

Final Report

to

Air Resources Board, State of California

"Isotopic Analysis of Smog Component Phases"

(ARB Contract No. A2-127-32)

by

Rainer Berger

Institute of Geophysics and Planetary Physics

University of California

Los Angeles, CA 90024

October 1, 1984

890
B47
1984

EXECUTIVE SUMMARY

"Isotopic Analysis of Smog Component Phases"

ARB Contract A-2-127-32

by

Rainer Berger

Institute of Geophysics and Planetary
Physics
University of California
Los Angeles, CA 90024

October 1, 1984

Summary

Over the years smog concentrations in certain parts of the State of California have decreased visibility so much that serious concern arose over the origin of visual pollution. Inasmuch as visibility reduction and odor pollution go hand in hand, the average citizen can see smog and qualitatively judge its intensity. Thus apart from the esthetic problems affecting the people of this state and the tourist industry, there are serious visibility concerns involving aircraft safety, certain types of aerospace testing and observation, and last not least adverse health effects on man, animals and crops.

With respect to the visibility problems, a small fraction of the total smog components can be blamed: suspended particles. These arise from the incomplete combustion of fuels, especially fuel oils and gasoline, but a significant portion was also thought to be the result of trees emitting terpenes and other resinous substances in small droplet form. In fact, there was voiced concern that the harvesting of agricultural crops might also have a contributing effect on smog. A simple test is to walk over a freshly mowed alfalfa or hay field, or through a sun-lit forest and smell all the organic compounds many of which enter the atmosphere in droplet form. As a result it became necessary to distinguish between particles (TSP) produced by living plant sources and those left from combustion of fossil fuels.

This differentiation can be made by isotopically analyzing particulate samples for their radiocarbon content. Carbon from fossil fuel sources contains no longer any measureable traces of radiocarbon. All has decayed by a nuclear process over millions of years of geologic time when the fossil fuels were first produced. However, carbon in all presently living things contains radiocarbon introduced during photosynthesis when plants fix carbon dioxide and water to produce carbohydrates: starch, tissue, wood, etc. Originally radiocarbon is produced in the stratosphere when cosmic ray particles break atoms of the atmosphere into their nuclear components: electrons, protons and neutrons. The neutrons react with nitrogen to produce radiocarbon which is oxidized to carbon dioxide, mixed virtually uniformly by the earth's wind

systems and then made available to all plants world-wide. As a result modern carbon particles are mildly radioactive and of known radiocarbon concentration.

In order to measure the radioactivity of carbon particles it was necessary to design, construct and test a special small volume counting device so that relatively small quantities of particles collected on air filters could be successfully analyzed. This was accomplished and the results are listed in the body of the full report.

As a result we now know that in all areas tested fossil fuel sources and their contaminating effects play a predominant role in TSP-pollution. This applies to the Los Angeles air basin as well to Lake Tahoe, Bakersfield or El Cajon east of San Diego. An exception to this rule are particles produced by field burning (Chico) or forestfires.

In southern California the concentration of carbon particles is controlled by the seasons. During the spring or summer and into the fall when onshore winds control the climate the highest particulate concentrations are found inland. In contrast, during Santa Ana episodes, particle concentrations rise markedly along the coast and reduce the quality of air to conditions similar to inland pollution during the summer.

It must be emphasized that the sampling record is not as continuous as one would like to see. This is due to inadequate collection amounts having been obtained earlier in this study. During the later stages of this work, provisions had been made to collect larger samples, and the problem of inadequate sample size was overcome.

As part of this measurement program, a high volume air sampler was successfully tested. Also contamination effects of the motors driving the sample collectors were investigated. Throughout the collection program such self-contamination was avoided and the results must be representative of the pollution levels encountered.

Finally it is proposed to continue the monitoring program to obtain a continuous record throughout the year. Many samples have already been collected and need to be assayed. Thereafter a monitoring program at a reduced level would keep a check on compliance with stricter emission laws notably aimed at Diesel engines known to be primary producers of particulates. Without such checks there could be no effective law enforcement aimed at improving the air quality and public health in this state.

