LEVELS OF PARTICULATE CARBONACEOUS MATERIAL IN SAO PAULO - BRASIL AN HISTORICAL DATA BASE

by

CLAUDIO DARWIN ALONSO

A thesis submitted to the Faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in Public Health in the Department of Environmental Sciences and Engineering.

Chapel Hill

1989

Approved by:

Parker C. Reist, Ph.D

. Kamens, Ph. D.

Morris A. Shiffman, Ph.D.

ABSTRACT

CLAUDIO D. ALONSO. Levels of Particulate Carbonaceous Material in Sao Paulo - Brasil, An Historical Data Base. (Under the direction of Dr. Parker C. Reist)

A calibration curve relating the carbon concentration to reflectance measurements was obtained. The curve was generated with data gathered in two different places and two different years. The curve was used to calculate the atmospheric carbon concentration in five Sao Paulo neighborhoods, from 1973 to 1988. It was possible to observe the seasonal variation of the data that show a maximum in the quarter ending in July or August, depending on the year or place. The long term trend analysis showed that the concentrations are decreasing in all sites. By comparing the Sao Paulo data to some cities in the United States, it was possible to verify that although the concentrations are decreasing, the levels are still extremely high.

SUMMARY

ACKNOWLEDGEMENTS

I would like to thank Dr. Parker Reist for his help during my study at Environmental Science and Engineering, specially when I was preparing this report.

I am also grateful to Jesuino, Maria Helena, Roberto, Carlos, Francisco, Hilton, Mario, Viviane and Rosana, for their aid in all technical material I needed from Brasil.

Thanks to Wandinha & Sons & Sons for the emotional support and to Linao wherever he is.

CETESB, through the Pollution Control Program - PROCOP - supported my education at The University of North Carolina and made this report possible.

TITLE: LEVELS OF PARTICULATE CARBONACEOUS MATERIAL IN SAO PAULO -BRASIL, AN HISTORICAL DATA BASE

by Claudio Darwin Alonso

1. INTRODUCTION

The presence of the particulate carbonaceous material suspended in the atmosphere has long been recognized. The study of this atmospheric component is important not only due to its high concentrations, but also due to its adverse effect on health and the environment.

Two broad classifications can be given to the particulate carbonaceous material. The first is based on the chemical characteristics of the components, dividing them into Organic Carbon and Elemental Carbon. The second is based on the origin of the compounds and divides them into primary and secondary carbon .

Organic carbon, no matter its physical state, can react in the atmosphere forming other compounds, but this is not true for elemental carbon. Organic compounds can be both primary and secondary components. Elemental carbon is uniquely a primary component carbonaceous aerosol. Furthermore, particulate organic carbon is not only emitted from combustion sources, but is also formed in the atmosphere through photochemical reactions.

According to Pitts(16), there is a production of reactive free radicals by pyrolysis of fuel hydrocarbons in the chemically reducing zone of a flame burning with an insufficient supply of oxygen. The C_1, C_2 and higher radicals combine rapidly in the reducing atmosphere to form partially condensed aromatic molecules. These kinds of compounds are known as PAH's (Polycyclic Aromatic Hydrocarbons). Today it is recognized that PAH's and its derivatives are animal, and possibly human carcinogens.(17)

Epidemiologic studies on the health effects of combustion products are difficult due to the substantial effect of confounding factors, especially smoking. Animal bioassays can provide important informations of the carcinogenic potential of air pollution. However, these assays are expensive, take a long time to be completed and require a large amount of samples.

The introduction in the mid-1970's of the rapid, relatively inexpensive in-vitro test for chemical mutagens by Ames and co-workers(6), made possible the study of the mutagenicity of the ambient particles in several cities (23,15,36). These studies showed that some organic compounds in the atmosphere are direct mutagens; they show mutagenicity without any previous activation by enzymes. On the other hand, some compounds such as benzo(a)pyrene need a liver enzyme activation to express mutageniciyy and are called promutagens.

Another consideration is that some PAH's react with near ambient levels of NO_2 $+HNO_3$ and with ozone forming nitro-PAH and oxy-PAH that are direct mutagens(17).

In the 1986 International Symposium on Toxicological Effects of Emissions from Diesel Engines (20) were presented a large number of works, most of them showing that diesel exhausts induce lung cancer in animals; in-vitro studies were also presented providing an increasing evidence for genotoxic effects of particles extracts and specific constituents. One of the conclusions of the symposium probably summarizes today's knowledge about the subject:"Taking all of the information together, it would appear appropriate to conclude that whole diesel exhaust is a probable human carcinogen"(24).

Although the harmfulness of elemental carbon has not been shown, it plays an important role in the lung deposition of toxic compounds including the organic carbons. As product of combustion, elemental carbon is mostly present in the atmosphere in the range of sub-micron sizes so it can penetrate deeply into the lung.

The chemical structure of "elemental carbon" in soots is similar to graphite, but with some surface oxygen-containing groups that may determine the adsorptive and catalytic properties of the particles(12).

Among the oxygen-containing functional group known in organic chemistry, the most often suggested are carboxyl groups, phenolic group and quinone carbonyl group. These surface groups would change the characteristics of adsorptivity of the soot if the particle were compared with a similar particle of graphite.

According to Charlson and Ogren(13) elemental carbon is emitted in the nuclei mode - range 0.05 to 0.1 µm - and has strong tendency to coagulate. In the atmosphere, these particles get in touch with other particles of the accumulation mode, and bigger particles of mixed composition can be formed.

In urban polluted areas it is estimated that this coagulation process lasts about one hour. Therefore, the soots in the atmosphere are chemically composed of elemental carbon and other kind of materials. This kind of chemical structure makes the soot particles good adsorbers, and as they have a small size they can easily carry into the lungs all the compounds adsorbed on them.

As with other fine particles, elemental carbon is expected to remain in the atmosphere for several days. This means that it can be well mixed in the air and travel long distances, both horizontal and vertically. It can also reaches high humidity locations and clouds.

Elemental carbon can be hygrophobic or not, depending on the other materials present in the particle. If hygroscopic, t can act as a nucleating agent for cloud formation, and in this case exerts a catalytic transformation from SO_2 to SO_4^{-2}.

Besides the chemical properties of the soots, some physical characteristics should be considered. Soot carbon is in the size range of the fine particles (most < 1.0 µm) also having a dark color. These characteristics impart a perturbation to the atmospheric radiation field. The particles that have the same size as the wave-length of visible light and can cause strong scattering of the light. The dark color shows that the particles also absorb intensely the visible light. It is postulated that the soot is a significant factor for the visibility degradation (32,29).Some authors (18,27) have also raised the possibility that soot, due to the fact that it is a light absorber, can trap the pollutants in an urban atmosphere by intensifying and maintaining an inversion aloft through differential heating of the air layers.

There are several methods to measure carbonaceous material in atmosphere. Among them the differences are not only in the techniques themselves, but also in the approach to the kind of material to be studied.

Studies of the molecular composition of particulate organics are carried out when the objective is to clarify aspects of the photochemical cycle or find out which type of compound is harmful to human health. These studies involve gas chromatography, mass spectrometry and other modern analytical methods.

The elemental carbon is mainly studied when the objective is to verify its relationships with atmospheric phenomena such as degradation of visibility and thermal effects.

The analysis of carbonaceous material in two broad classes, organic carbon and elemental carbon, has been done for use in chemical element balance for source apportionment. Most of the described techniques are based on the thermal evolution and oxidation of the different types of carbon, using infra-red detectors for a direct measurement of the evolved CO_2 or converting the CO_2 to CH_4 for detection with a flame ionization detector(27,8,34).

The use of thermal-optical methods have also been described(19,21) as well as a reflectance-GRALE (gamma ray analysis of light elements) method for the determination of the carbon content in the atmospheric soots(14). The main problem in these methods is that both species, elemental and organic carbon, are defined according to the analytical procedure and not according to their chemical properties.

In some methods the organic carbon is defined as the fraction that is volatilized at a temperature in the range from 450°C(33,2) to 550°C(8). In this step different carrier gases are used: oxygen-free Helium(8,33) or oxygen-argon mixtures(2). All these different approaches are used not only to minimize the charring that occur during the organic analysis step but also to guarantee the complete volatilization of the organic compounds. The second step in these procedure is to burn completely the carbon in the sample, in general at temperatures 700°C, in order to obtain the total carbon. Elemental carbon is obtained by the difference between total and elemental carbon.

In the thermal-optical method(19-21) the analysis is performed in three steps by using different carrier gases in each step, in order to minimize the above mentioned effects.

In the reflectance-GRALE method(14) the calibration curve for elemental carbon is obtained by taking a standard prepared by the combustion of polystyrene, paraffin and butane; the sample is heated at 300°C to loose the organic carbon. Although it was demonstrated in this method that no charring occurs, there is some uncertainty in the measurement of the elemental carbon, since at 300°C not necessarily all organic carbon would be volatilized.

Differences in procedure can cause differences in results. A study was carried out to compare two different thermal methods. A large difference was observed in the results obtained, according to Will as referenced by Stevens(33).

As a consequence of all differences in the analytical methods, the terms organic carbon and elemental carbon reflect only an operational definition of the data obtained. Although there is some uncertainty about exactly what the methods are measuring, the measurements of atmospheric carbon is considered to be very important in characterizing sources of atmospheric pollution, since the only generic source of organic and elemental carbon is burning of fuels.

There are several methods available for measurement of the particle concentration in the atmosphere. Among these, some use gravimetric procedure as in Hi-Vol and dichotomous samplers, and others use optical properties of the dust deposited on a filter paper such as the smoke shade and the paper tape sampler. As a matter of fact the blackness of a filter deposit has been used for over 70 years as a gross indicator of the amount of pollution in the air (smoke shade method).

The smoke shade method relates the concentration of particulate matter in the atmosphere to the filter reflectivity. It seems reasonable that the reflectivity of the filter should be more related to the carbon content since the carbon has the dominant color among the atmospheric particles. Bailey and Clayton (7) showed that the relation indeed exists in the London atmosphere. The importance of this observation is that it is possible to verify how the generic source of air pollution "combustion" has been affecting the air pollution of an urban area in a historical data base.

2. OBJECTIVE

CETESB - Companhia de Tecnologia de Saneamento Ambiental- the environmental agency of Sao Paulo state, has long been measuring the particulate matter in the atmosphere by the smoke shade method. It has been possible to retrieve all the reflectance values of the samples collected since 1973. Considering that these reflectance measurements can be related to the carbon content in the atmosphere, and also that carbon has been shown as an important pollutant in Sao Paulo city, this work has the following objectives:

1. To obtain a calibration curve relating reflectance to carbon concentration, with validation to the area of study.

2. To observe the historical behavior of the carbon contents in particulate matter in Sao Paulo atmosphere.

3. CHARACTERISTICS OF SAO PAULO METROPOLITAN AREA - SPMA

Characteristics of the Sao Paulo Metropolitan Area (SPMA) are described in the CETESB Air Quality Annual Report (9) which is summarized below.

The SPMA is located on the Atlantic plateau on the Tropic of Capricorn, 80 km from the seaboard, with an area of about 8,000 km^2. The urban region of the area is 5,000 km^2 and is 700m to 900m above sea level with ridges which tower up to 1200m. The general topography is rather complex and the air flow is strongly influenced by local conditions.

The climate in the SPMA can be summarized as a dry winter (June to September) and a wet summer (December to February). From September to April the area is dominated by a southern moist wind with frequent occurrences of frontal systems passing through, resulting in precipitation, low level cloudiness and low availability of solar radiation. During the winter, high pressure builds up northward in the eastern Atlantic, producing light winds from the coast, strong thermal inversion of the subsidence type and clear skies. Precipitation becomes far less frequent and pollution problems increase.

Approximately 15.3 million people live in the SPMA and nearly 70% of the population lives in Sao Paulo City. The remaining population in the area is distributed among the smaller cities and districts. Presently the SPMA is the largest industrial zone in Brasil.The population and industrial growth has been rapid with little planning of the physical structure of the cities in the region.

With 47,000 industries, the SPMA has 46% of the industries of the Sao Paulo state(28). Of particular interest is the presence of heavy industries in the region such as iron and steel works, cement plants, sulfuric acid plants, fertilizer plants, refineries, petrochemical plants, chemical manufacturing, etc.

The emission source inventory for the SPMA was calculated with the help of data obtained from the actual sources activity data base, for the reference year 1985, and the emission factors were calculated from the Compilation of Emission Factors of the U.S.Environmental Protection Agency or, in some cases, obtained from source tests (e.g., for the light duty vehicles). A summary of the emission estimates of particles by source is presented in table 1.

Table 1 - Emission estimates of particles in SPMA

SOURCES EMISSION	(1000 TON/YEAR)
Industrial Processes	59
VEHICLES	
gasoline exhaust *	4.3
alcohol exhaust *	-
Diesel exhaust **	9.9
motorcycle exhaust	0.1
taxi	0.2
tires	6.4

* light duty vehicles
** heavy duty vehicles

Although there are some emissions due to open fire burning the estimates are not reliable.Brazil is unique in that it has a significant fleet of light duty vehicles using alcohol (ethanol) as fuel. Furthermore ethanol is added to gasoline with the present blend being 22% ethanol and 78% gasoline. Both changes produce a decrease in the carbon monoxide emission levels and an increase in the aldehydes emissions compared to the use of gasoline alone. The nitrogen oxides emissions are maintained almost constant. There is no estimate for emission of particles from alcohol-fueled cars but some initial observations show that these cars emit less particles than gasoline-fueled cars. The evolution of vehicles and fuel use in the SPMA is shown in table 2.

Table 2 - Evolution of the fleet of vehicles in SPMA

TYPE OF VEHICLE	YEAR 1981	YEAR 1987	VARIATION
	(multiply x 1 000)		
gasoline	2,100	1,700	-21%
alcohol	84	850	1011%
Diesel	161	190	118%
motorcycle	89	200	225%
taxi	36	35	-3%

3.1 Air Quality Measurements in SPMA

Presently CETESB has been operating a manual air monitoring network since 1973 and an automatic network since 1981. Besides these networks, several special studies have been carried out to clarify the behavior of some pollutants in the atmosphere.

3.1.1.Manual Network

The manual network is composed of 6 sampling stations which measure SO_2 and particles as "smoke " (since 1973), and 11 sampling stations which measure total suspended particles using a high volume (Hi-Vol) sampler (since 1983). The manual network today is operated mainly to keep the historical records and maintain continuity with the daily measurements collected by the automatic network.

3.1.2. Automatic Network

The automatic network is composed of 22 fixed sampling stations and 2 mobile vans, with automatic generation and transmission of data to a central station. This network measures SO_2 (all stations), inhalable particles (all stations), CO (7 stations), hydrocarbons (1 station), nitrogen oxides (6 stations), O_3 (6 stations) and wind speed and direction (10 stations).

3.1.3. Special Studies

Among the special studies carried out in the SPMA, those related to measurements of particles are of special interest for this work. The main studies were concerned with lead content in the SPMA atmosphere(4), the distribution of particulate matter around a heavy traffic way(3), the size characteristics of the SPMA dust(5), the atmospheric particulate carbon in the SPMA(1) and the one year receptor modeling for apportionment of sources of particulate matter(11).

3.2. Characteristics of the Air Quality in the SPMA

3.2.1. Sulfur dioxide

The concentrations of SO_2 are decreasing in all sites of measurements in the lasts 5 years and do not exceed both the daily and annual standards (365μg/m^3 and 80μg/m^3).

3.2.2.Carbon Monoxide

Carbon monoxide levels routinely exceed the air quality standard (9ppm/8h) at almost all sampling sites by a large amount.

3.2.3.Ozone

The ozone air quality data indicate that the O_3 standard (160μg/m^3/1h) is constantly violated. The three highest one hour samples observed in 1987 were 455 μg/m^3, 326 μg/m^3 and 300 μg/m^3.

3.2.4.Suspended Particulate

Observed values are far above the standards for particulate levels (80 μg/m^3 daily and 240 μg/m^3 annual geometric mean) showing that the particulates are one of the serious problems of air pollution in the SPMA. Special attention has been given to this pollutant and several studies have been carried out to verify aspects of the problem. The result of these studies are summarized below.

The levels of Lead were measured in 2 different years; in 1978, just before the alcohol program had started and in 1983 when the gasoline was already mixed with alcohol and 10% of the car fleet was "alcohol" fueled. The results showed an astonishing decrease of lead concentration in all stations. The worst level station (Sao Caetano) had the maximum quarterly concentration of 1.6 µg/m^3 in 1978 reduced to 0.3µg/m^3 in 1983.

The TATUAPE(5) study was carried out by placing 5 tape samplers (hourly measurements) in an axis perpendicular to a heavy traffic way. It was possible to observe that the concentration peaks were coincident with the traffic peaks at all 5 stations. By comparing the results of all stations it was possible to see that the concentrations decreased to about 30% of the roadway value at a distance of 200m from the central station but increased again due to the proximity of another heavy traffic way nearby.

The largest study of particulate matter carried out in Sao Paulo (ECA-SP) was done in 1986-1987 and generated so much data that some data are still being processed. One of the objectives of the study was to characterize the size composition of the suspended particles. The results(1) are summarized in Table 3.

TABLE 3
Size composition of suspended particle (annual average)

STATION	FP %	CP %	>10	Conc. Hi-Vol µg/m^3 (AGA)	Conc. Inal µg/m^3 (AAA)
S.Caetano	22.3	20.8	56.9	175	86
D.Pedro	31.4	18.9	49.7	142	79
Ibirapuera	35.4	22.8	41.9	69	45
Osasco	26.4	19.1	54.4	124	62

FP = Fine Particles(<2.5µm)
CP = Coarse Particles(2.5µm<d<10µm)
AGM= Annual Geometric Average
AAA= Annual Arithmetic Average 1

The ECA-SP also provided information about the carbon content in the suspended particles. Some of these data are summarized in table 4.

TABLE 4
Total Carbon content in the suspended particles (annual average)

STATION	CONTENT OF TOTAL CARBON IP µg/m³	IP %	Hi-Vol µg/m³	Hi-Vol %
S.Caetano	30.4	35.6	45.9	22.9
D.Pedro	39.4	50.6	53.9	34.2
Ibirapuera	16.6	36.4	22.5	28.1
Osasco	28.6	46.0	41.7	30.2

IP=Inhalable Particles(<10µm)
% = Percent of total carbon in the total mass concentration

The Sao Paulo data for carbon in HI-Vol samples were plotted along with some results obtained in the USA(31), Figure 1.

