent source, the sea spray. The same was observed with K in São Cristóvão, which probably comes from construction works and dust from unpaved roads, since this element is a main constituent of rocks and soil dust (17). The larger particle size of the particles generated by mechanical means may account for this difference in behavior for these two elements. (4) The high correlation coefficients between Ni and V, Fe and Mn, and Cd and Cu indicate that one source exists for each pair of these elements: oil combustion, soil dust, and incineration, respectively (6, 7).

General Conclusions

(1) TSP concentrations in both areas studied in Rio de Janeiro varied around $100 \mu\text{g}/\text{m}^3$, well above the maximum recommended by the Brazilian air quality standards ($80 \mu\text{g}/\text{m}^3$). The trace metals from anthropogenic sources were

Table IV. Correlation Coefficients between Concentrations of Metals, TSP, and Dispersion Factor in Copacabana

	Pb	Cu	K	V	Ni	Fe	Mn	Cd	Na	Cr	Zn	TSP	DF
Pb	1.000	0.537	a	0.326	0.306	0.214	a	0.649	a	0.496	0.416	0.349	-0.280
Cu		1.000	0.303	0.596	0.547	0.525	0.689	0.603	a	0.372	0.555	0.660	-0.454
K			1.000	0.314	0.397	0.290	0.282	0.239	-0.617	0.222	0.239	0.202	a
V				1.000	0.613	0.553	0.653	0.398	a	a	0.363	0.532	-0.335
Ni					1.000	0.557	0.583	0.459	a	a	0.425	0.438	-0.257
Fe						1.000	0.809	0.265	a	a	0.326	0.691	-0.396
Mn							1.000	0.340	-0.536	a	0.373	0.695	-0.460
Cd								1.000	a	0.470	0.455	0.394	-0.253
Na									1.000	a	a	a	0.548
Cr										1.000	0.412	0.234	a
Zn											1.000	0.381	a
TSP												1.000	-0.435
DF													1.000
N	109	110	103	95	104	109	110	107	15	98	78	110	110

^a Not significant at 5% level.

Table V. Correlation Coefficients between Concentrations of Metals, TSP, and Dispersion Factor in São Cristovão

	Pb	Cu	K	V	Ni	Fe	Mn	Cd	Na	Cr	Zn	TSP	DF
Pb	1.000	0.552	a	0.338	0.317	0.212	0.299	0.399	a	0.500	0.596	0.451	a
Cu		1.000	a	0.500	0.454	0.518	0.662	0.495	-0.491	0.310	0.693	0.641	-0.283
K			1.000	a	a	a	a	a	a	a	a	a	a
V				1.000	0.454	0.600	0.676	0.336	a	a	0.453	0.647	-0.476
Ni					1.000	0.425	0.470	0.276	a	0.335	0.322	0.438	a
Fe						1.000	0.796	0.271	a	a	0.418	0.725	-0.410
Mn							1.000	0.449	a	a	0.515	0.747	-0.408
Cd								1.000	a	0.223	0.286	0.436	a
Na									1.000	a	a	a	a
Cr										1.000	0.268	0.212	a
Zn											1.000	0.576	-0.250
TSP												1.000	-0.567
DF													1.000
N	117	113	115	103	116	118	117	115	18	106	91	118	118

^a Not significant at 5% level.

found in lower concentrations than in other cities, indicating a larger contribution from natural sources: sea spray and soil dust. However, the levels of Pb, Mn, V, Cr, and Zn are already relatively high, and control measures should be enforced to prevent them from increasing even further.

(2) The prohibition of garbage incineration in Rio did not produce the expected decrease in TSP concentration. However, a decline was noticed in Cd and Cr concentrations, especially in Copacabana, an area more affected by this source of particulate matter. The high content of atmospheric Pb following the changes of lead content of the gasoline shows a need for control of motor vehicle emissions. This picture, however, will change as a consequence of the energy crisis. Gasoline prices are increasing very rapidly, and ethyl alcohol is being used regularly as a fuel, both pure and mixed with gasoline in Rio de Janeiro.

(3) São Cristovão, an industrial area by the Rio bay, presented more regular seasonal variations of TSP and metal concentrations than Copacabana, with peaks during the May to August periods. Except for Na and K, the metals analyzed showed significant correlations with each other and with TSP concentration in both districts, indicating that the particles in which they are contained have a similar behavior in the atmosphere.