Abstract

Over the years smog concentrations in certain parts of the State of California have decreased visibility so much that the phrase visual pollution was coined. In fact, the total suspended particle load of the atmosphere is there for every citizen to see and most noticeable as an indicator of smog. Apart from the esthetic effect there are serious concerns about visibility affecting aircraft safety, certain types of aerospace testing and observation, and potential direct impacts on the welfare of man, animals and plants.

In this study the origin of the carbonaceous fraction of the total suspended particle load was analyzed using the principle that carbon from fossil fuel sources contains no measurable quantities of the radioactive isotope carbon-14, whereas all recent carbon derived from the biosphere does. Thus carbon from diesel or other fossil combustion sources can be differentiated from carbon which is part of pollen, tree emissions or organic dust.

Samples were collected by ARB personnel in a number of locations in the state, principally in the Los Angeles Metropolitan air basin while the radiometric analyses were carried out at UCLA. The results of this study can be briefly summarized as follows:

In all areas analyzed, except for Chico, fossil fuel sources are the predominant polluters. In the air basins of Southern California the concentration of carbon particles is controlled by the seasons ranging from below the detection limit ($0.1 \mu\text{g}/\text{m}^3$) to $21 \mu\text{g}/\text{m}^3$. While in the summer from west to east, the average concentrations at Pacific Palisades, downtown Los Angeles and Upland are 0.6, 10.3 and $118 \mu\text{g}/\text{m}^3$ respectively, the winter data for the same locations are 4.2, 10.0 and 7.8. Thus during Santa Ana conditions, the air quality directly on the coast at Pacific Palisades is greatly reduced.

In addition, an Electric Power Research Institute massive high-volume air sampler was tested for obtaining size-segregated samples. As a result it was found that the smallest and most dangerous

particles are principally composed of fossil carbon (77%). Therefore it is recommended to carry out further analyses using size-segregated samples in the state to monitor the most dangerous fraction of particles impacting public health and visibility.

Acknowledgements

Dr. John Holmes, Chief-Research Division ARB-Sacramento, must be credited for major design aspects of the entire study.

Mr. Eric Fujita, Dr. Douglas Lawson and Dr. Jack Suder, ARB-Sacramento were very helpful in monitoring the project.

I am also indebted to P. Harrington and his associates of the ARB staff, El Monte, for providing the particulate filters and the Electric Power Research Institute for the use of the massive volume air sampler. David McJunkin and Roberta M. Johnson, UCLA, assisted competently in preparing and assaying the samples. Donald Sullivan, La Jolla, was very helpful in assuring top performance of the electronic counting equipment. Terry Jackson, UCSD, measured expertly a number of relevant atmospheric CO₂ samples for reference purposes. Glennis McConahy, UCLA, deserves recognition for typing the final manuscript.

This report was submitted in fulfillment of ARB Contract A2-127-32 "Isotopic Analysis of Smog Component Phases by UCLA under the sponsorship of the California Air Resources Board. Work was completed as of October 1, 1984.

Disclaimer

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

Table of Contents

	<u>Page</u>
Title Page	
Abstract	1
Acknowledgements	3
Disclaimer	3
Table of Contents	4
List of Figures	5
List of Tables	6
Summary and Conclusions	7
Recommendations	9
Report; Introduction	11
Sample Collection	12
Radiometric Analysis	13
Stable Isotope Analyses	17
Results and Discussion	17
References	43
List of Publications	44
Glossary of Terms	45

List of Figures

Seasonal variations of total solids and carbon at	<u>Figure</u>	<u>Page</u>
Pacific Palisades	1	31
Downtown Los Angeles	2	32
El Monte	3	33
Upland	4	34
Chico	5	35
Lake Tahoe	6	36
Bakersfield	7	37
El Cajon	8	38
California Surface Wind Patterns		
Spring	9	39
Summer	10	40
Fall	11	41
Winter	12	42