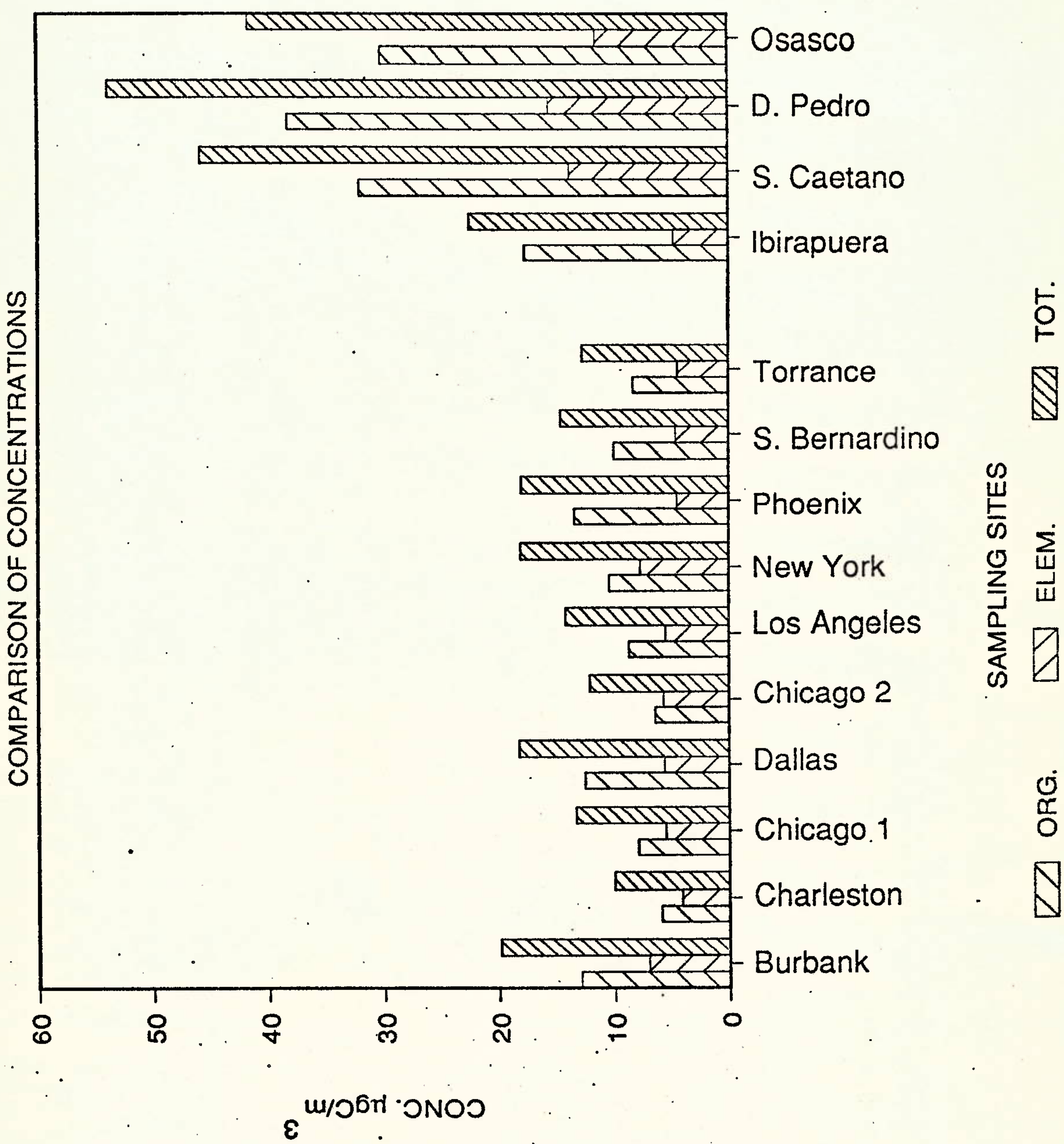
The results obtained from the receptor model "chemical Mass Balance" in the ECA-SP and related to combustion processes are presented in the table 5.

TABLE 5
Sources of combustion according to the receptor model

SOURCE	STATION S.Caetano IP	S.Caetano TSP	D.Pedro IP	D.Pedro TSP	Ibirapuera IP	Ibirapuera TSP	Osasco IP	Osasco TSP
Vehicles	40.0%	27.0%	50.0%	38.0%	35.0%	23.0%	41.0%	30.0%
Ind.Oil	3.5%	<7.6%	3.6%	<4.0%	4.0%	<2.7%	2.3%	<5.6%
Carb. Sec	7.0%	<7.6%	9.7%	<4.0%	13.0%	9.2%	17.0%	4.5%

As a general and final comment about the air quality in the SPMA we can say that the main pollutants in the region are those related to the emissions of vehicles and also that

FIGURE 1 - S.PAULO AND SOME U. S. CITIES



the particulates play an important role in the deterioration of air quality.

4. EXPERIMENTAL

4.1 Sampling and analysis

4.1.1. Smoke Shade Sampler.

The sampling equipment is similar to that described by WHO(37) and consists in the following parts:

1. Inlet - a 60-degree funnel with a diameter of 5cm. The funnel is installed facing downward in the sampling site.

2. Filter holder -Millipore Holder model No.XX IEA XX 5004700 with an nominal filtration area = 9.4cm^2.

3. Critical orifice - nominal flow rate of 2 L/min. A hypodermic needle was used as a critical orifice.

4. Pump - diaphragm type, capable to maintain the critical conditions in the orifice.

All parts are connected with a 6.4mm inner diameter plastic tubing (Tygon) in the order described above. The sampling height is 2.6m and is uniform in all stations. The tubing size from the funnel to the filter holder is 2.3m.

The sampling procedure consists of placing a clean sheet of filter in the holder, turning on the pump and sampling, usually for 24 hours. For the reflectance analysis Whatman No. 1 filter paper was used. For carbon analysis a fiber glass filter (Gelmam A/E) was used. The filter was previously heated to 450^{0}C to reduce the blank carbon value.

4.1.2. Reflectance Analysis

Percentage reflectance was measured by an Evans Electroselenium Ltd Smoke Stain Reflectometer, capable of measuring percentage reflectance between 0 and 100. A clean sheet of Whatman No. 1 filter paper is placed in the white plaque provided with the equipment and the galvanometer is adjusted to 100. A sampled filter is placed in the same plaque and its reflectance is then measured

The reflectometer is periodically checked with the "standard grey plaque" provided with the equipment. The results are reported in "Darkness Index" (DI),

$$DI = 100 - Reflectance$$

4.1.3. Carbon Analysis

This analysis was carried out by using the Carbon Analyzer Xertex-Dorhmann model DC85. The sample is loaded in a platinum boat in a flux of carrier gas. The boat is then advanced to a high temperature "oxidation zone" where the carbonaceous material is volatilized and/or burned to CO_2. The complete oxidation of the gases to CO_2 is guaranteed by a bed of "catalyzer" CuO. The CO_2 is then measured by a non-dispersive infrared detector. Results of Total Carbon and Volatile Carbon are obtained according to the operational conditions as described in Table 6. The elemental or non-volatile carbon is obtained by an arithmetical subtraction of total carbon minus volatile carbon.

Table 6
Analytical conditions for carbon determinations

CONDITIONS	VOLATILE CARBON	TOTAL CARBON
Oxidation Zone (temperature)	450^{0}C	700^{0}C
Catalyzer (temperature)	700^{0}C	700^{0}C

Carrier Gas   Argon with 2% of Oxygen
Flow = 200 ml/min

In the analysis of the filter samples, a disc of 0.121cm is removed from the filter and loaded into the platinum boat. A different disc is used for each condition. The final result is reported in surface concentration, $\mu g/cm^2$.

The equipment is calibrated with a solution of potassium biphtalate (2000 µgCarbon/ml) for a response of 2000 ppm (the equipment was originally made for water analysis). A punch of an unused filter is used for blank measurement. The calibration procedure is repeated in the beginning and end of the day. Periodically the equipment is checked with a real atmospheric sample, kept as a standard, in order to verify the behavior of the catalyzer or to verify the appropriate functioning of the equipment when any kind of maintenance is done or when a new cylinder of gas is used. This "standard" is a Hi-Vol sample kept at ambient temperature. Repeated analysis of this standard showed an average of 1652.5 ppm and a standard deviation of 69.4

ppm(4.2%) and these numbers are used as guidelines for acceptance or not of the good functioning of the equipment.

4.2. Data collection

The calibration curve was built up with real atmospheric samples. The samples were collected in two different sites and in two different periods. The first site "PINHEIROS" is located in a residential area at about 200m from a very heavy trafficway and 30m from a light trafficway. The samples were collected in the winter of 1988 (PIN-88). This set was obtained by sampling over a 24 hour period. The data do not show an even distribution of values in the range that was intended for study. To obtain more samples which it was hoped would give more evenly distributed values, a second period of study was planned. This was done in "CERQUEIRA CESAR"(CC-89), located in a residential-commercial area and the sampler was at 20m away from a corner highly influenced by two heavily travelled roadways. The sampling was performed in the 1989 winter with several samples being taken over a 48hr period. In the 1989 winter samples were also collected in the five different sites where the historical data were to be analyzed. These samples were not to be part of the calibration curve but were to be used as proof of the validity of the curve obtained. Two absolutely equal samplers were located at each study site. One sampling device collected samples through Whatman No. 1 filter paper and the other through a Gelman

A/E glass fiber filter sheet. All samples were taken under a nominal flow of 2 L/min.

4.3. All Data Calibration curve

All data used to develop the calibration curve are given in the Appendix A. There it is possible to see the site, date and analytical results of each sample. The curve that best fits the data was obtained following the procedure described by Kleinbaum et al.(32).

The complete series of data were initially treated by mixing all of the 1988 and 1989 data. Several models were tried using the least-squares method and a summary of these models are given in table 7.

TABLE 7
Summary of the least squares models

MODEL	a	b	c	r^2	residual average
Linear y=a+bx	-3.864	0.6170	-	0.931	0.000
Exponential $y=ae^{bx}$	3.266	0.0436	-	0.956	0.038
Power $y=ax^b$	0.259	1.178	-	0.956	-0.281
Polynomial y=a+bx+cx	2.246	0.1477	0.00726	0.956	0.003

The regression analysis was done using the Darkness Index as independent variable (x) and Total Carbon Surface Concentration (μg/cm²) as dependent variable (y). Among the exponential, power and polynomial models, which have the same r^2, the best choice is the polynomial because it has the lowest residual average. The linear model has the poorest r^2 but also presents the lowest residual average. For this reason a comparative study of the residuals was carried out with the linear and polynomial models to decide which one best fits the data. The plots of both curves are presented in figures 2(a) and 2(b). The ith residual, e_i, is

FIGURE 2a-STRAIGHT LINE MODEL

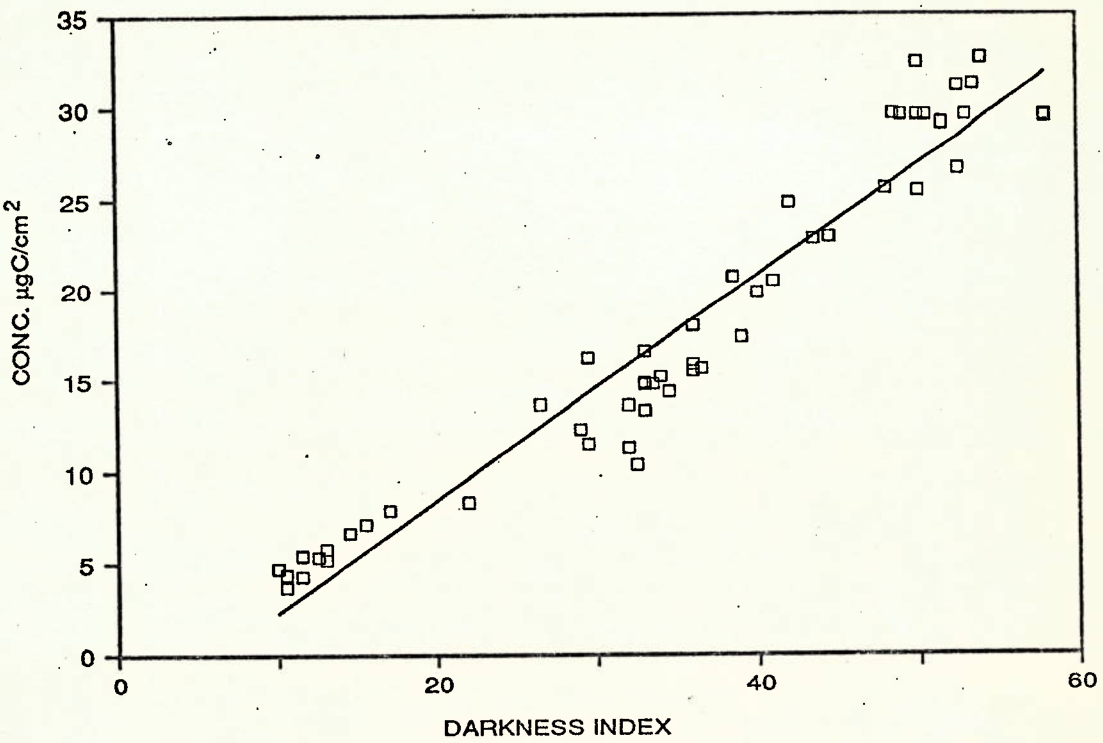
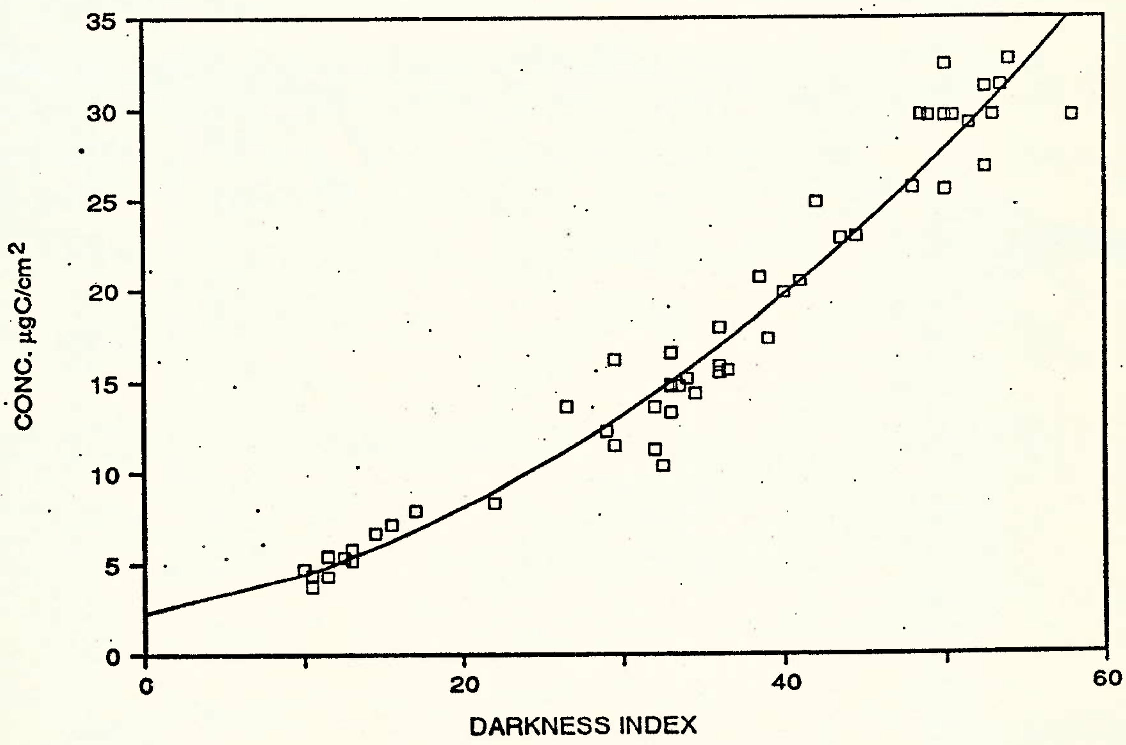


FIGURE 2b- POLYNOMIAL MODEL



defined as the difference between the observed value, Y_i, and the model predicted value, Y_s.

$$e_i = Y_i - Y_s$$

The estimate of population variance, S^2, computed from the sample of n residuals is:

$$S^2 = \frac{1}{(n - k - 1)} \Sigma e_i^2$$

where k is the number of independent variables. The standardized residual is:

$$Z_i = e_i / S$$

The Z_i value was calculated for both models and the plots of (Z_i *X* Measured Carbon) are presented in figures 3(a) and 3(b). A summary of the dispersion of the standardized residuals is presented in Table 8.

Table 8
Dispersion of the standardized residuals

Parameter	Linear	Polynomial
Positive residuals	26	27
Negative residuals	25	24
std. dev. S	2.42	1.96
0 - 1 S	35 (68.6%)	39 (76.5%)
1 - 2 S	14 (27.4%)	9 (17.6%)
2 - 3 S	2 (4.0%)	3 (5.9%)

In the table 8 and figures (3a - 3b) it is possible to see that both curves present approximately the same number for the positive and negative residuals. Meanwhile, the Z_i of the polynomial curve is more evenly spread around the

FIGURE 3a- STRAIGHT LINE MODEL RESIDUALS

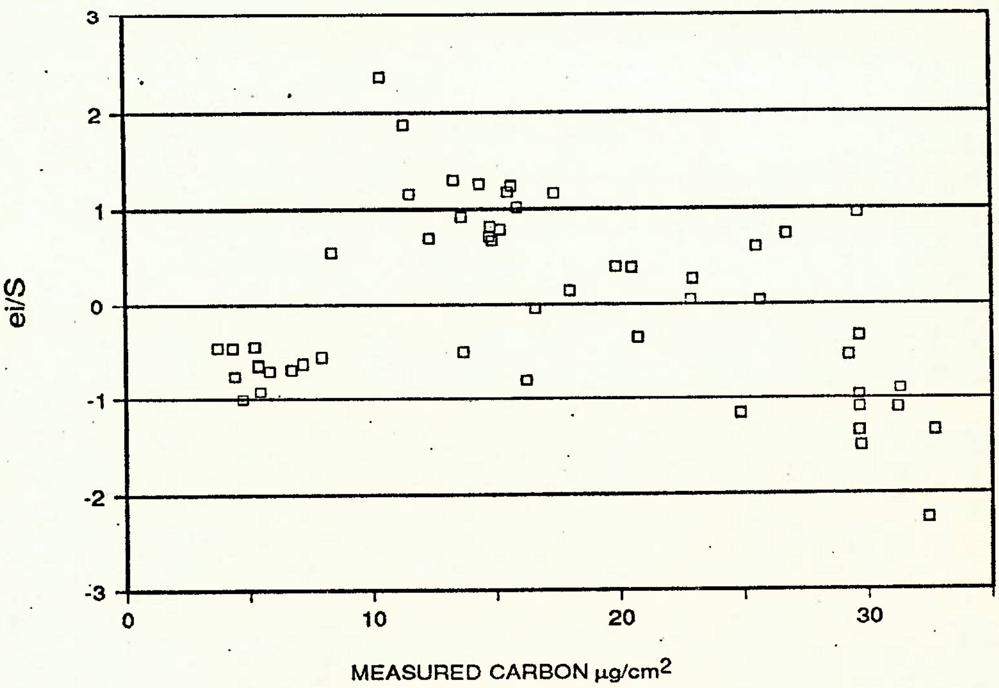
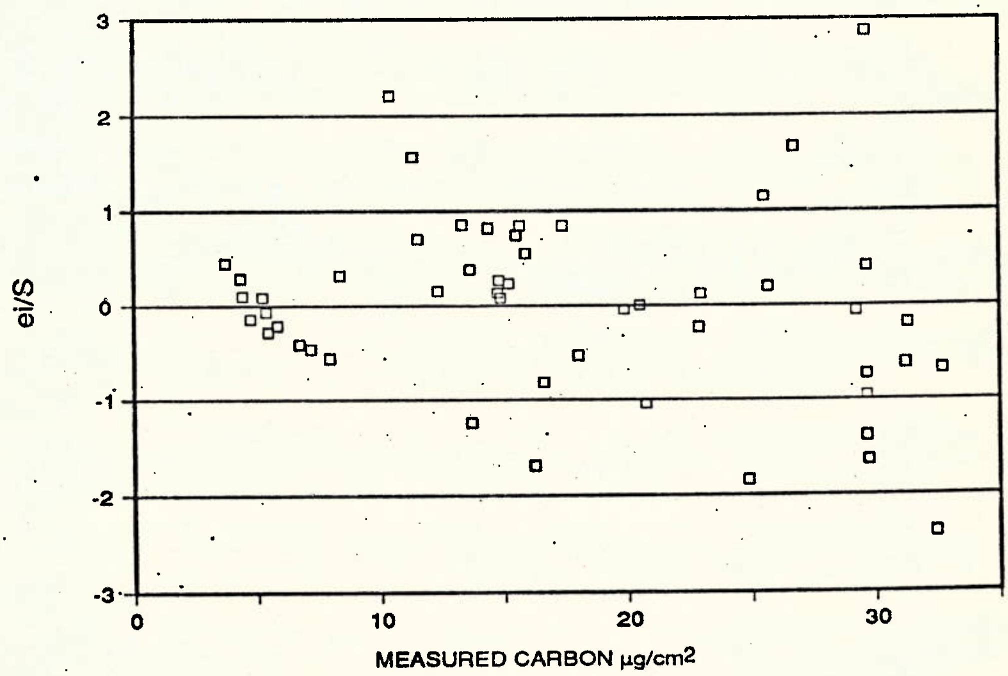


FIGURE 3b- POLYNOMIAL MODEL RESIDUALS



zero value. Also there are more data in the 0-1 standard deviation range for the polynomial than for the linear model. The standard deviation of the residuals are smaller in the polynomial than in the linear model. These reasons lead to the conclusion that the polynomial model is the best among the models which were tested.