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Diesel-Particulate Collection for Biological Testing. Comparison of Electrostatic Precipitation and Filtration

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■ The extent to which a particle collection method can influence the chemical composition and biological activity of diesel-particulate extracts was investigated. Undiluted diesel particles were collected from the exhaust of a GM 5.7-L diesel engine at specific collection temperatures by electrostatic precipitation (ESP) and filtration. The percent of extractable organic compounds by dichloromethane for the ESP sample was higher than the filter sample and was dependent on collection temperature. Chemical fractionation of the extracts into nine components was achieved according to a solvent partitioning scheme. The biological activities of these extracts and their fractions were examined in the *Salmonella typhimurium* mutagenicity test. No significant difference was found in the overall biological activities of the filter and ESP samples, although the specific activities of some extract fractions were different.

Introduction

With the expected increased usage of light-duty diesel engines, the potential health effects of diesel exhaust emissions should be determined. In addition to chronic-exposure studies with dilute diesel exhaust, the chemical and biological characteristics of diesel particles and the extracts would provide relevant information for the assessment of health hazards associated with inhaled diesel particles. Short-term bioassays, such as the Ames test, have shown that diesel-particulate extracts are mutagenic with varying degrees of biological activity dependent on engine types and fuels. Most of the biologically active compounds found on diesel particles are suspected to be hydrocarbon compounds either formed during the combustion process or adsorbed and condensed on the particles during the collection process. Experimental artifacts may exist if the diesel particles are not collected under proper conditions. The standard sampling method using appropriate filter papers may not be satisfactory for diesel-particle collection if the biological activity of the particles is to be studied. The high pressure drop across the filter can lead to losses of volatile organic compounds on the particles on the filter due to the partial vacuum. Another serious problem associated with filter sampling may be the chemical conversion of organic compounds on the particles by engine exhaust gases, such as nitrogen oxides and other reactive hydrocarbon compounds. Pitts et al. (1) reported that filters spiked with benzo[a]pyrene were found to be partially converted to nitro-substituted

compounds by 1 ppm nitrogen dioxide in laboratory studies. These factors may play important roles in the relative biological potency of diesel particles and their extracts.

In order to provide a comparison with filter sampling, we used electrostatic precipitation (ESP) in parallel to examine the role of the collection method on the chemical and biological properties of diesel exhaust particles. The collection efficiency of ESP is almost as high as filtration, although the mechanisms of collection are distinctly different. Electrostatic collection of particles offers a low pressure drop across the collector and allows the exhaust gases to pass over the collected particles instead of through them. Thus, losses of volatile compounds due to the partial vacuum and the mass transfer of gaseous hydrocarbons and nitrogen oxides to the particles should be reduced since only a small fraction of the gases is in contact with the diesel particles.

The objective of this study is to determine the effect of the particle collection method on the chemical composition and biological activity of diesel-particulate extracts. In this study, a GM 5.7-L diesel engine was operated at 65-km/h road-load conditions. Type 2D federal compliance diesel fuel was used, and a regular oil change was performed every 3000 mi with 30W lubricating oil. Diesel particles collected by either ESP or filtration were extracted in a Soxhlet apparatus with dichloromethane. The diesel-particulate extracts were chemically fractionated into nine components according to a solvent partitioning scheme. The biological activity associated with the extracts and their various fractions was studied by using the Ames test.

Experimental Methods

Collection of Diesel Particles. The sampling system for diesel-particulate collection is shown in Figure 1. A GM 5.7-L diesel engine was controlled by a water brake dynamometer at 1350 rpm and 96 N·m, representing 65-km/h road-load cruise conditions. The exhaust from the engine passed through a normal passenger-car exhaust system. A gate valve downstream of the muffler controlled the total diesel exhaust airflow and the collection temperature in the electrostatic precipitator. Parallel filter samples were obtained from the filter sampling ports using 47-mm Pallflex filter paper.

The basic principle of ESP collection of particles is a two-stage process: particle charging and particle collection. Particles entering the precipitator are charged electrically in a unipolar ion field provided by the corona discharge in the