List of Tables

	<u>Table</u>	<u>Page</u>
Control Test at El Monte	1	13
Proportional Counter Performance	2	15
Particulate Carbon-Isotope Analysis	3	16
Origin of Carbon Data for:		
Palisades	4	23
Downtown Los Angeles	5	24
El Monte	6	25
Upland	7	26
Chico	8	27
Lake Tahoe	9	28
Bakersfield	10	29
El Cajon	11	30

Summary and Conclusions

In this study the origin of the carbon fraction in total aerosol particles was investigated. There is no question that in all the areas analyzed, except for Chico, fossil fuel sources play the predominant role. The concentration of carbon particles is often controlled by the seasons in the air basins of Southern California as apparent from the comparison below.

	<u>Start</u>	<u>End</u>	<u>No. of Days</u>	<u>Fossil Carbon</u>		
				<u>Pacific Palisades</u> $\mu\text{g}/\text{m}^3$	<u>Downtown Los Angeles</u>	<u>Upland</u>
Summer 1982	6/8	6/21	10		9.4	9.0
	7/19	7/30	10	1.6	15.0	8.9
	8/9	8/20	10	<u>0.2</u>	<u>6.5</u>	<u>17.6</u>
	Average			0.6	10.3	11.8
Winter 82-83	11/30	12/13	10	7.6	15.9	14.2
	1/25	2/7	9	3.7	4.3	1.9
	2/7	2/21	11	<u>1.5</u>	<u>10.5</u>	<u>7.3</u>
	Average			4.2	10.0	7.8
% Carbon in TSP	Summer 82			3.0	15.3	12.8
	Winter 82-83			6.7	17.0	14.0
% Fossil Carbon in Total Carbon	Summer 82			25	95	87
	Winter 82-83			64	75	67

Inspection of these data shows that not only the east-of-the-coast lying communities such as downtown Los Angeles and Upland are affected but also those on the coast itself (Pacific Palisades) when Santa Ana conditions prevail. In other words, the air quality at times during the winter months at Pacific Palisades located directly on the ocean can be almost as bad as that in downtown Los Angeles or Upland during the summer.

When the state-wide data are inspected they show average carbon concentrations ranging from the about 1-21 $\mu\text{g}/\text{m}^3$. In one case involving straw burning near Chico, the percentage of carbon in particulates reached 34% based on 42.9 $\mu\text{g}/\text{m}^3$ of total particulates containing 14.7 $\mu\text{g}/\text{m}^3$ C.

However, due to the non-continuous data points presented so far as a result of sometimes inadequate sample amounts received from the air collection units, more sampling is necessary to present ultimately a complete seasonal record of carbon particulates in the air basins of California.

In addition, a massive high-volume air sampler on loan from the Electric Power Research Institute (EPRI) was tested whose impaction plates are coated with teflon. Since this plastic contains fluorine which was thought to interfere with radiometric assay, a test sample was run and found to be measureable in the UCLA system. Therefore, this type of sampler can be utilized in future monitoring providing either necessary quantities in less time or large enough samples when the ambient particle concentration is low.

Furthermore this air sampler allows size-segregated analyses with the following preliminary results:

	Size (μ)	Weight (g)	(%)	Biol.C (g)	(%)	Fossil C (g)	(%)
Large impactor	20-3.5	0.7408	30.6	0.4297	58	0.3111	42
Small impactor	3.5-1.7	0.6540	27.0	0.3401	52	0.3139	48
Precipitator	up to 1.7	<u>1.030</u>	<u>42.4</u>	<u>0.2369</u>	23	<u>0.7931</u>	77
		2.4248	100	1.0067		1.4181	

This table shows that much more information is obtainable by size-segregated samples than by ordinary air sampling techniques which combine all fractions into one single sample. Taking these data as indicative of the isotopic carbon content of particulates, then the smallest fraction is composed mainly of fossil carbon. This suggests that it is due mainly to motor vehicles and in particular to diesels. The smallest-sized particles are known to be the most harmful from a public health point of view since they readily enter the smallest lung capillaries. Thus the EPRI massive high-volume sampler permits us to follow and monitor the most dangerous fraction of carbon particles which is not possible with the conventional units used so far.