4.4.Partial Data Calibration curve

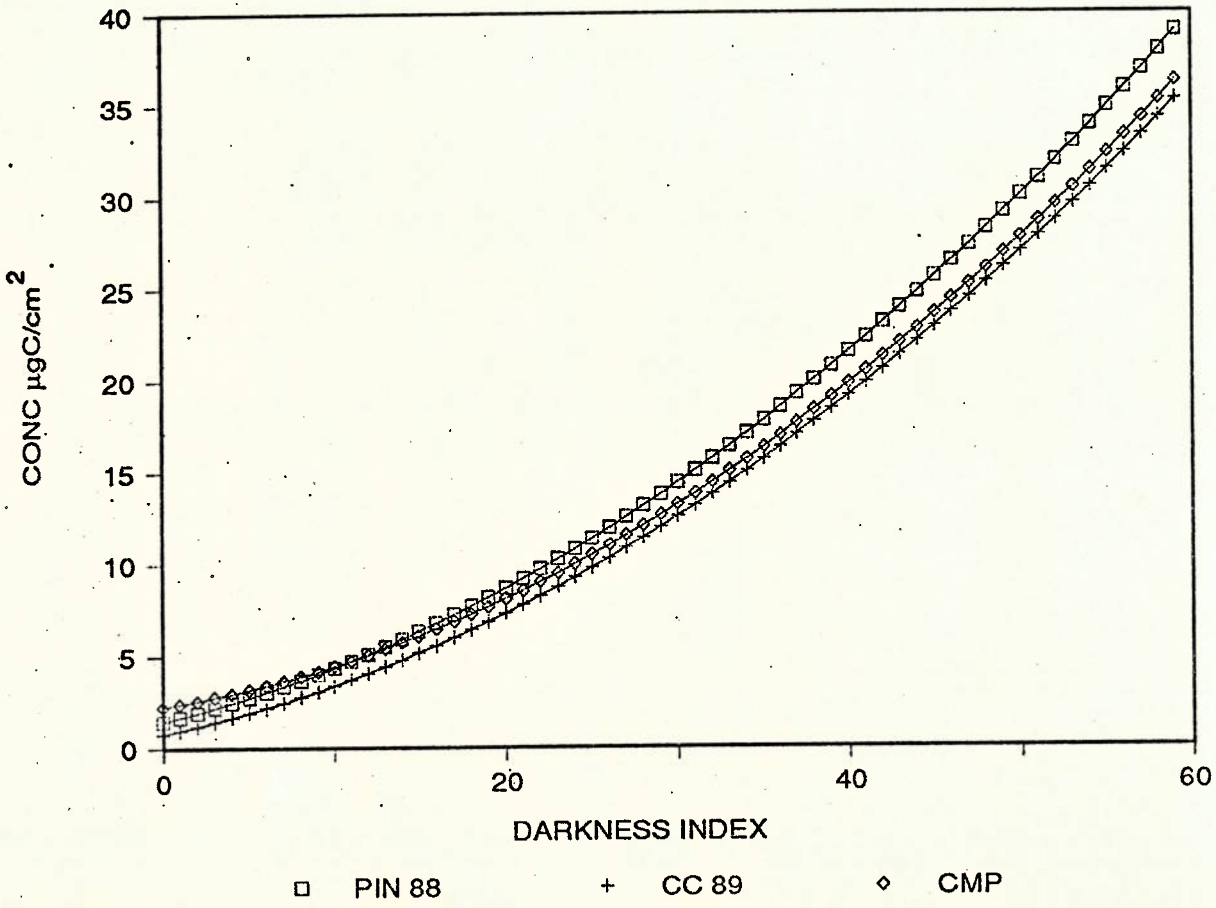
To verify wether the sampling period or sampling site affects the calibration curve, the regression of complete data (CMP) was compared to the regression of the two sampling periods PIN-88 and CC-89. The second degree equations for the models are presented in table 9.

TABLE 9
Polynomial equations for each set of data

Site and period	a	b	c	r^2
Pinheiros 1988 (PIN-88)	1.451	0.2203	0.00725	0.986
C. Cesar 1989 (CC-89)	0.765	0.1958	0.00658	0.934
Complete data (CMP)	2.246	0.1477	0.00726	0.956

The 3 curves are displayed in figure 4. The CMP curve is closer to the PIN-88 curve until approximately DI=25. After this point the CMP starts to be closer to CC-89. If one looks closely at the data of the partial curves it is possible to see that 50% of the PIN-88 data are smaller than DI=25 and only 3.5% of the CC-89 data are in this range. This observation suggests that the complete (CMP) curve fits

FIGURE 4- POLYNOMIAL MODEL
TOTAL AND PARTIAL SETS



basically with the PIN-88 data in the beginning and with CC-89 in the upper range.

To verify how close the CMP is to each separate curve it was calculated from the equations using the values for different points of DI as well as the difference of each point from the CMP curve. Differences were normalized with respect to the standard deviation of the residuals obtained in the CMP analysis (1.96). Table 10 shows the results of these calculations.

TABLE 10
Differences among the 3 curves

DI	CMP	PIN-88		CC-89	
	µg/cm²	µg/cm	nd	µg/cm²	nd
10	4.4	4.4	0.0	3.4	0.51
20	8.1	8.7	0.31	7.3	0.41
30	13.2	14.4	0.61	12.6	0.31
40	19.8	21.5	0.87	19.1	0.36
50	27.8	30.1	1.17	27.0	0.41

nd= normalized differences

The normalized difference shows that the partial curves are different from the complete curve in values smaller than 1 standard deviation. Only in the case of DI 50 in PIN-88 was a value slightly greater than 1 observed. For this reason the curves were considered equivalents and it was assumed that the complete curve is valid for all stations and all years.

4.5. Test of the curve

Several data were generated with the purpose of testing the calibration curve and for that reason were not used in the calculations of the model. Four data points were gathered at each site where it was intended that the historical analysis would be carried out using a total of 20 data points.

The experiment was conducted in the same way as that for the calibration curve. Directly measured carbon results were compared to those obtained by use of the calibration curve. A table with the results are presented in appendix B. An analysis of the table shows that 65% of the normalized residuals are on the negative side and 35% on the positive side. The normalized residuals shows also that 50% of the data differ less than 1 standard deviation from the curve and the other 50% is in the range between 1 and 2 standard deviation. This result was considered satisfactory for the purpose of this work.

4.6. Particle size

Although characterization of the particle size collection characteristics of the smoke shade sampler was not the objective of this work, an attempt was made to verify at least the size range of the collected particles. This is important because there are no standards for carbonaceous particles in the atmosphere and a reasonable way to verify the importance of the levels found in Sao Paulo is to compare them with levels found in other cities with similar characteristics. Although the ECA-SP study provided a basis of comparison, the recent studies report carbon content in samples obtained with Hi-Vol or Dichotomous samplers having a defined cut diameter. Thus any comparison has meaning only if it is done with samples having essentially the same size distribution.

A few sampling were carried out with parallel collection using a dichotomous sampler and the smoke shade sampler. These data are presented in appendix C. The smoke shade mass concentration was obtained by using the standard reflectance curve(22) and the dichotomous mass concentration via gravimetric analysis. The total carbon concentration was measured in all samples with the thermal method previously described.

From these results it is possible to conclude that both mass concentration and carbon concentration are greater in samples collected with the smoke shade sampler. To make this comparison easy, smoke shade data versus the dichotomous data were plotted and the plots are presented in figures 5(a) and 5(b). The dichotomous concentration is the sum of fine and coarse particles concentration, the so called inhalable particles (IP).

To confirm the above results, which were obtained in Cerqueira Cesar, two other sets of samples were collected in

FIGURE 5a-CARBON CONCENTRATION MEASURED

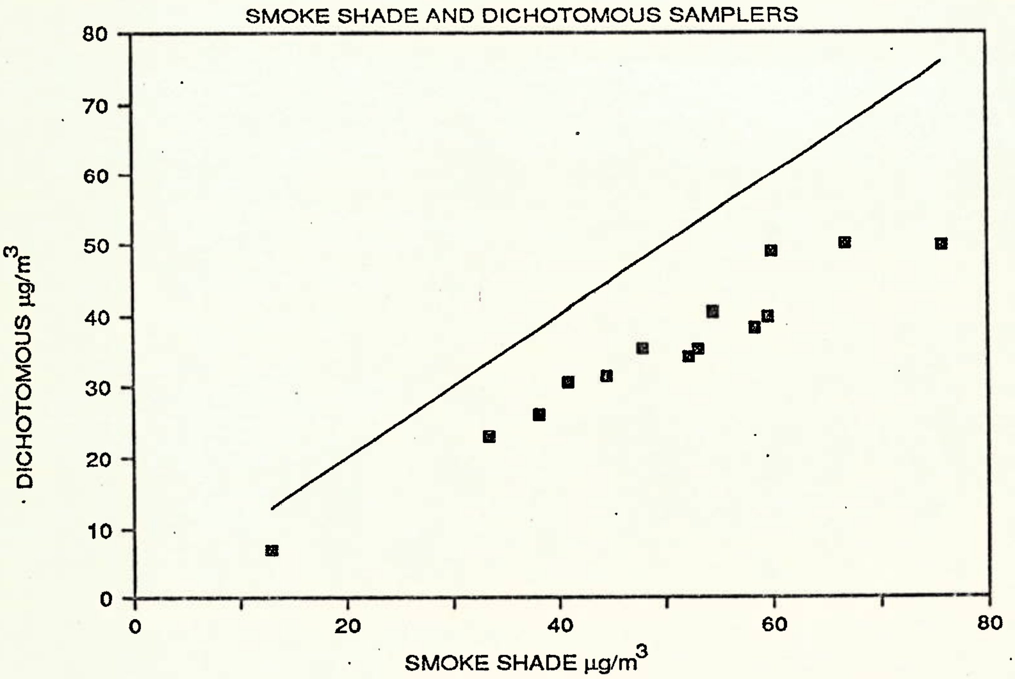
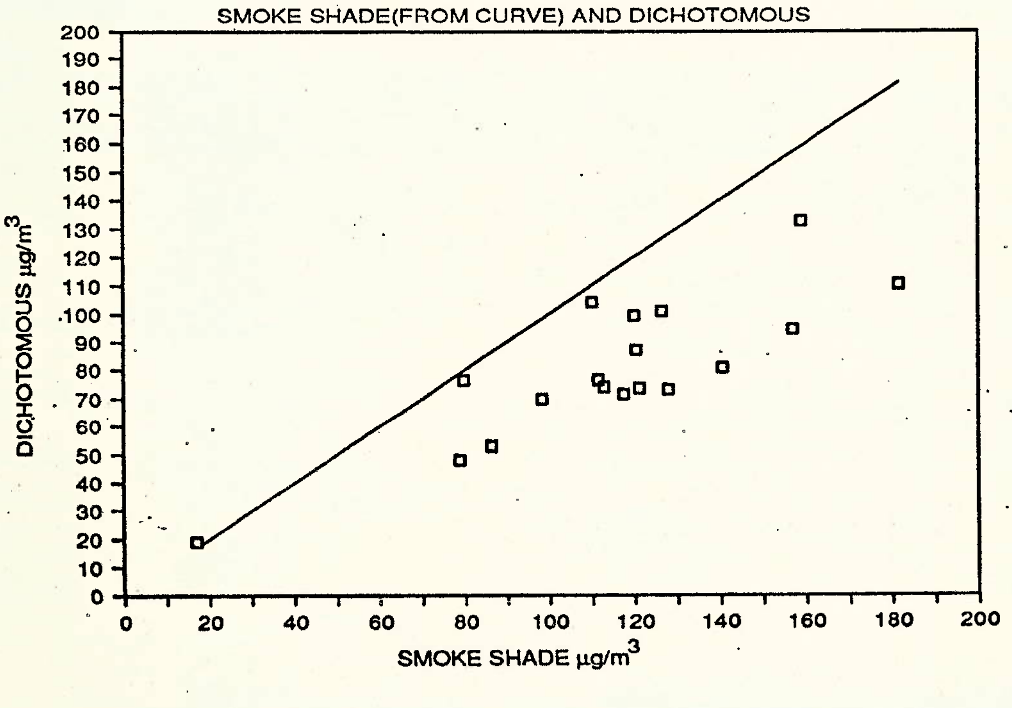


FIGURE 5b -MASS CONCENTRATION



Pinheiros. This new set of data is shown in Table 11 and is important to note that Hi-Vol samples were collect also. These data confirm that the smoke shade sampler does get particles in sizes greater than the dichotomous sampler and smaller than samples collected by the Hi-Vol sampler.

Table 11
Comparison of mass concentration obtained by 3 different methods.

DATE	IP µg/m3	S.Shade µg/m3	Hi-Vol µg/m3
Aug-24-89	56	73	105
Aug-25-89	105	132	154

Initially it was expected that the carbon concentration would be greater in the fine fraction but smaller in the inhalable fraction because of previous reports in the literature(35). But, as showed above, the smoke shade results are greater than the sum of fine and coarse particles (IP) in the dichotomous sampler. The configuration of the sampler was considered and some calculations were done in order to verify the reasons for this behavior.

McFarland et al.(25) evaluated in a wind tunnel study a funnel-shaped inlet similar to that adopted by the British Standard Institution. They found that for a wind velocity of 8 Km/hr the cut point size for the inlet is 10.8 µm when the sampling flow is 1.5 l/min. Unfortunately the funnel diameter is not specified. The sampler used in the present study is 45 mm in diameter and the sampling flow is 2 l/min. The average city wind speed is 9 Km/hr. From the funnel dimensions and flow rate the inlet velocity was calculated to be:

$$V = \frac{Q}{A} = 2.1 \text{ cm/sec}$$

where Q= flow = 2000 cm^3/min and A= the funnel area=15.9 cm^2.

The particle equivalent diameter for this velocity according to the Stokes-Cunningham sedimentation law is:

$$\tau_g = \frac{Cc\ \rho\ d_p^2\ g}{18\ \mu}$$

resulting in dp= 26.5μm

where Cc = Cunningham correction
ρ = particle density =1 g/cm^3 for equivalent diameter
d_p = particle diameter
g = gravitational acceleration
μ = air viscosity
τ = relaxation time

The resulting dp just says that in still air particles larger than 26.5 μm will not be captured by this inlet. Certainly other factors act on the inlet to change the collection characteristics of the inlet and wind speed seems to be the most important(26).

Some other components of the sampler can act to select the particles that reach the filter. The first curve of the tubing can capture particles. This was analyzed assuming that the particle has a behavior as in a cyclone with a number of turns equal to 0.5 (the curve is 180ł). The penetration of particles of several diameters was calculated using the formula(30):

$$\varepsilon = \frac{\pi N_t V_c \tau}{B_c/2}$$

where $P = 1 - \varepsilon$

ε = efficiency
P = penetration
N_t = number of turns
V_c = gas velocity
B_c = tube diameter
τ = relaxation time

The tubing also has 40 cm of horizontal length and some deposition of the particulate matter is to be expected. This mechanism was analyzed using the model of Natanson (Ref.25) and the same particle sizes used by McFarland. The penetration of particles through a horizontal tube with viscous air is:

$$P = 1 - \frac{2}{\pi} \{ 2 \phi \, SR + \sin^{-1} \phi^{1/3} - \phi^{1/3} \, SR \}$$

$$\phi = \frac{2 \, Vt \, L}{4 \, D \, U}$$

$$SR = (1 - \phi^{2/3})^{1/2}$$

P = penetration
V_t = terminal velocity
L = tube length
D = tube diameter
U = flow velocity in tube

The penetration for both cyclone and deposition are presented in table 12.

TABLE 12
Penetration of particles due to deposition and cyclone mechanism

Mechanism	Size µm	1.4	2.7	6.5	9.7	11.0	15.0	20.0	25.0
Cyclone	P=	0.997	0.988	0.935	0.861	0.824	0.688	0.484	0.264
Deposition	P=	0.997	0.989	0.935	0.856	0.815	0.656	0.389	0.046

It is can be seen in the table that both mechanisms show approximately the same penetration in the range from 1.4 to 15 µm. In the system used in these studies the deposition mechanism is more effective than the cyclone for collecting larger particles (smaller penetration). The total penetration for both mechanisms is given by the product of each partial penetration (P_{dep} X P_{cyc}). The total penetration for 11.0 µm is 0.672 and for 15 µm is 0.451. This means that for these combined models the expected cutpoint is between 11 and 15 µm.

Based on the experimental values with additional theoretical support, it can be concluded that the sampler used in this study has a cutpoint higher than the dichotomous sampler.

5. ANALYSIS OF THE HISTORICAL DATA

As previously described, CETESB has smoke shade data from several sites since 1973. It was possible to estimate the carbon concentration for those sites by using the method described previously. Five out of six stations were chosen for the study, and the criteria of choice was the sampling period. The sixth station had less data than the others.

5.1.Site description

5.1.1. Aclimacao

The site is located in a residential/commercial area. The sampling equipment is installed in a home garden at about 12m from the edge of a road. Traffic is considered moderate to heavy.

5.1.2. Moema

The neighborhood is basically residential but the sampling equipment is located at 45m away from a main avenue with a big shopping center and other commercial activities. The traffic is moderate to heavy and it seems (no statistics available) that the number of buses is not as high as at other sites of this study.

5.1.3. Praca da Republica

This site represents the downtown area with busy commercial activity. The traffic is heavy. The sampler is located 21 m from traffic lane.

5.1..4 Tatuape

The site is basically commercial/residential but there is some small influence of industries. The sampler is located in the gardens of a public library at 35 m from a very heavily travelled avenue.

5.1..5 Campos Eliseos

This station was located near a central bus station till 1978. In October of that year the fire station (which was the location of the sampler) was demolished and the sampler had to be moved to its present site. Since then the sampler has been installed in a home garden 15m away from the traffic lane. The traffic is very heavy, probably the heaviest of the all sites studied.

5.2. Data collection

The data were generated on a daily basis until 1982. After the automatic network started stable data generation, the manual network began operation on a 6-day cycle. For this study the automatic data were retrieved on a 6-day cycle in order to maintain the same data basis for the whole period.

The data available are from September 1973 to December 1988 except for the site Praca da Republica where the data series began in 1974. The completeness of the data is an important factor in the data analysis. Fortunately the malfunctioning of the network was minimal and in most of the years 100% of the data are available. In several years there was a maximum of 3 data failures (5.7% of the year's data).

The only real problem occurred in the Aclimacao site in 1986 when no data were generated in August and September. An estimation was done for August 1986 by using the average of the same months in 1985 and 1987. The same procedure was used for September. The annual average practically does not change with and without estimation of the missing data (with=33.6 $\mu g/m^3$ and without=33.1$\mu g/m^3$). This fact led to the conclusion that the estimation is acceptable.

5.3 Data Analysis

Analysis and interpretation are not only a function of the objectives of the monitoring program, but also of the specific nature and quality of available data. The Tatuape study(3) focused on the variation of the concentration during the day, and so the sampling was scheduled on a 1 hour basis.

In the beginning of the manual network the objective was to verify the attainment of the air quality standards; therefore, the samples were taken daily on a 24 hour sampling period. Now the manual network is operated with an objective of verifying the trends of particulate matter and for reasons of economics the samples are taken for 24 hours every six days. As a consequence, the data available permit the seasonality and annual trends to be shown.

The daily maximum becomes less important, although it can be estimated by statistical techniques. Obviously the accuracy of the monthly and annual average decreases when the sampling frequency is not 1/day, but it has been shown(38) that the annual average has a deviation of less than 2% when samples are taken every other day, and about 5% when the samples are taken every twelfth day.

5.3.1. Seasonal and Long Term Trends

The air quality in a region depends on the emission of pollutants and the climatological conditions for their dispersion. An analysis of the pollutants' emission related with transportation is not easy. In the case of Sao Paulo the change in the car fuel, the inauguration of the subway in the seventies and an economic crisis in the eighties are important factors that need to be taken in account. The city is still growing disorderly and it is impossible to foresee what will happen in a near future. This means that any analysis of long term trends should be viewed as a study of past to verify which factors are important in changes or trends, but not as a mathematical approach to predict the future.

5.3.1.1 Seasonal Pattern

To verify the seasonal trend, quarterly moving averages were calculated. This kind of average has some advantages over the monthly average. In the first place, the data are smoothed out.. In the second, the data are averaged in a three month period, the size of a season. Third, the number of samples is bigger and this becomes very important because the sampling schedule brings us only 5 to 6 samples each month. With the increase of the sample size it is possible to have samples taken in different days of the week, mainly week-ends, when the pattern of emissions is different.

Plots of the quarterly moving averages for each site are presented in figures 6 to 10. It is seen in the plots that the yearly maximum concentration occurs in the quarter that ends in July or August, depending on the year or the station. Some maximum are observed in June in the Moema site. The Campos Eliseos site shows a sudden change in 1979 because, as mentioned previously, the station location was changed.

The plots show the seasonality of the data and the levels of measured carbon in each site, but with this display it is difficult to compare the results from one site to another. To verify whether the variability of the sites are the same or not, all data were normalized according to the following equation:

$$N_d = (Q_d / Y_m) - 1$$

N_d=Normalized data
Q_d=Quarter data
Y_m=Year mean.

Plots of the normalized data are presented in figures 11 to 15. With normalization it is easy to see the variability of the data in relation to the mean. The sites Aclimacao, Tatuape and Republica have an intermediate annual average concentration, ranging between 30 and 55 $\mu g/m^3$ (see next item). The data variability of these 3 sites are approximately the same. Campos Eliseos presents the highest