Recommendations

First, the body of data obtained so far is not continuous due to lack of adequate samples in certain time periods. These seasonal holes should be closed by further collections and analysis.

Second, the UCLA laboratory still has a large number of filter samples that have not yet been analyzed due to the fact that funding ended at the beginning of 1984 even though we have continued to work on this project until now in the interest of providing the best continuous set of data obtainable. It must be realized that the University is not in session during 3½ summer months. Moreover, we are still receiving samples now from the El Monte Haagen-Smit Laboratory. It is suggested that we receive funding to complete the entire set of samples so that a truly comprehensive data set is available.

Third, inasmuch as the EPRI massive high volume air units provide size-segregated samples, it would be desirable to conduct a study for a full year in one of the smoggiest locations, either downtown Los Angeles or Upland, to understand better size distribution and origin of carbon particles. UCLA could purchase an EPRI-type unit for such a study within the framework of an ARB contract.

Four, since the ARB is charged with a monitoring function of air quality, a continued study of carbon particles at a meaningful level is recommended to assess the success of air quality control legislation over the next several years.

Five, no studies have been conducted of air quality in large buildings with self-contained climate control. Because a sizeable population is affected in office structures, large department stores and living complexes, the ARB should begin monitoring air pollution inside which is not now carried out by any agency at all.

Six, the emissions of jet aircraft at major airports such as Los Angeles International Airport are clearly visible to everybody. However no data exist at airport locations in terms of air quality or lack of it.

Seven, the same problems exist at locations downwind from oil refineries in the state as well as oil fields onshore or off-shore. Given the southern California climate, especially oil facilities near or in urban centers need to be assessed for carbon particle emissions.

Introduction

Recently, Appel et al. (1983) found that 20% of the total suspended particle load in air is carbonaceous and the major single class constituting TSP-loads at three California locations. Inasmuch as smog occurs in both the urban and rural areas of the state, the question was raised to what extent plant emissions from, for example, pine trees contribute to the overall smog problem. In fact a scenario was presented a few years ago where terpene-emitting conifers would produce more smog-causing chemicals in wet growth years, whereas during dry periods less plant emissions and therefore less smog-production could be expected (Sandberg, Basso and Okin 1978; Bufalini 1979; Miller, Pitts and Winer 1979; Sandberg, Basso and Okin 1979). On the other hand state agencies like the ARB have long been concerned with smog-producing emissions from fossil fuel combustion by automotive and industrial sources. Thus it became necessary to determine to what extent aerosols are composed of recent biospheric (contemporary) and fossil fuel emission products.

This distinction can be made by analyzing total suspended particles (TSP) for their radiocarbon content. Fossil fuels contain carbon without a measureable trace of the radioactive isotope carbon-14 or radiocarbon, since its half-life is only 5730 ± 30 years. Due to the great age of petroleum or coal resources all carbon-14 has decayed and is no longer detectable. In contrast, all recent biospheric carbon contains radiocarbon. This isotope is constantly produced in the upper atmosphere, oxidized to $^{14}\text{CO}_2$ and fixed via photosynthesis in all plant matter. From there it finds its way also into animals and men resulting in a near uniform distribution of the isotope in the worldwide biosphere. By assaying TSP samples for radiocarbon it is possible to calculate the fossil and contemporary carbon contributions to the aerosol particles and thus determine their origin (Lodge, Bien and Suess 1960; Berger, Johnson, and Holmes, 1983).

Sample Collection

The TSP-samples were collected by ARB-personnel using chemically and isotopically clean quartz fiber filter papers at several locations in California, predominantly in the Los Angeles Metropolitan Region. The filters were placed in front of fans which drew air at a measurable rate through the quartz fiber paper.

All sampling was performed with size selective inlet (PM15) hi-volume samplers unless otherwise indicated by TSP (Total Suspended Particulates). These TSP samplers were used in El Monte as part of a re-entrainment test to insure that carbon from the sampler motor brushes was not contaminating the samples. TSP samplers were also used at Lake Tahoe early in the project since SSI samplers were not available..

The sampling period at Pacific Palisades, Los Angeles, El Monte and Upland generally ran from 1000-1800 Monday through Friday. During this time of day the wind is generally onshore. El Cajon operated during the same hours but seven days a week due to timer limitations.

Sampling periods at Tahoe, Bakersfield, and Chico were generally 24 hours a day for the entire period indicated due to equipment limitations. The Upland sampler was temporarily moved to Tahoe between July and September of 1983 allowing for 18-hour sampling intervals. More than 8 hours a day sampling was needed in Tahoe due to a low loading rate.

To test the purity of the filters, blanks were run at UCLA and found to contain no detectable carbon content either chemically or radiochemically. Moreover, the sampling methodology used was tested in the field by checking the effect of the cooling air of the electric motors driving the collection fans.

At one point it was feared that the abrading carbon brushes of the motors might introduce carbon particles into the filters producing erroneous results. However, it was determined that such concern was groundless.

In an experiment motor exhaust was ducted away from the

air sampling unit and compared to a non-ducted experiment. The carbon assay for both filters was identical within experimental error. If however, the motor exhaust was directly ducted onto the filter surface an effect was noticed lowering the biospheric carbon level as expected. This is due to the fossil carbon origin of the electric motor brushes. The results of this test are summarized below in Table I.

Table I
Control Test at El Monte, CA.

<u>Lab No.</u>	<u>Conditions</u>	<u>Radioactivity</u>
UCLA-2451-D	Exhaust not ducted	0.61 cpm
-2451-A	Exhaust ducted into filter	0.36 cpm
-2451-B	Exhaust ducted away	0.52 cpm
-2451-C	Exhaust not ducted	0.54 cpm
-2449	Electric motor brush carbon	no activity

UCLA-2451 A and D were collected from 10/18/83 to 10/28/83 and UCLA-2451 B and C from 9/27/83 to 10/14/83.

In some cases the amount of TSP collected on the quartz filters was insufficient for radiocarbon analysis due to variations in TSP-loading of the air samples. This explains why the sampling record is not always continuous.

Radiometric Analysis

Since TSP concentrations are typically low in the $100 \pm 50 \mu\text{g}/\text{m}^3$ range a special small volume proportional counter was designed, constructed and tested. For a complete fill or optimum detection conditions only 100 mg of carbon are needed. The counting chamber is located inside an anticoincidence guard assembly which in turn is protected from ambient environmental radiation by a 7.5-ton radioactively clean steel shield. The anticoincidence guard allows the subtraction of cosmic ray flux which still penetrates the steel shield due to its high energy particles from space.

The electronics which permit the actual radiocarbon assay

consist of an all-solid-state unit with three anti-coincidence and three coincidence channels. The entire counting system is powered by ultra-stable high voltage power supplies. Its counting characteristics are summarized briefly in Table 2. For the purpose of standardization three standards are used: (1) By international convention 95% of the count rate of National Bureau of Standards oxalic acid for radiocarbon laboratories (equivalent to the biosphere of 1890 prior to the CO_2 contamination of the atmosphere by industrialization), (2) CO_2 derived from marble (measures the intrinsic radioactivity in the counter wall and electronic noise effects), and (3) a CO_2 -gas sample derived from a deck plank of the funerary boat of Sesostris III which has an historically known age of 1800 B.C. The latter standard is used to assure that the dating equipment performs accurately. For practical purposes the age of the Sesostris sample is calculated using its count rate and that of the oxalic acid and marble background. As can be seen from Table 2, the equipment performs very well because the age of the Sesostris CO_2 -gas can be calculated to date close to its historical age of 1800 B.C. This type of standardization procedure is carried out repeatedly to insure continued accurate radiocarbon assays.