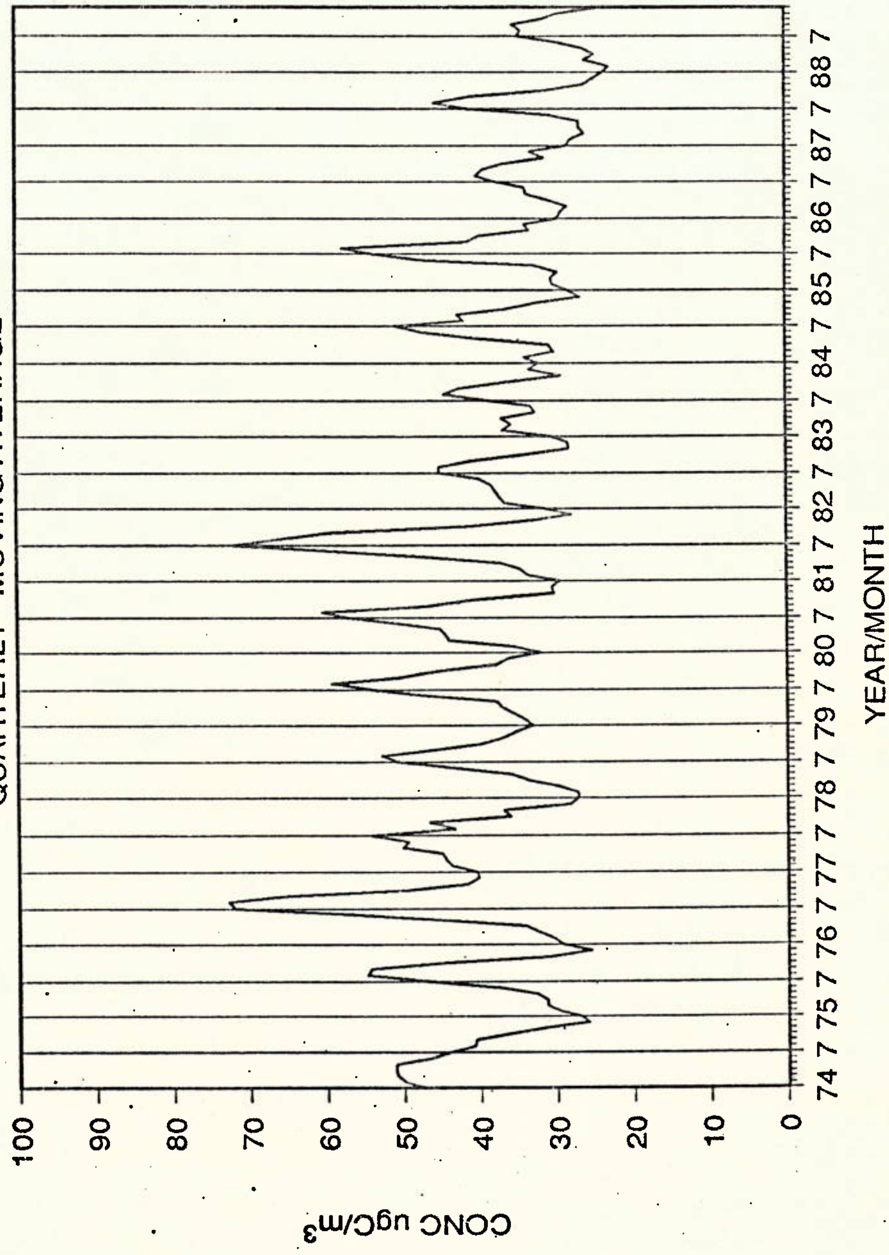


FIGURE 6 - ACLIMACAO

QUARTERLY MOVING AVERAGE

FIGURE 7 - CAMPOS ELISEOS

QUARTERLY MOVING AVERAGE

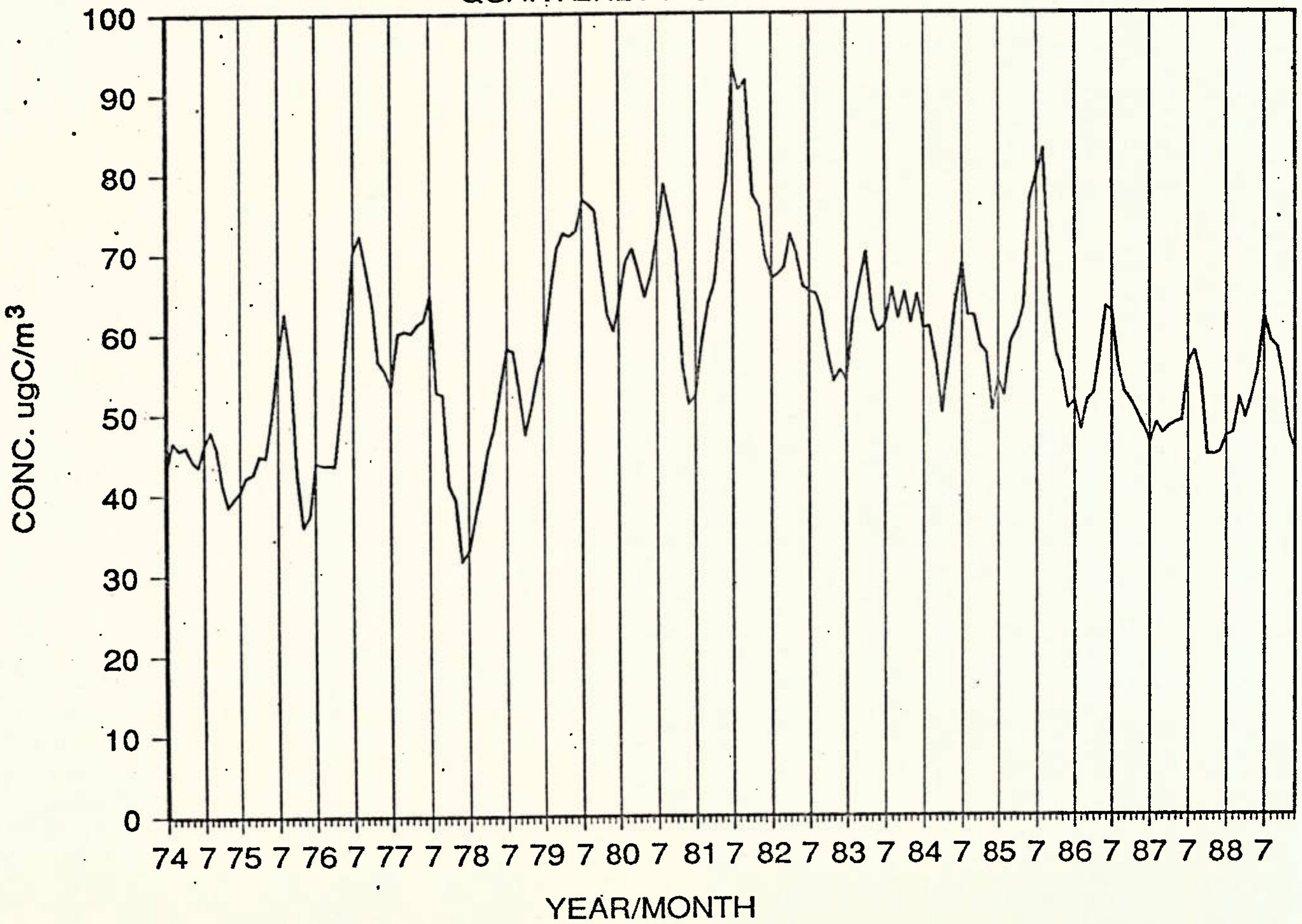


FIGURE 8 - MOEMA

QUARTERLY MOVING AVERAGES

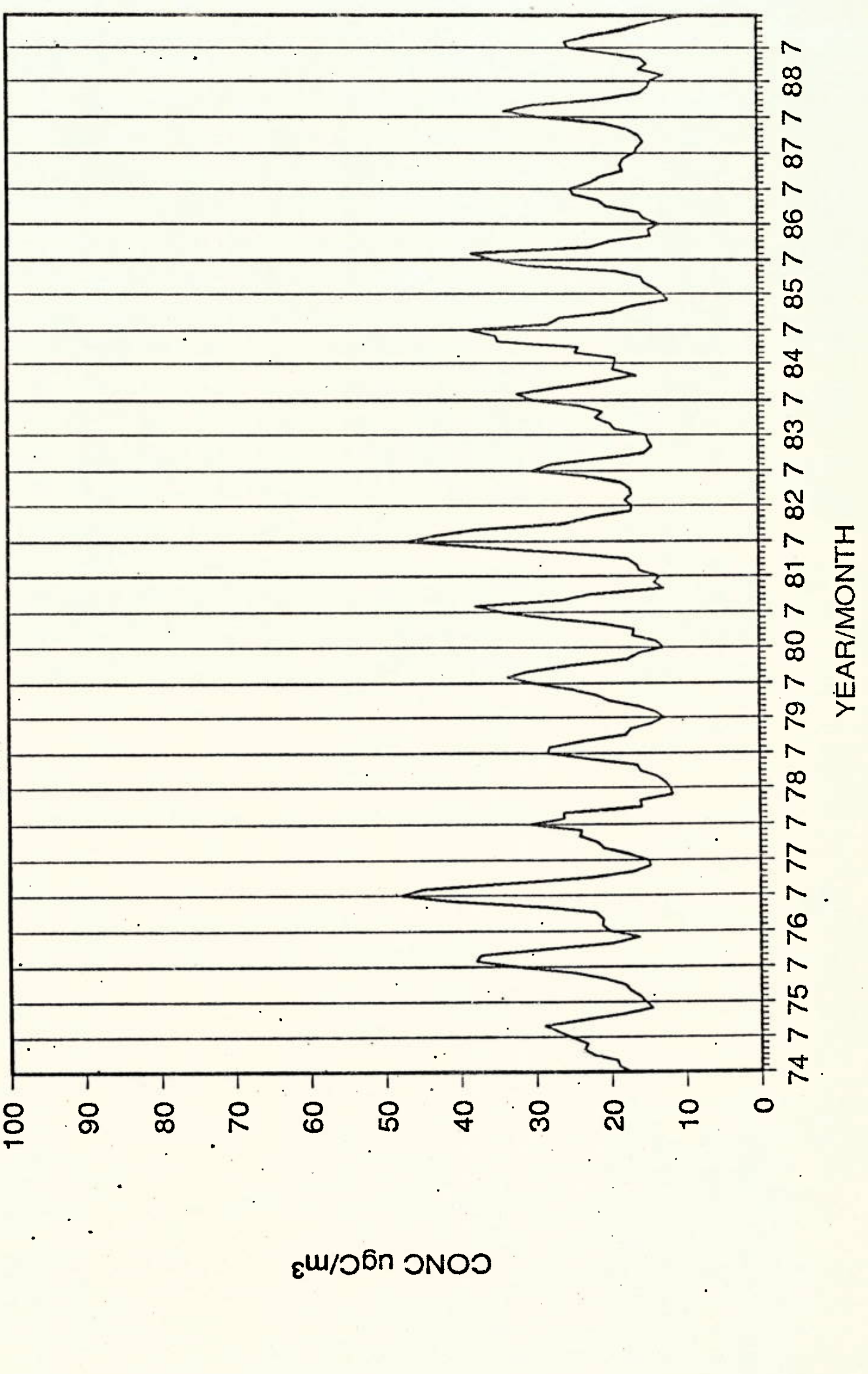


FIGURE 9 - PRACA da REPUBLICA

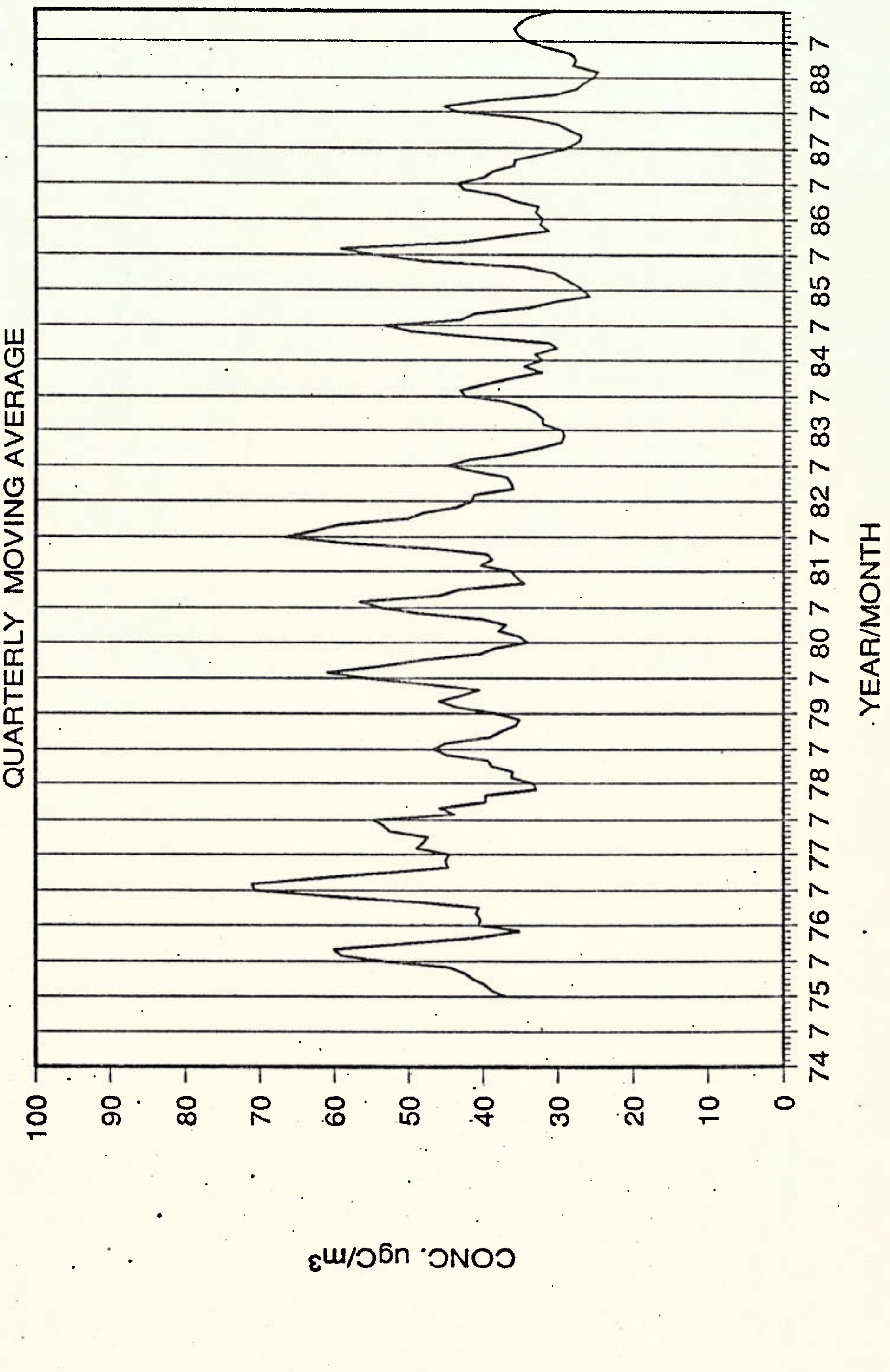


FIGURE 10 - TATUAPE

QUARTERLY MOVING AVERAGE

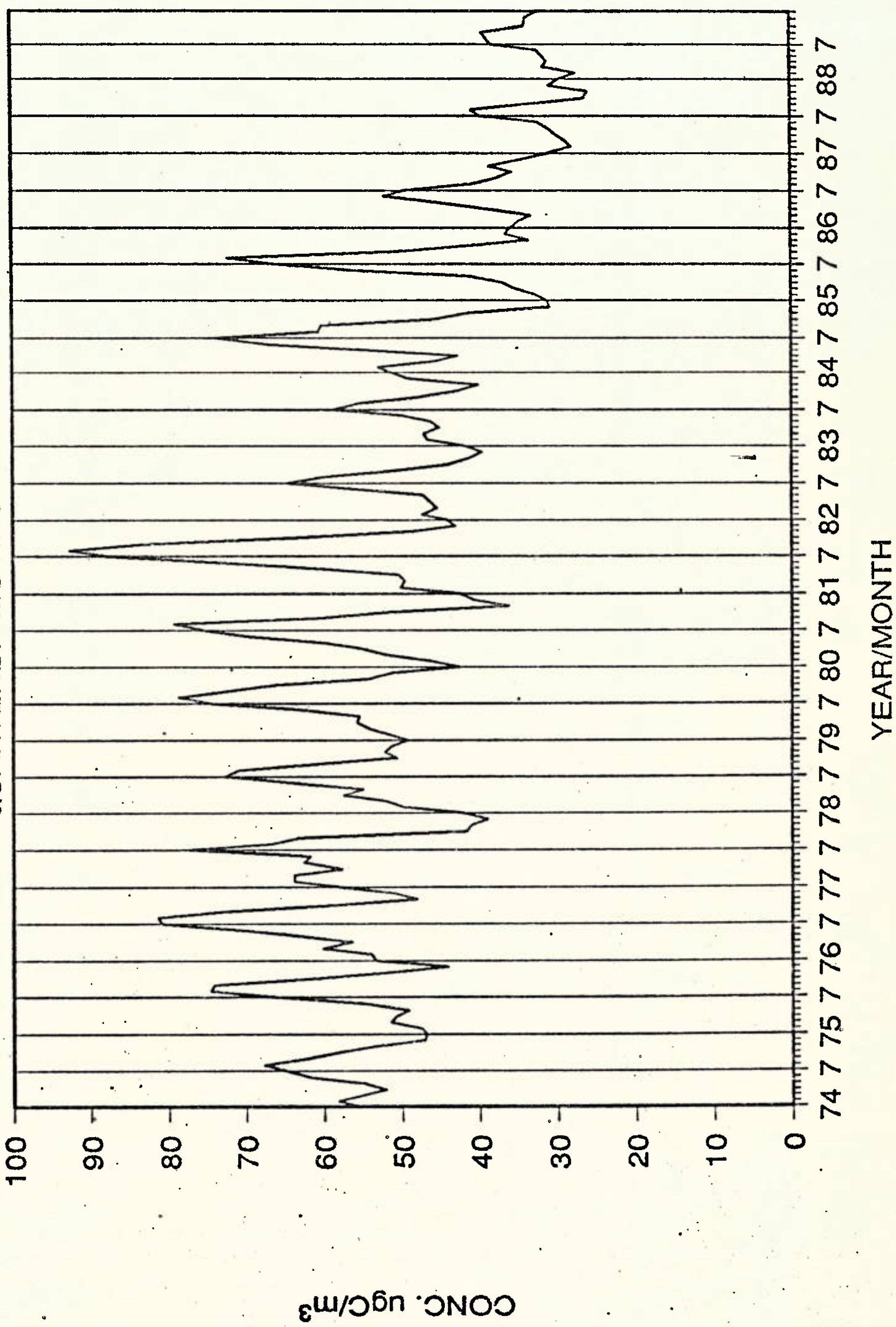


FIGURE 11 - ACLIMACAO

NORMALIZED QURTERLY AVERAGES

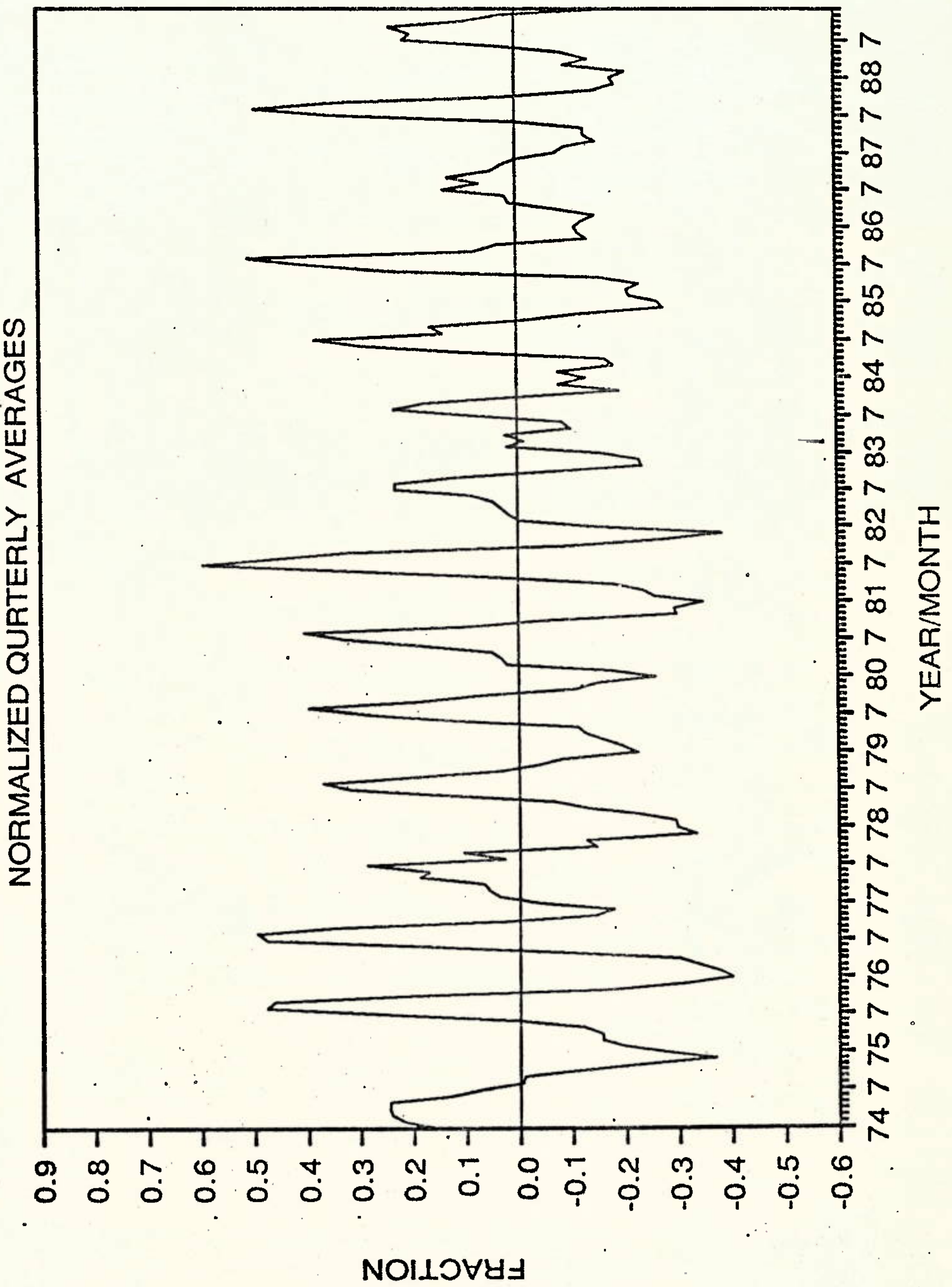


FIGURE 12 - CAMPOS ELISEOS

NORMALIZED QUARTERLY AVERAGES

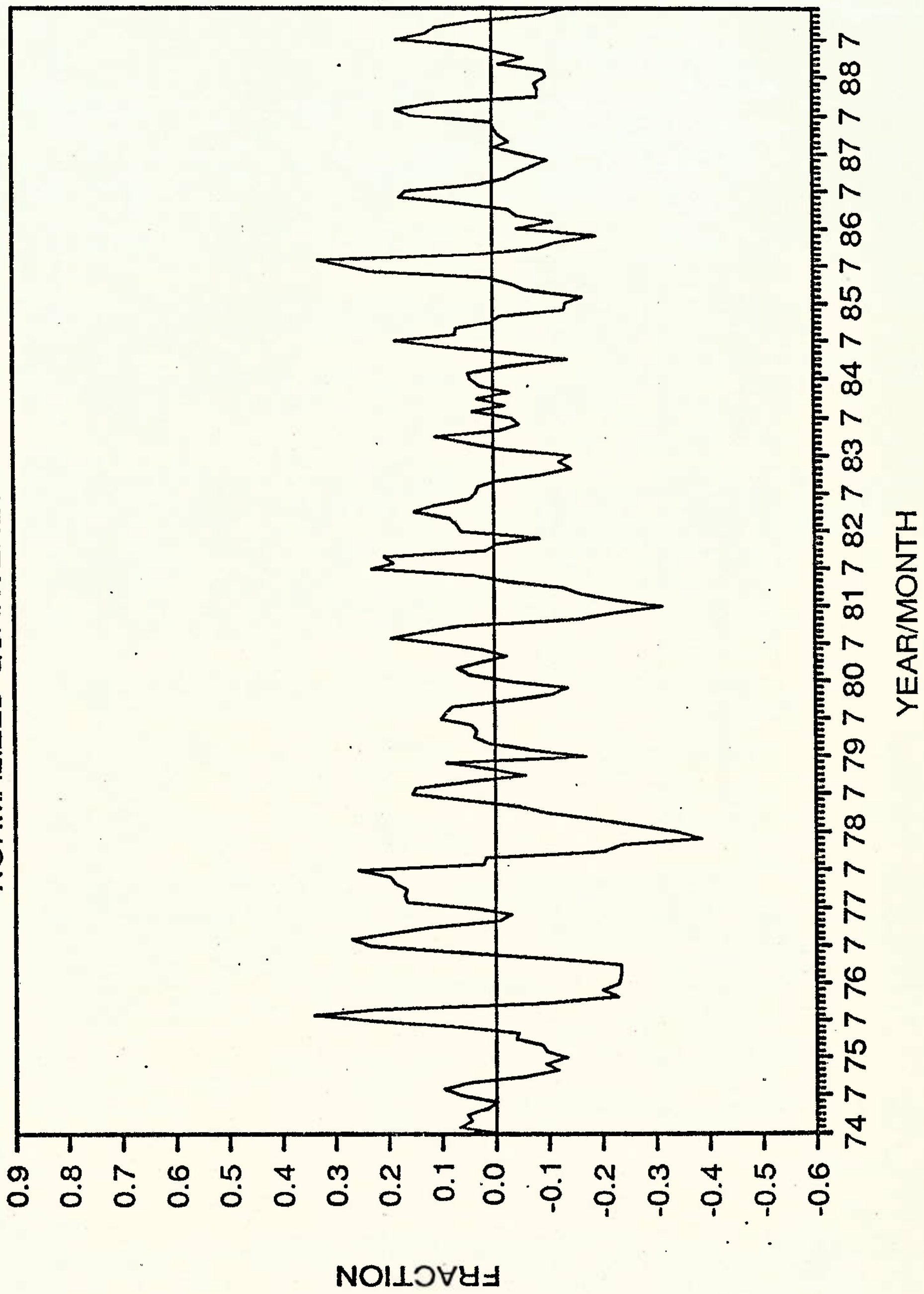


FIGURE 13 - MOEMA

NORMALIZED QUARTERLY AVERAGES

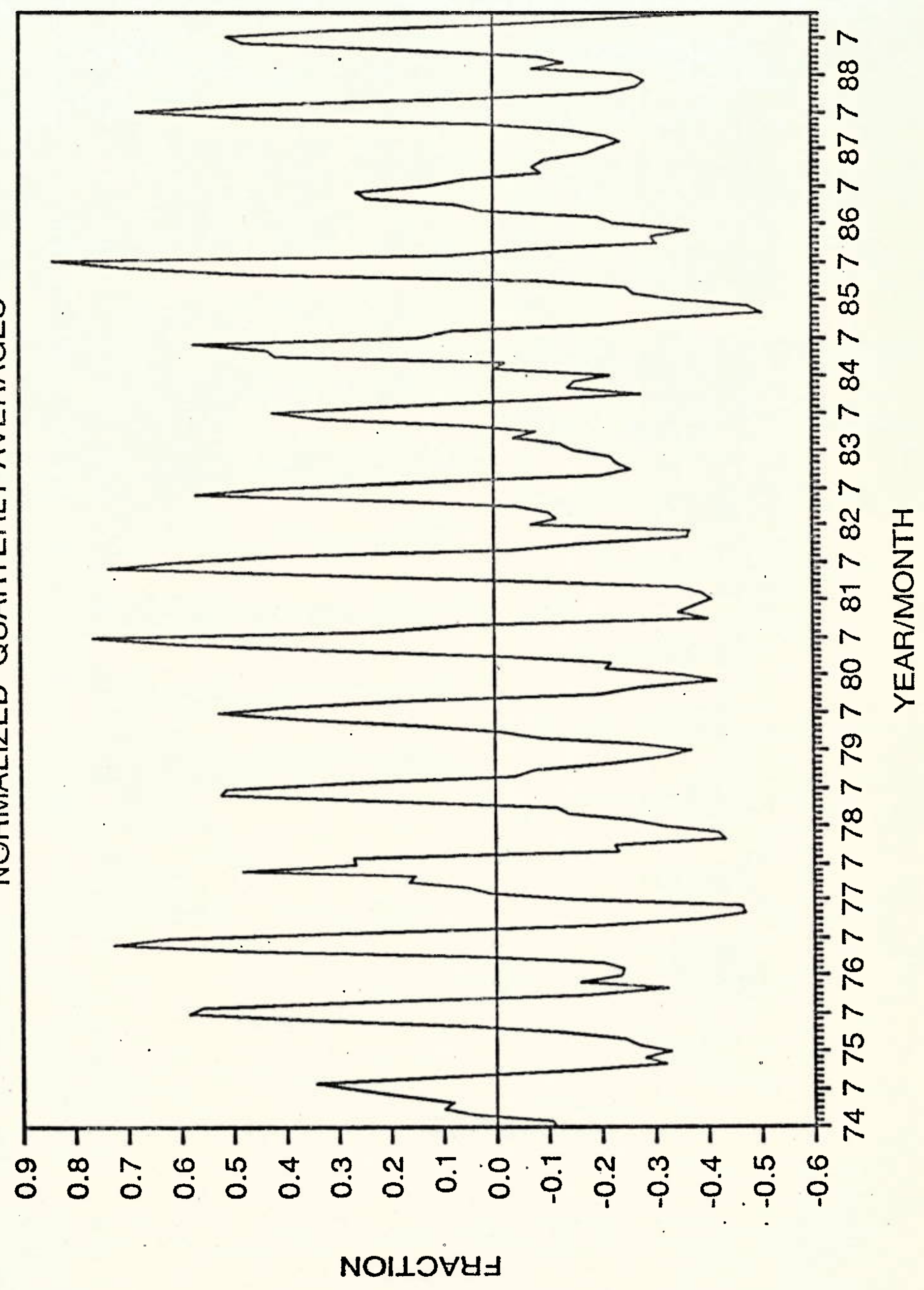


FIGURE 14 - PRACA da REPUBLICA

NORMALIZED QUARTERLY AVERAGES

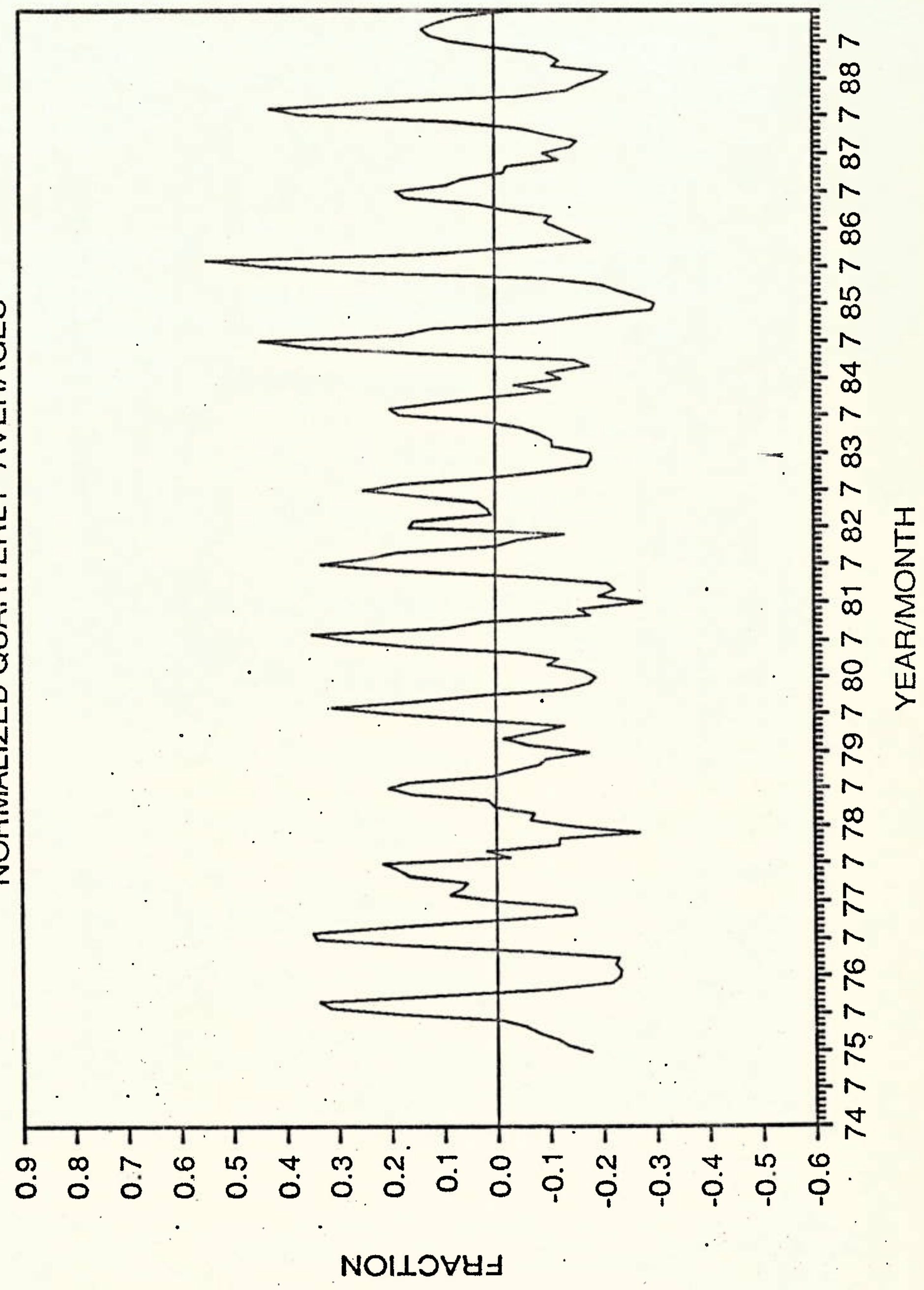
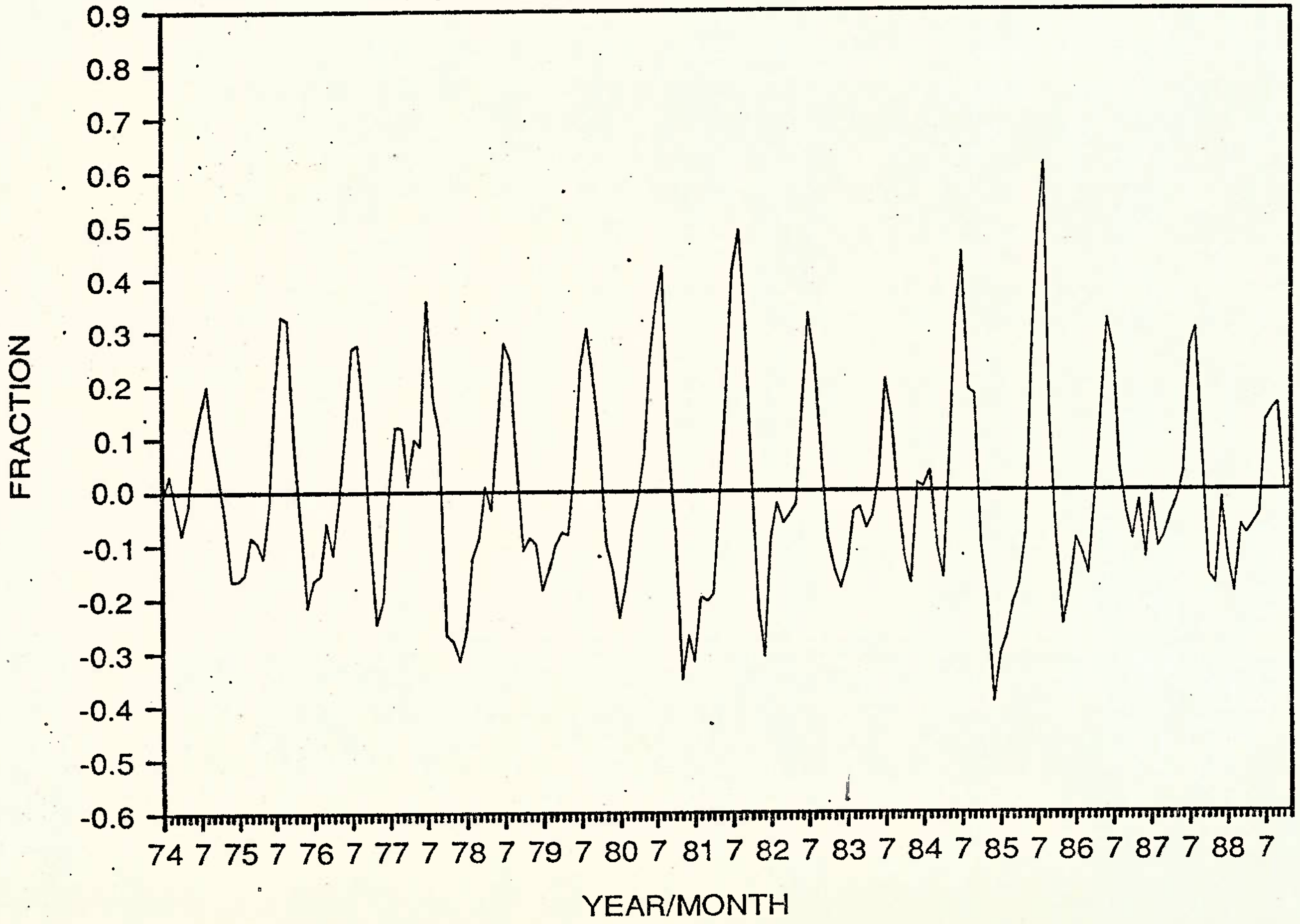


FIGURE 15 - TATUAPE

NORMALIZED MONTHLY AVERAGES



annual average, ranging between 55 and 80 μg/m^3, and the variability is the lowest observed in the data of all stations. The last site, Moema, presents the lowest annual average (range 20-30 μg/m^3) and also the highest variability. These observations suggest that the variability of concentration due to seasonal effects is somehow inversely proportional to the observed annual average.