The sample measurement protocol in its entirety is as follows: Depending on the filter loading which varies from about 0.5 to 1.5 g 1-2 quartz filters are placed into an isotopically clean Vycor-quartz tube and burnt in a stream of analytically pure oxygen. The resulting CO_2 is purified by passing through silver nitrate and chromic acid solutions and is then dried. Any CO is converted to CO_2 by hot copper oxide. Finally, all electro-negative impurities that interfere with proportional counting, such as O_2 , NO_2 or halogens are removed by repeated passage of the gas over hot, clean elementary copper. Subsequently the clean CO_2 sample gas is stored in high pressure steel cylinders.

Inasmuch as all biospheric and fossil carbon samples contain ppm-quantities of uranium which is present worldwide, a certain amount of radon gas is continuously produced in the smog particulates. As soon as they have been burnt to CO_2 no more radon is

Table 2

Performance of 200 ml-Proportional Counter

Background, consisting of radioactive contamination
in counter materials and electronic noise,
determined by measuring pure carbon dioxide
from Missouri marble (radioactively dead)

0.870 ± 0.005 cpm*

Recent biosphere, equivalent to the count rate
of 95% of the activity of National Bureau of
Standards oxalic acid for radiocarbon labor-
atories

1.010 ± 0.015 cpm*

Historical sample, a deck plank from the funerary
boat of Sesostris III who died near 1800 B.C.

0.645 ± 0.015 cpm*

equivalent to 1800 B.C. after
tree ring calibration

*Net counting rates in counts per minute (cpm)

See R. Berger, 1983, for counter construction details.

Table 3

Smog Particulate Carbon Isotope Analysis

<u>UCLA No.</u>	<u>Origin</u>	<u>Collection Date</u>	<u>Loading Rate (g/min)</u>	<u>Biospheric Contribution (%)</u>	<u>Fossil Fuel Contribution (%)</u>	<u>$\delta^{13}\text{C}$ (‰)</u>
2211A	Riverside	9/29/78	0.00019	42 ± 2%	58 ± 2%	-26.33
2211B	"	10/03/78	0.00031	41 ± 2%	59 ± 2%	-29.72
2211C	"	10/06/78	0.00022	34 ± 2%	66 ± 2%	-27.42
2211D	"	10/10/78	0.00019	*	*	-26.30
2211E	"	10/13/78	0.00025	45 ± 2%	55 ± 2%	-26.90

The calculations of biospheric and fossil fuel contributions are based on the radiocarbon concentration of CO₂ in the troposphere of 1978 which was +35% above the reference level of 95% NBS Oxalic Acid for radiocarbon laboratories (Berger, in press; Levin, Münnich and Wiess, 1980).

added by the inorganic or ash portion found in most natural samples. This uranium daughter then decays with a half-life of 3.8 days. In order to eliminate any counting errors due to radon, samples are stored for a period of one month to permit complete radon decay. In practice this means that each sample takes about 4-5 weeks to analyze. However, analyses are run in a staggered mode so that roughly every few days a new sample is processed. Total counting time per sample varies from 2 to 4 days. Standardization of the counter requires on the average 6 days if no adjustments are necessary.

Stable Isotope Analyses

It might be argued that beside the aerosol particles the glass filters also may have adsorbed inorganic dust which in the Los Angeles area might contain inorganic carbonates. In order to check such a possibility a number of samples were analyzed for their $^{13}\text{C}/^{12}\text{C}$ ratio (Table 3). This is a good indicator of the origin of carbon. In inorganic soil-derived carbon the $^{13}\text{C}/^{12}\text{C}$ ratio is close to 1, whereas land plants metabolizing by the biological C-3 pathway or petroleum have a ratio of about -25‰ with respect to the internationally accepted PDB standard. All samples measured had values much closer to 25 than 1. Consequently, carbonate contamination of the aerosol samples can be ruled out.

Results and Discussion

For purposes of overview the data obtained in this study are listed numerically at the end of the report in Tables 4-11 and graphically presented in Figures 1-12. The composition of TSP ranges from 0 to 100% biological or fossil carbon content depending on sample location and season. Seasonal variations in the predominant surface wind flow patterns in California are shown in Figures 17-20.

Next follows a discussion of the data from the different sampling locations beginning with Metropolitan Los Angeles which includes Pacific Palisades, Downtown Los Angeles, El Monte and Upland stations.

Pacific Palisades

The air samples were collected in Will Rogers State Park. Carbon concentrations ranged from about 1-8 $\mu\text{g}/\text{m}^3$ of air sampled. The total solids adsorbed on the filters varied from 57.2 to 149.6 $\mu\text{g}/\text{m}^3$. Figure 1 shows a seasonal effect resulting in highest carbon and total solids loading during the fall and winter months when Santa Ana conditions prevail with offshore winds. Table 4 indicates a range of biologic to fossil carbon ratios from one extreme to the other. During the spring and summer months (Figures 9 and 10) onshore winds during the day result in the lowest carbon concentrations of the year. Thus the air quality in Pacific Palisades is seasonally controlled with an optimum during the spring and summer.

Downtown Los Angeles

The sampling location is the Department of Water and Power Building in the downtown center of the City of Los Angeles. The data analyzed so far show carbon concentrations up to about twice as high as in Pacific Palisades near the ocean. There does not seem to exist a pronounced seasonal effect as in Palisades. Total solids collected on the air filters range from about 57 to 102 $\mu\text{g}/\text{m}^3$ of air. Yet there is a preponderance of fossil carbon suspended in downtown air as evident from Table 15.

El Monte

Samples were collected at the Haagen-Smit ARB facility in El Monte east of downtown Los Angeles. Concentration levels of carbon and total solids in air are very similar to the downtown environment. There appears to be an indication of a seasonal effect (Table 16) with high TSP concentrations in October 1983. However the data base is too incomplete to establish a clear-cut relationship. Again more often than not fossil carbon predominates in the air over El Monte.

Upland

At Upland TSP concentrations appear to fall into two distinct categories, either predominantly biologic or mainly fossil carbon (Table 19). Moreover the carbon and total solids concentration in ambient air are similar to El Monte or Downtown samples, perhaps slightly higher. There is some seasonal effect discernible in the data obtained so far: carbon concentrations appear to be highest during the summer (Figure 7). Carbon concentrations at Upland on the average are similar to those at the Palisades during the strongest Santa Ana conditions.

For the Los Angeles Metropolitan Region then the following pattern emerges: During the spring and summer as air predominantly flows from west to east filter loading increases in the same direction. During the winter carbon concentrations inland are of an average level around $10\mu\text{g}/\text{m}^3$ where as on the coast they have reached their maximum. Thus the TSP loads follow in overall pattern the smog distribution observed.

Chico

In northern California 2 sets of measurements were made in 1982 to assess the impact of air pollution in Chico during the fall of 1982.

The filter analysis of the Chico samples reveal predominantly biologic carbon concentrations. Total carbon levels are about $10\pm 5\mu\text{g}/\text{m}^3$ of air and total solids range from c. 28 to $43\mu\text{g}/\text{cm}^3$ of air analyzed. If field burning was the principal reason for obtaining these samples, it is surprising to find that about one quarter of the carbon collected is of fossil origin.