5.3.1.2 Annual trends.

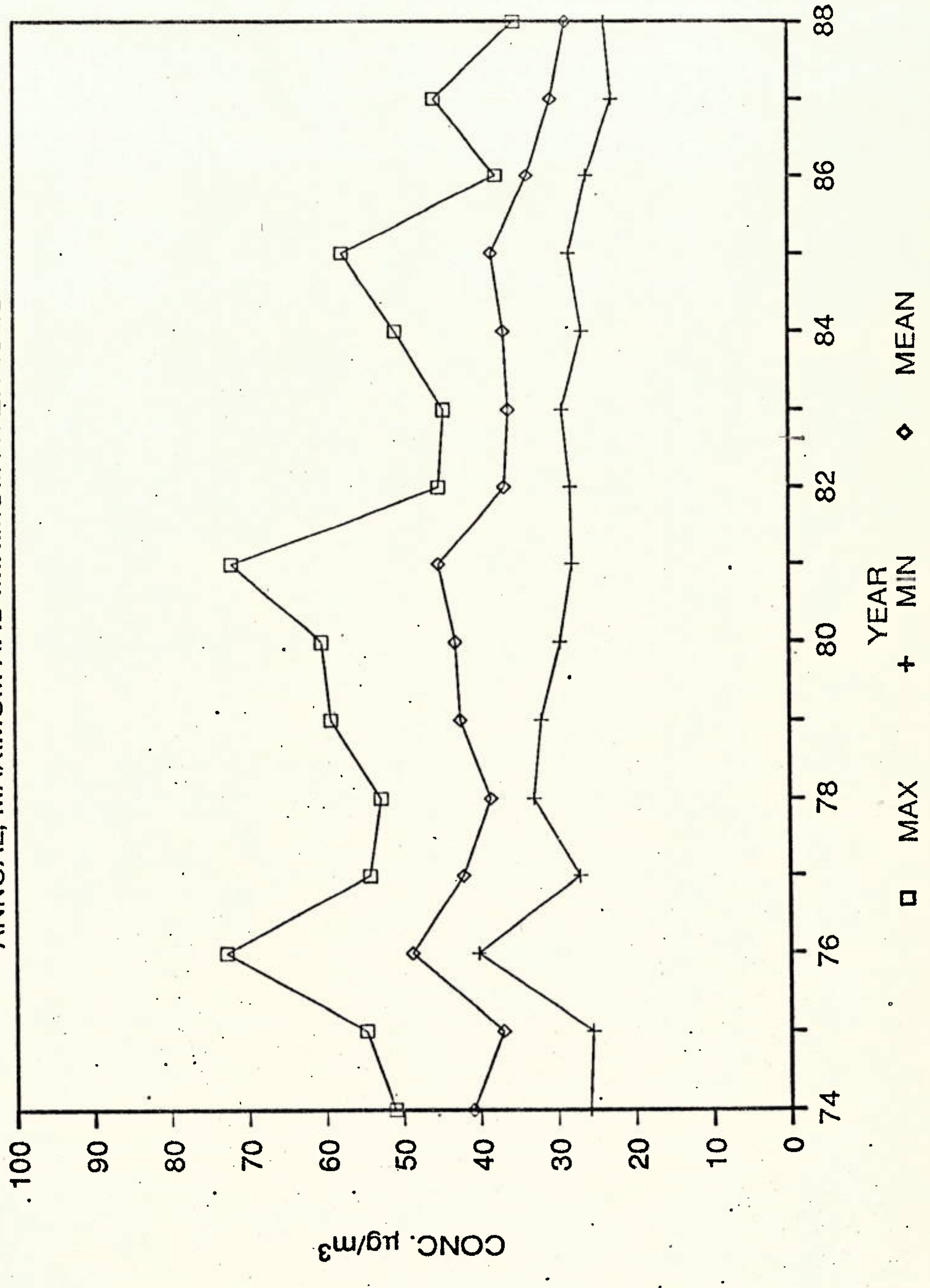
Annual trend analysis is based on the plots presented in figures 16 to 20. The annual as well as the maximum and minimum quarterly averages were plotted (data in appendix D). The minimum averages occur in different months, in general between November and January, depending on the year and the station. Therefore some "summer" data could be the same in 2 different years if the minimum were calculated in a calendar year. Then, the minimum average was calculated between two subsequent maximum data points; for example the minimum observed between September 1975 and August 1976 was recorded as the 1975 minimum.

Another observation about the data is that Campos Eliseos' averages were recorded only from the year that the sampler was moved (1979).

The first observation that should be mentioned is concerned with the overall trend of the annual average. This trend analysis depends on the time-frame considered. A sudden drop in the first year's concentration could maintain

FIGURE 16 - ACLIMACAO

ANNUAL, MAXIMUM AND MINIMUM AVERAGES



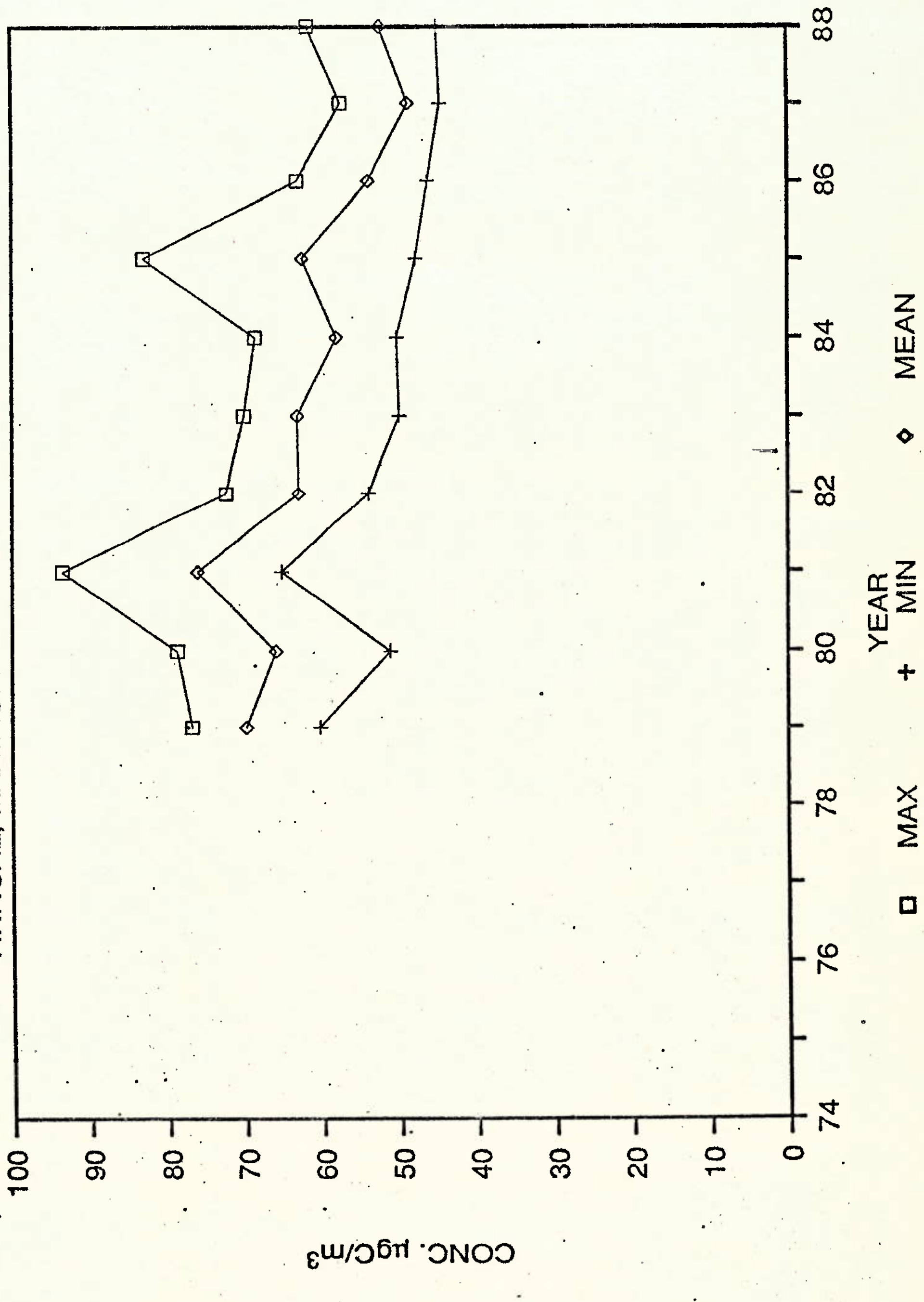


FIGURE 17 - CAMPOS ELISEOS

ANNUAL, MAXIMUM AND MINIMUM AVERAGES

FIGURE 18 - MOEMA

ANNUAL, MAXIMUM AND MINIMUM AVERAGES

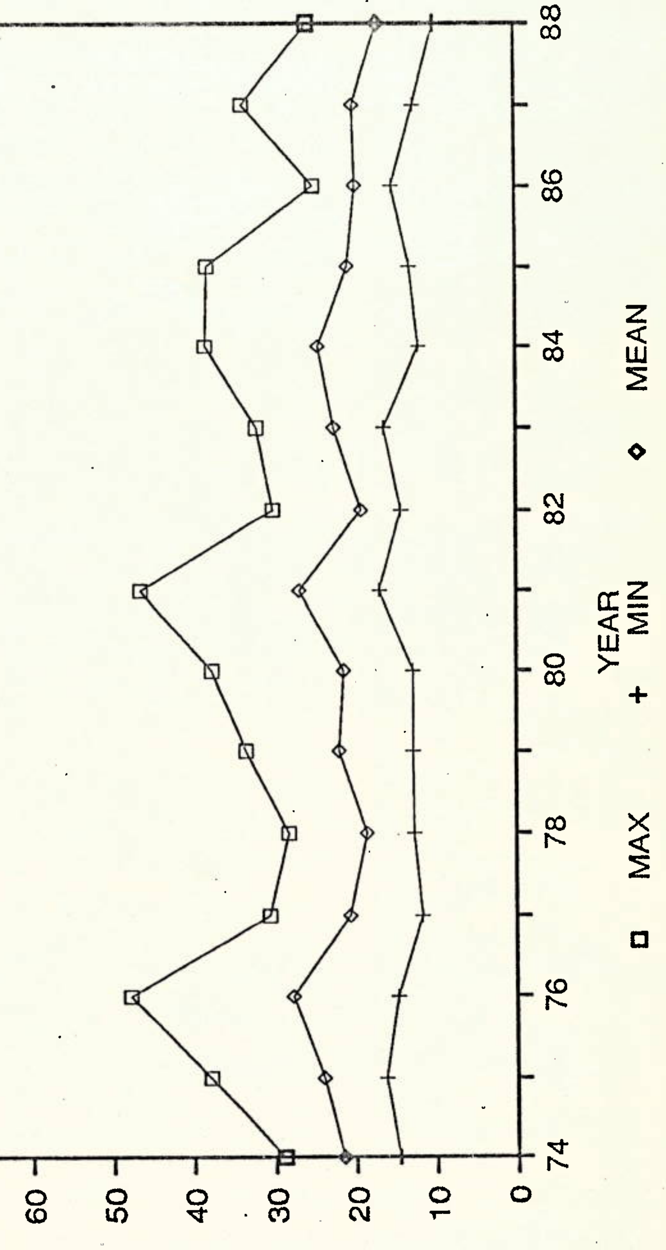


FIGURE 19 - PRACA da REPUBLICA

ANNUAL, MAXIMUM AND MINIMUM AVERAGES

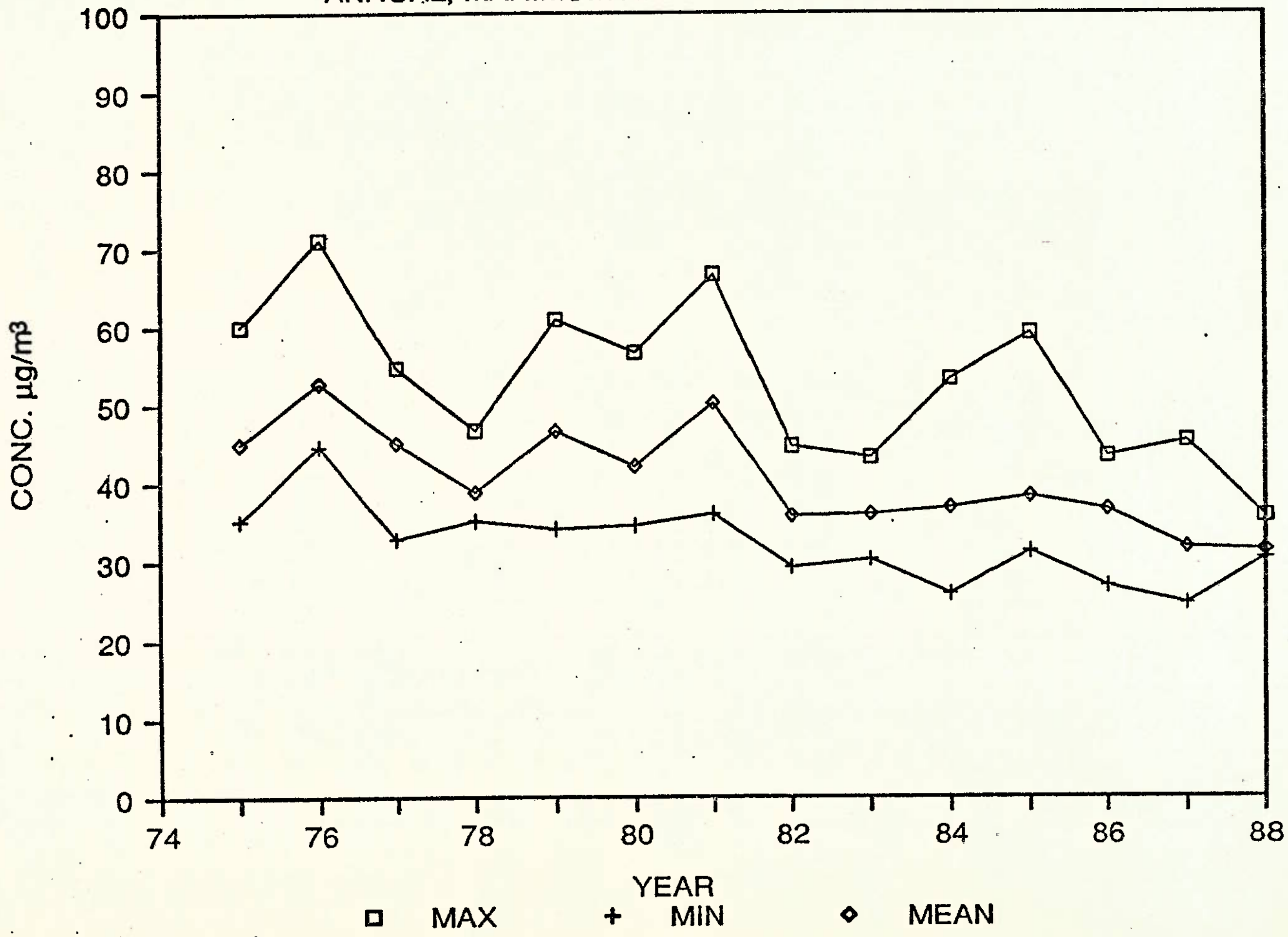
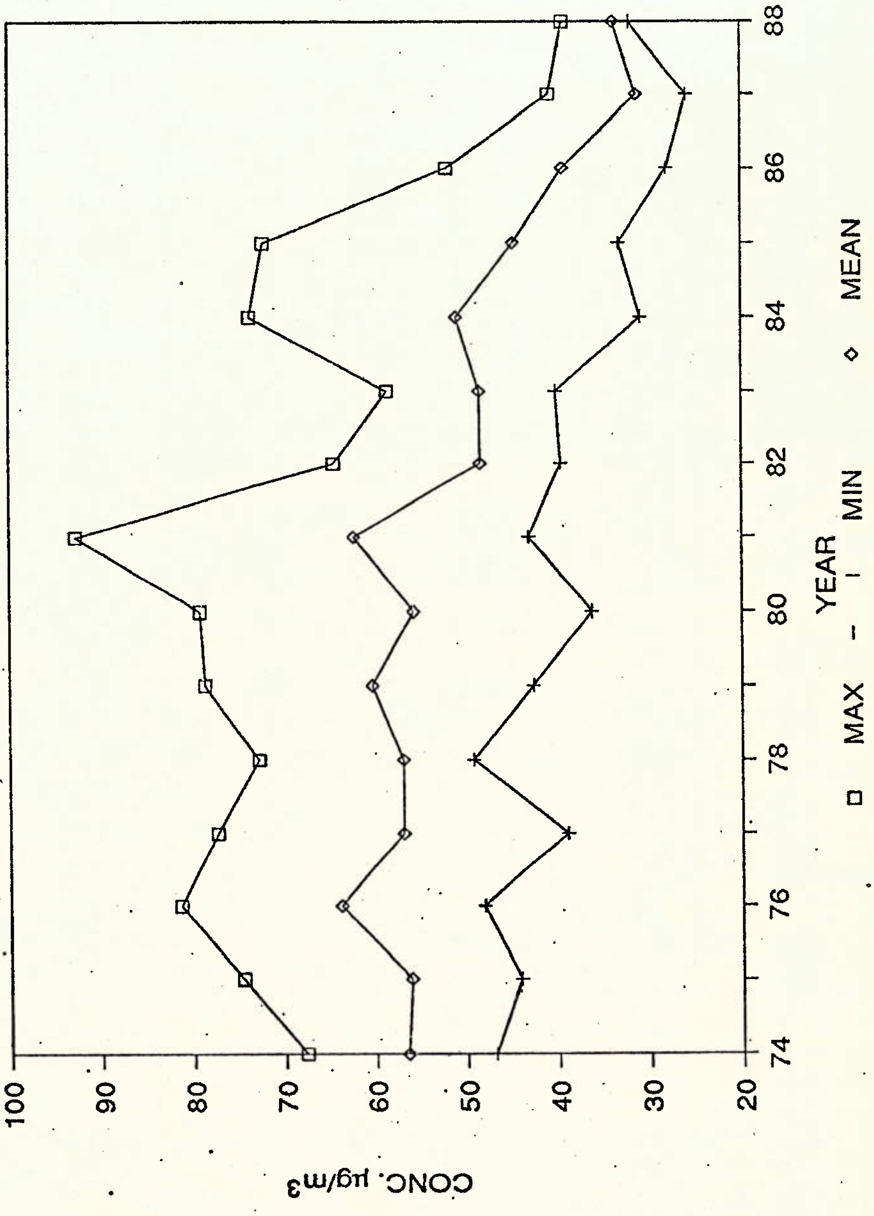


FIGURE 20 - TATUAPE

ANNUAL, MAXIMUM AND MINIMUM AVERAGES



a negative trend in a whole series, even if in later years the trend is stable. For this reason our data were analyzed in two different time-frames; the whole series and the latest 6 years. The choice of 6 years was based on changes in traffic patterns due to the inauguration of the subway, as will be discussed further on.

The technique used for measuring the statistical significance of trends was the Daniel's test for trends using the Spearman rank correlation coefficient as described by WHO(36).

"Given a time period $(t_1,...,t_n)$ and their corresponding value of yearly average $(y_1,...,y_n)$ ranked from the lowest to the highest, the test statistic is calculated as the rank-correlation coefficient:

$$r_s = 1 - (6 \Sigma d_i^2)/(N^3 - N)$$

where d_i is the difference between the t variable (time starting with period one to period N) and the t' variable ranked by measured concentration for the i^{th} observation. The absolute value of r_s, the coefficient of rank correlation, is compared with the critical value W_p in a statistical table of Spearman rank correlation coefficients. If $r_s > W_p$ then a trend is declared significant. A negative value of r_s indicates a downward trend". The calculated values of the test as well as the Spearman coefficient are presented in table 13.

TABLE 13
Results of the trend test

SITE		COMPLETE SERIES			6 YEAR SERIES		
	Yrs	r_s	W_p	Trend	r_s	W_p	Trend
Aclimacao	15	-0.70	0.44	YES	-0.77	0.83	NO
C.Eliseos	10	-0.93	0.56	YES	-0.89	0.83	YES
Moema	??	-0.42	0.44	NO	-0.88	0.83	YES
P.Republica	14	-0.80	0.45	YES	-0.60	0.83	NO
Tatuape	15	-0.80	0.44	YES	-0.88	0.83	YES

It can be concluded from table 13 that in the complete series, all stations show negative trends, although Moema's trend is not statistically significant. The 6 year series results show a negative trend in C.Eliseos,Moema and Tatuape, but Aclimacao and P.Republica show some decrease in the data although without statistic significance. The plots and the tabled results show a general decrease in particulate carbon pollution in SPMA.

Calculation of the decreasing rate in the atmospheric carbon was carried out using a linear regression model. Regressions were also calculated on the maximum and minimum quarterly averages to verify whether the overall reduction (annual average) occurs due to similar reduction in "summer" and "winter" or whether the reduction occurring in one particular season is more important. The reduction rate as well as the regression r^2 for the complete series and for the latest 6 year series are presented in tables 14 and 15.

Table 14
Reduction rate of particulate carbon in the complete series

SITE	REDUCTION RATE $\mu g/m^3$ year Annual	Maximum	Minimum	r^2 annual rate
Aclimacao	0.86	1.35	0.44	0.51
C.Eliseos	2.39	2.45	1.79	0.76
Moema	0.27	0.40	0.14	0.17
P.Republica	1.24	1.56	0.93	0.63
Tatuape	1.88	2.22	1.40	0.71

Table 15
Reduction rate of particulate carbon in the latest 6 years

SITE	REDUCTION RATE $\mu g/m^3$ year Annual	Maximum	Minimum	r^2 annual rate
Aclimacao	1.72	2.30	1.18	0.74
C.Eliseos	2.59	2.70	1.24	0.70
Moema	1.20	1.70	0.80	0.78
P.Republica	1.12	2.18	0.20	0.63
Tatuape	3.92	6.14	1.72	0.86

The tables show that the regression model as applied is useful for averaging out the reduction rate occurred during the past years, but has low significance as a predictor model because the r^2 is poor.

Although both the "winter" maximum and the "summer" minimum show a reduction rate, the winter reduction plays the most important role. The reduction which occurs in the winter quarter series is always bigger, and in some stations it is about the double of that observed in the summer quarter.

Some stations present a remarkable difference in the reduction rate when the complete and the 6 year series are compared. The Tatuape station shows the most spectacular reduction and this fact will be discussed in the next section.

A final observation about the data is that in all stations a kind of cycle seems to occur. By observing the maximum quarterly data in the plots it is possible to see that for every 5 year cycle, beginning in 1977, the data reaches a lower value and in the next years they rise again starting a "new cycle". This presumption is speculative because the data series is still too small to permit a secure generalization. On the other hand it can indicate an important weather cycle and so attention has to be paid to it in future data analysis.

5.4 Data Interpretation.

5.4.1 Seasonal Data

The seasonal behavior of air pollution has a special meaning in highly polluted cities such as Sao Paulo. In the months in which unfavorable meteorological conditions for atmospheric dispersion occur, the pollutant concentration increases and special enforcement should be carried out. Then, the determination of the "polluted season" becomes highly necessary. In terms of particulate carbon this was determined in this study.

Finally, it should be emphasized that the usage of heating systems is practically nonexistent in the SPMA, therefore, the winter data is not affected by any kind of special seasonal sources.

5.4.2 Long Term Data

Two categories of source should be considered in an attempt to understand the behavior of the data series; stationary and mobile sources. Most of the particulate control program in Sao Paulo was directed to stationary sources. A significant reduction was achieved in terms of particulates as a general pollutant(10), but this did not affect proportionally the particulate carbon at the sites studied. This can be seen in table 16.

TABLE 16
Reduction in industrial emission and in atmospheric concentration
1979 data=100%

YEAR	1979	1983	1987
Emission (ton X 10^3/year)	156	70	48.5
Reduction	-	55%	69%
Concentration ($\mu g/m^3$)*	48.2	41.3	32.5
Reduction	-	14.3%	32.6%

* average of all station data

From 1979 to 1983 a 55% reduction in the industrial emission occurred, but only 14.3% reduction in the atmospheric concentration was noticed. From 1983 to 1987 a smaller reduction in the emission was followed by a greater reduction in the concentration. This fact shows that concentrations at the sites of measurement have low components of industrial emission and are mainly affected by other sources (the mobile sources). The reasoning presented above is perfectly in accordance with the results obtained by the use of receptor models, which showed that the main source of carbonaceous material in the SPMA is transportation (11).

An analysis of the pollution caused by transportation should take in account that the Brazilian fleet has light duty vehicles using only gasoline or alcohol as fuel. Diesel fuel is restricted to buses and trucks. The main factors that could have caused the observed reduction in the atmospheric concentration are discussed below.

Gasohol

The usage of a mixture of gasoline and alcohol as car fuel started in 1979. An important aspect that should be emphasized is that the gasohol program was implemented at once. So a sudden drop in the concentrations would be expected to occur if the contribution of car emissions is important. It should be recalled that the lead concentration in the SPMA atmosphere dropped drastically as a consequence of the alcohol program. Yet the carbon concentration did not decrease in the two subsequent years after the beginning of the program. Thus the usage of gasohol instead of gasoline does not appear to affect the atmospheric carbon concentration in the SPMA.

Enforcement

Laws for emission control of mobile sources have only recently been established. The 1980 federal regulation sets the black smoke emission limits for in-use diesel vehicles. The effectiveness of this law depends on the degree of enforcement achieved. The enforcement is stronger in the winter so this could explain that the reduction in carbon concentration is greater in the winter than in the summer.

Subway Inauguration

Some subway stations were inaugurated near the sampling sites during the study period. The Praca da Republica subway station was inaugurated in April 1982 in the same square where the air sampler is located. An analysis of the Praca da Republica plot (fig. 16) and reduction rates (tables 15 and 16) does not show any influence of the subway on the data. This site is in the very downtown and the subway probably did not change the traffic pattern in that area.

6. FINAL COMMENT

The decrease in the carbonaceous material concentration is a fact demonstrated in this work. It is also a fact that during all the period of this study, legislation about vehicle emissions had not yet come into force, so that control was based only on a regulation for in-use diesel vehicles. This kind of control as well as the changes in traffic pattern due to inauguration of some subway branches are the reasons thought to be the responsible for the observed reduction in the concentrations of the carbonaceous material in the SPMA.

Despite the fact that concentrations of the carbonaceous material in the SPMA have been decreasing during the last 15 years, the levels still are very high. To emphasize this statement data has been presented which compares the levels of total carbon in some U.S. cities to those obtained in SPMA, including the results of this study (Figure 21).

7. CONCLUSIONS

7.1 About the method

One of the objectives of this work was to estimate the carbonaceous material concentration using a historical data base. To do this a method had to be established that would take into account the fact that the data available were based on reflectometric measurements. The method here presented has a curve that relates the reflectance with total carbon concentration obtained by the thermal method.

The total carbon was the specie of choice for two reasons. First, it was the curve that presented the best correlation coefficient. Second, the thermal method splits the organic carbon and elemental carbon species into operational definitions. The total carbon has better consistency for comparisons, and our intention was to compare the Sao Paulo data to data of some U.S. cities. The calibration curve presented an acceptable accuracy when tested at the five sites where the historical data were to be analyzed. By comparing the 1987 estimated data to other Sao Paulo 1987 data it was possible to see that there was very good consistency (see figure 21). The comparison shows that the estimation is quite reliable.

7.2 About the historical data

7.2.1 Seasonal analysis

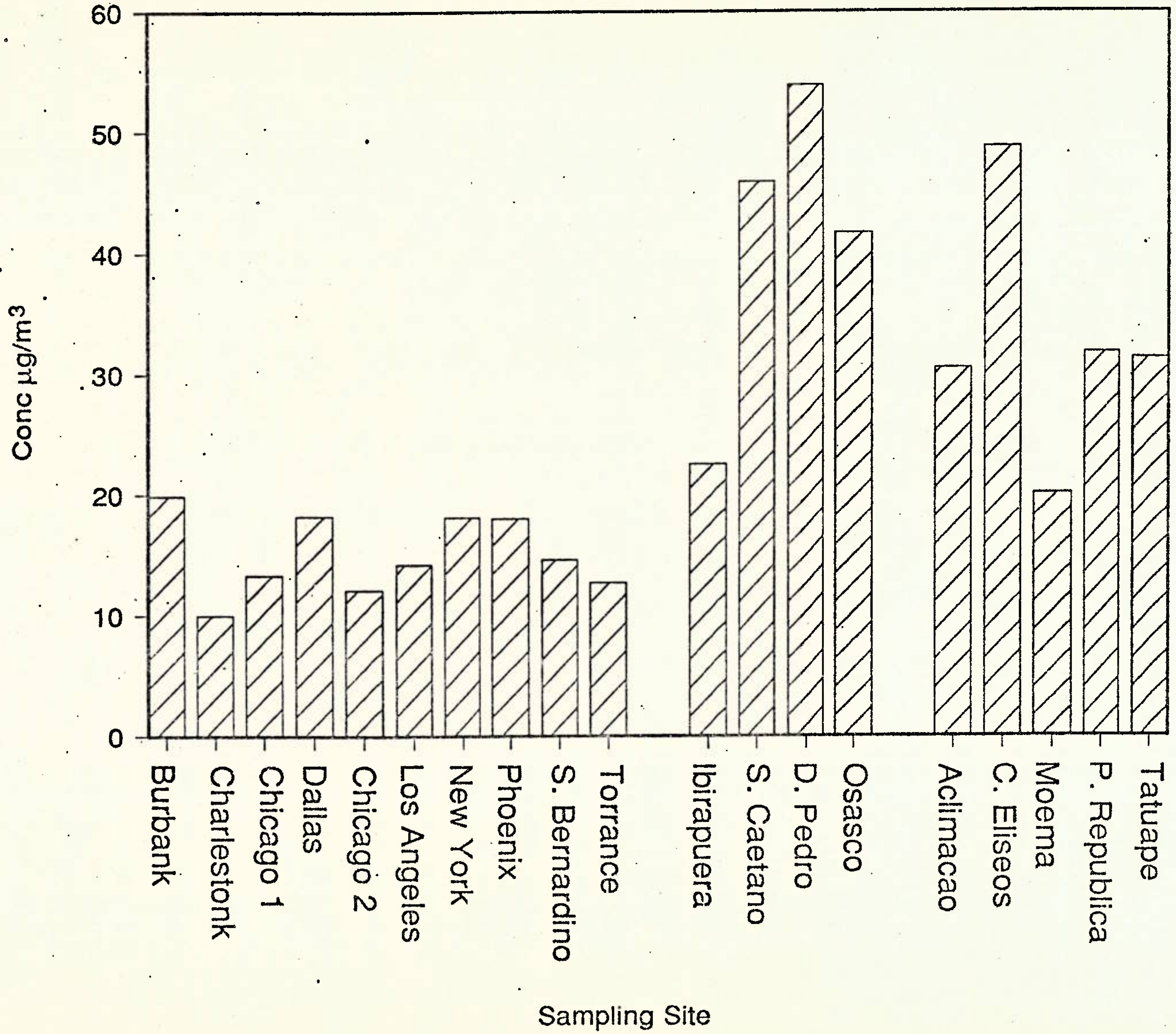
By analyzing the historical data for total carbon it was possible to verify the seasonal behavior of this pollutant. It was observed that the most polluted season refers to the quarter ending in July or August depending on the year and the station. The season with the lowest data is not well defined, but in general are those ending in November, December or January depending on the year and the station.

7.2.2 Annual Trend

Analysis of the annual trends showed that all stations have decreasing total carbon data in the complete period as well as in the latest six year series. Although this trend presents no statistical significance for one site in the

FIGURE 21 - S. PAULO AND SOME U. S. CITIES

CONCENTRATIONS OF TOTAL CARBON



completed series and for two sites in the 6 year series, it shows that at least these levels are not rising.

By looking at the complete study,it is possible to see that the Tatuape site showed the greatest reduction rate in the 6 year series. By comparing the annual average to the winter and summer data in each station, it is possible to conclude that the reduction rate is greater in the winter.

An attempt was made to explain the behavior of the data. It was possible to verify that the industrial emission reduction was not followed by an equivalent reduction in the atmospheric carbon concentrations. On the other hand, the inauguration of a subway branch in the Tatuape region, that caused an reduction in bus traffic, was followed by a sharp decreasing in the concentrations in that site. This observation leads to the conclusion that carbonaceous pollution is mostly due to traffic, what is supported by the ECA-SP study. A better and quantitative analysis would be possible if statistical data of traffic and a better estimate of emissions were available.

BIBLIOGRAPHY

1- Alonso, C.D., Martins, M.H.R.B., Romano, J.," Teores de Material Particulado Carbonaceo na Atmosfera da Grande Sao Paulo" ,ECA-SP No 2, CETESB, Sao Paulo, Brasil, 1988 .

2- Alonso, C.D., Romano, J.,"Medicao de Carbono Particulado no Ar"., Presentation at 40th Reuniao Anual da Sociedade Brasileira Para o Progresso da Ciencia, Sao Paulo, Brasil, June 1988.

3- Alonso, C.D., Romano, J., Acquaviva, W., Santos, M.S., "Estudo de Material Particulado na Atmosfera de Tatuape", Presentation at 38th Reuniao Anual da Sociedade Brasileira Para o Progresso da Ciencia, Curitiba, Brasil, June 1986.

4- Alonso, C.D., Romano, J., Barbosa, H.,"Teores de Chumbo nas Atmosferas Urbanas da Grande Sao Paulo", Presentation at 13th Congresso Brasileiro de Engenharia e Saneamento Ambiental;Maceio, Brasil(1985).

5- Alonso, C.D., Romano, J., Martins, M.H.R.B., "Teores de Material Particulado Fino, Grosso, Inalavel e Total na Atmosfera da Grande Sao Paulo", ECA-SP No 1, CETESB, Sao Paulo, Brasil, 1988.

6- Ames, B.N., Durston, W.E., Yamasaki, E., Lee, F.D., "Carcinogens are Mutagens: A Simple Test System Combining Liver Homogenates for Activation and Bacteria Detection", Proceedings of National Academy of Sciences, Vol.70, pp 2281, 1973.

7- Bailey, D.L.R., Clayton, P., "The Measurement of Suspended Particulate and Carbon Concentrations in the Atmosphere Using Standard Smoke Shade Method",Warren Spring Laboratory, Stevenage, England 1980.

8- Cadle, S.H., Groblicki, P.J., Stroup, D.P.," Automated Carbon Analyzer for Particulate Samples", Anal.Chem., Vol.53, pp2201-2206,1980.

9- CETESB, "Qualidade do ar na regiao metropolitana de Sao Paulo e em Cubatao", CETESB, Sao Paulo, Brasil, 1987.

10- CETESB, "Padroes de Emissao por Tipologia de Fonte". CETESB, Sao Paulo, Brasil, 1987.

11- CETESB, Aplicacao de Modelo Receptor em Amostras de Sao Paulo, ECA-SP No 3, CETESB, Sao Paulo, Brasil 1989.

12- Chang, S.G., Brodzinsky, R., Gundel, L.A., Novakov, T., "Chemical and Catalytic Properties of Elemental Carbon" in Particulate Carbon, Atmospheric Life Cycle, pp 160-179, Wolff, G.T., Klimischi, R.L.(Eds.), Plenum Press, New York, 1982.

13- Charlson, R.J., Ogren, J.A., "The Atmospheric Cycle of Elemental Carbon", "Particulate Carbon, Atmospheric Life Cycle, pp 3-16, Wolff, G.T., Klimischi, R.L.(Eds.)Plenum Press, New York, 1982.

14- Delumyea, R.G., Chu, L., Macias, E.S.," Determination of Elemental Carbon Component of Soot in Ambient Aerosol Samples", Atmospheric environment, Vol.14, pp647-652, 1980.

15- Finlayson-Pitts, B.J., Pitts J.N. ,Atmospheric Chemistry: Fundamentals and Experimental Techniques, John Wiley & Sons, New York, 1986,pp 48.

16- Finlayson-Pitts, B.J., Pitts, J.N.,Atmospheric Chemistry: Fundamentals and Experimental Techniques, John Wiley & Sons, New York, 1986, pp 847.

17- Gibson, T.L., "Sources of Nitroaromatic Mutagens in Atmospheric Polycyclic Organic Matter", Journal of the Air Pollution Control Association, Vol.36, pp 1022, 1986

18- Hidy, G.M.," The Importance of Elemental Carbon -Session Summary" Particulate Carbon, Atmospheric Life Cycle, pp 75-76, Wolff, G.T., Klimischi, R.L.(Eds.)Plenum Press, New York, 1982.

19- Huntzicker, J.J., Johnson, R.L., Shah, J.J., Cary, R.A., "Analysis of Organic and Elemental Carbon in Ambient Aerosol by a Thermal-Optical Method" ,Particulate Carbon, Atmospheric Life Cycle, pp 79-85, Wolff, G.T., Klimischi, R.L.(Eds.)Plenum Press, New York, 1982.

20- Ishinishi, N. Koisumi, A., McClellan, R.O., Strober W.(Eds.), Carcinogenic and Mutagenic Effects of Diesel Engine Exhaust, Elvesier, Amsterdam, 1986.

21- Johnson, R.L., Shah, J.J., Cary, R.A., Huntzicker, J.J., "Atmospheric Aerosol: Source/Air Quality Relationships", ACS Symposium Series No. 167,1981, American Chemical Society.

22- Kleinbaum, D.G., Kupper, L.L., Muller, K.E., Applied Regression Analysis and Other Multivariable Methods, 2nd edition, 1988, PWS-KENT Publishing Company, Boston.

23- Lioy, J.P., Daisey, J.M., Toxic Air Pollution: A Comprehensive Study of Non-Criteria Air Pollutants, pp 125-166, Lewis Publishers, Inc, Chelsea-Michigan, 1987.

24- McClellan, R.O., "Conclusions and Recommendations of the International Satellite Symposium on Toxicological Effects of Emissions from Diesel Engines, Tsukuba", in Carcinogenic and Mutagenic Effects of Diesel Engine Exhaust, pp 529-534, Elvesier, Amsterdam, 1986.

25- McFarland, A.R., Ortiz, C.A., Rodes, C.E., "Wind Tunnel Evaluation of The British Smoke Shade Sampler", Atmospheric Environment, Vol.16, pp 325-328, 1982.

26- McFarland, A.R., Wedding, J.B., Cermak, J.E., " Wind Tunnel Evaluation of a Modified Andersen Impactor and an All Weather Sampler Inlet" Atmospheric Environment, Vol11:535-539, 1977.

27- Mueller, P.K., Fung, K.K., Heisler, S.L., Grosjean, D., Hidy, G.M., "Atmospheric Particulate Carbon Observations in Urban and Rural Areas of the United States", Particulate Carbon, Atmospheric Life Cycle, pp 343-368, Wolff, G.T., Klimischi, R.L.(Eds.)Plenum Press, New York, 1982.

28- Oliveira, G., Lima, E.R., Godinho, R., "Tendencias do Dioxido de Enxofre na Regiao Metropolitana de Sao Paulo" Presentation at V International Clean Air Congress, Buenos Aires, Argentina,1980.

29- Pierson, W.R., Russel, P.A., "Aerosol Carbon in the Denver Area in November 1973", Atmospheric Environment., Vol.13, pp 1623-1628, 1979.

30- Reist, P.C., Introduction to Aerosol Science, MacMillan Publishing Company, New York, 1984.

31- Shah, J.J., Johnson, R.L., Heyerdahl, E.K.Huntzicker, J.J., "Carbonaceous Aerosol at Urban and Rural Sites in the United States ", Journal of the Air Pollution Control Association, Vol.36, pp 254-257, 1986

32- Shaw, G.E.,"Perturbation of the Atmospheric Radiation Field from Carbonaceous Aerosols"Particulate Carbon, Atmospheric Life Cycle, pp 53-68, Wolff, G.T., Klimischi, R.L.(Eds.)Plenum Press, New York, 1982.

33- Stevens, R.K., McClenny, W.A., Dzubay, T.G.," Analytical Methods to Measure the Carbonaceous Content of Aerosols", Particulate Carbon, Atmospheric Life Cycle, pp 111-126, Wolff, G.T., Klimischi, R.L.(Eds.)Plenum Press, New York, 1982.

34- Tanner, R.L., Gaffney, J.S., Phillips, M.F., "Determination of Organic and Elemental Carbon in Atmospheric Aerosol Samples by Thermal Evolution", Analytical Chemistry,Vol.54, pp,1627-1630, 1982.

35- U.S. Environmental Protection Agency (1987);Federal Register Vol.52 No.126, pp 24641, 1987.

36- Valente, G.U., Sato, M.I.Z., Coelho, M.C.Coimbrao, C.A., Sanches, P.S., Alonso, C.D., "Aplicacao do Teste de Ames na Avaliacao da Mutagenicidade dee Material Particulado no Ar",Presentation at 40th Reuniao Anual da Sociedade Brasileira Para o Progresso da Ciencia, Sao Paulo, June 1988.-6

37- World Health Organization, Selected Methods Of Measuring Air Pollutants;World Health Organization, Geneva, 1976.

38- World Health Organization, "Analyzing and Interpreting Air Monitoring Data" World Health Organization, Geneva, 1979

APPENDIX A

MEASUREMENTS FOR CALIBRATION CURVE

PINHEIROS - 1988

Date	DI	Total Carbon ug/cm2	Elemental Carbon ug/cm2	Organic Carbon ug/cm2
jun 12-13	29.0	12.3	2.4	10.0
jun 13-14	22.0	8.4	1.0	7.3
jun 14-15	11.5	4.3	1.6	2.7
jun 15-16	13.0	5.2	2.2	3.0
jun 16-17	12.5	5.4	0.2	5.2
jun 20-21	33.5	14.8	2.3	12.6
jun 21-22	50.5	29.6	8.0	21.6
jun 22-23	36.0	18.0	4.4	13.6
jun 28-29	49.0	29.6	3.8	25.8
jun 30-01	50.0	32.4	7.8	24.7
jul 01-02	42.0	24.9	4.3	20.5
jul 05-06	52.5	31.2	8.7	22.5
jul 06-07	43.5	22.9	6.3	16.6
jul 07-08	14.5	6.7	0.9	5.9
jul 08-09	10.5	4.4	0.6	3.8
jul 14-15	13.0	5.8	1.0	4.8
jul 15-16	17.0	7.9	1.9	6.1
jul 19-20	29.5	16.2	4.7	11.5
jul 20-21	11.5	5.5	0.8	4.7
jul 21-22	26.5	13.7	3.7	10.0
jul 25-26	10.0	4.7	2.2	2.6
jul 26-27	10.5	3.7	1.3	2.4

MEASUREMENTS FOR THE CALIBRATION CURVA
C. Cesar - 1989

Date	DI	Total Carbon ug/cm2	Elemental Carbon ug/cm2	Organic Carbon ug/cm2
apr 25-26	33.0	13.3	5.0	8.4
apr 26-27	53.0	29.6	12.7	16.9
apr 27-28	50.0	25.5	10.8	14.7
may 02-03	34.5	14.4	5.8	8.6
may 03-04	53.5	31.3	14.3	17.0
may 08-10	36.5	15.7	5.7	10.0
may 10-11	40.0	19.9	6.8	13.1
may 11-13	48.0	25.7	8.6	17.0
may 16-17	33.0	14.9	4.6	10.3
may 17-18	33.0	16.6	5.3	1.3
may 18-19	32.0	13.7	5.1	8.5
may 19-20	29.5	11.5	4.3	7.2
may 22-23	44.5	22.9	10.2	12.7
may 23-24	54.0	32.7	11.3	21.4
may 24-26	51.5	29.2	9.2	20.0
may 26-28	15.5	7.2	1.8	5.4
may 28-30	41.0	20.5	7.4	13.1
may 30-31	36.0	15.5	5.4	10.1
may 31-01	33.0	14.8	5.8	9.0
jun 01-02	34.0	15.2	5.3	9.9
jun 02-03	48.5	29.7	10.1	19.6
jun 03-05	50.0	29.6	7.7	22.0
jun 05-06	36.0	15.9	6.1	9.8
jun 06-07	52.5	26.7	12.0	14.8
jun 07-08	58.0	29.6	12.6	17.0
jun 11-13	32.0	11.3	4.2	7.2
jun 13-14	32.5	10.4	3.8	6.5
jun 17-19	38.5	20.7	6.4	14.4
jun 12-20	39.0	17.4	5.7	11.7

APPENDIX B

SMALL STUDY IN 5 SITES

SAMPLE No.	DI	Total Carbon Measured ug/cm2	Total Carbon Calculated ug/cm2	Res. Calc. (-) Meas.	RES NORM (R/1.96)
Aclimacao					
1	17.5	10.0	7.1	-2.9	-1.5
2	33.0	18.3	15.0	-3.2	-1.6
3	21.0	11.3	8.5	-2.8	-1.4
4	12.0	9.0	5.1	-3.9	-2.0
C.Eliseos					
1	46.5	25.7	24.8	-0.8	-0.4
2	38.0	15.7	18.3	2.7	1.4
3	44.0	20.9	22.8	1.9	0.9
4	36.5	16.3	17.3	1.0	0.5
Moema					
1	33.0	18.4	15.0	-3.4	-1.7
2	17.5	6.5	7.1	0.5	0.3
3	30.0	15.8	13.2	-2.6	-1.3
4	14.5	7.9	5.9	-2.0	-1.0
P.Rep.					
1	24.5	11.5	10.2	-1.3	-0.7
2	36.5	21.0	17.3	-3.7	-1.9
3	24.0	11.6	10.0	-1.6	-0.8
4	36.0	18.5	17.0	-1.5	-0.8
Tatuape					
1	23.5	8.8	9.7	0.9	0.5
2	35.5	17.0	16.6	-0.4	-0.2
3	32.0	12.1	14.4	2.3	1.2
4	44.0	20.0	22.8	2.8	1.4

APPENDIX C

DATA FROM SMOKE SHADE AND DICHOTOMOUS

DATE	MASS CONC S.SHADE ug/m3	MASS CONC DIC ug/m3	CARBON S.SHADE CONC ug/m3	CARBON DIC CONC ug/m3
MAY 08-10	79	48.21	33.4	23.06
MAY 10-11	118	71.64	53.1	35.29
MAY 11-13	121	73.54	47.9	35.38
MAY 16-17	121	87.24	58.4	38.35
MAY 17-18	110	104.41	59.6	39.86
MAY 18-19	112	76.47	52.2	34.14
MAY 19-20	98	69.95	44.5	31.52
MAY 22-23	182	110.32	75.8	49.75
MAY 24-26	157	94.67	60.0	48.99
MAY 26-28	17	18.94	12.9	6.99
MAY 28-30	86	52.94	38.1	26.10
MAY 30-31	127	101.14	54.5	40.48
MAY 31-01	113	74.15	54.3	*
JUN 01-02	120	99.67	56.2	*
JUN 03-05	128	73.34	53.1	*
MAY 05-06	141	81.06	62.1	*
MAY 17-19	80	76.27	40.9	30.51
MAY 19-20	159	132.81	66.8	50.07

APPENDIX D

ANNUAL, MAXIMUM AND MINIMUM QUARTERS AVERAGES

ACLIMACAO			
YEAR	ANNUAL AVERAGE µg/m3	MAXIMUM QUARTER AVERAGE µg/m3	MINIMUM QUARTER AVERAGE µg/m3
74	41.0	51.1	25.9
75	37.0	54.7	25.5
76	48.7	72.8	40.1
77	42.1	54.2	27.1
78	38.5	52.7	32.9
79	42.4	59.2	31.9
80	43.0	60.4	29.4
81	45.1	71.9	27.8
82	36.6	45.0	28.1
83	36.0	44.4	29.2
84	36.6	50.6	26.6
85	38.2	57.6	28.2
86	33.6	37.6	26.0
87	30.5	45.6	22.7
88	28.6	35.3	23.6

CAMPOS ELISEOS			
YEAR	ANNUAL AVERAGE g/m3	MAXIMUM QUARTER AVERAGE g/m3	MINIMUM QUARTER AVERAGE g/m3
74			
75			
76			
77			
78			
79	69.8	76.8	60.3
80	66.0	78.7	51.2
81	76.1	93.5	65.2
82	63.0	72.3	53.9
83	63.2	70.0	50.0
84	58.1	68.6	50.3
85	62.5	83.0	47.9
86	53.9	63.2	46.3
87	48.8	57.6	44.7
88	52.3	61.7	45.0

MOEMA			
YEAR	ANNUAL AVERAGE g/m3	MAXIMUM QUARTER AVERAGE g/m3	MINIMUM QUARTER AVERAGE g/m3
74	21.5	28.9	14.6
75	23.9	37.9	16.2
76	27.7	47.8	14.7
77	20.6	30.6	11.7
78	18.5	28.2	12.7
79	22.0	33.5	12.8
80	21.4	37.7	12.8
81	26.9	46.5	17.0
82	19.2	30.1	14.3
83	22.6	32.1	16.4
84	24.5	38.4	12.1
85	20.8	38.2	13.2
86	19.8	25.0	15.3
87	20.1	33.7	12.6
88	17.0	25.7	10.0

PRACA DA REPUBLICA			
YEAR	ANNUAL AVERAGE g/m3	MAXIMUM QUARTER AVERAGE g/m3	MINIMUM QUARTER AVERAGE g/m3
74			
75	44.9	60.0	35.2
76	52.7	71.0	44.5
77	45.0	54.6	32.9
78	38.8	46.6	35.1
79	46.6	60.9	34.1
80	42.0	56.7	34.6
81	50.1	66.6	36.0
82	35.7	44.6	29.3
83	36.0	43.1	30.2
84	36.8	53.2	25.9
85	38.3	59.2	31.3
86	36.6	43.3	26.8
87	31.8	45.3	24.7
88	31.4	35.7	30.4

TATUAPE				
YEAR	ANNUAL AVERAGE g/m3	MAXIMUM QUARTER AVERAGE g/m3	MINIMUM QUARTER AVERAGE g/m3
74	56.5	67.7	46.9
75	56.1	74.6	44.1
76	63.8	81.4	48.1
77	56.9	77.3	39.0
78	56.9	72.8	49.2
79	60.3	78.6	42.6
80	55.7	79.2	36.3
81	62.2	92.7	43.1
82	48.3	64.4	39.6
83	48.5	58.6	40.1
84	51.0	73.7	30.9
85	44.7	72.2	33.2
86	39.3	52.0	28.0
87	31.3	40.8	25.9
88	33.9	39.3	32.1