Lake Tahoe

This environmentally sensitive area was sampled repeatedly during 1982 and 1983. During the spring and fall high carbon concentrations were measured from 15.3 to $21.2\mu\text{g}/\text{m}^3$. This carbon was predominantly of fossil origin. In contrast, during the summer

carbon concentrations were lower at 4.6 to 6.7 $\mu\text{g}/\text{m}^3$, but most of the carbon was also of fossil sources except for one period in late July 1983 when biologic carbon predominated at 80% biologic over 20% fossil sources. Inspection of Table 23 suggests spread-out distributions of biologic and fossil carbon from 80% biologic to 53% fossil sources. On balance, fossil-fuel-derived carbon plays at Lake Tahoe an equal if not greater role than carbon derived from recent biologic sources such as trees and shrubs. This very fact is surprising in view of the forests surrounding this mountain resort area.

Bakersfield

In south central California Bakersfield is a center of oil production and refining. Therefore, series of samples were collected to assess the impact of this industry on the southern San Joaquin Valley.

Carbon levels range from 5 to 19 $\mu\text{g}/\text{m}^3$ of air with total solids loading from 47 to 147 $\mu\text{g}/\text{m}^3$. During the winter season, Bakersfield appears to be subject to a seasonal increase in carbon and total particles concentration. So far there are not yet available data for an entire calendar year to fully confirm this observation. It is not certain whether the prevailing winds during the summer dilute TSP concentrations or if stagnant air during the winter allows an increase. Bakersfield air samples are the most difficult to measure in the laboratory, because they require an unusual amount of chemical cleaning to reduce electro-negative impurity levels. While winter samples may be sometimes mainly of recent biologic origin (64 to 94% bio) they can also contain as much as 60 to 80% fossil carbon. The main emphasis in Bakersfield TSP-carbon tends to lie on the fossil origin side as apparent from Table 25.

El Cajon

In southern California, the second largest city in the state, San Diego, experiences air pollution particularly in its eastern

environs such as El Cajon.

In El Cajon typically carbon concentrations are under $10 \mu\text{g}/\text{m}^3$ of air and total suspended solids range from 27 to $40.5 \mu\text{g}/\text{m}^3$. All samples contain mostly fossil fuel carbon (Table 27). There appears to be operating also a seasonal effect as seen in Tables 26 and 28. However the data base is not yet sufficiently developed to clearly state the case for definite seasonal control. However, as more data becomes available this question can also be solved.

From a general point of view, it is difficult with the present incomplete data set to make clear-cut seasonal comparisons with other pollutants such as carbon monoxide, nitrogen dioxide, ozone, sulfur dioxide or lead, sulfates and nitrates. Such a comparative evaluation must wait until a complete seasonal set of measurements has been obtained for TSP concentrations and their carbon component.

Notes for Tables 4-11

Dates collected: May not be inclusive

$\mu\text{g}/\text{m}^3$: Particulates per cubic meter at air sampled; both total particulates and carbon particulates are expressed in micrograms ($\text{g} \times 10^{-6}$)

NC: Not counted, insufficient sample

% Bio: Contribution from contemporary biosphere, remainder is from fossil fuel

% Fossil: Contribution from fossil fuel sources

Errors of the %Bio or %Fossil column are $\pm 2\%$ for a full fill of counter

Table 4

Palisades

<u>UCLA No.</u>	<u>Date Collected</u>		$\mu\text{g}/\text{m}^3$			Carbon	
			<u>Total</u>	<u>C</u>	<u>%C</u>	<u>%Bio</u>	<u>%Fossil</u>
2428A	4/28 - 4/30	82	80.9	4.3	5.3	100	0
2428 B&C	5/4 - 5/13	82	86.5	2.8	3.2	99	1
2428E	5/18 - 5/31	82	66.2	<1.2	<2.0	NC	-
2428F	6/8 - 6/21	82	57.2	1.2	2.1	100	0
2430A	6/28 - 7/9	82	62.0	<1.3	<2.0	NC	-
2431A	7/19 - 7/30	82	82.6	2.3	2.8	32	68
2433B	8/9 - 8/20	82	89.6	3.6	4.0	94	6
2433I	9/20 - 10/18	82	142.1	4.9	3.4	72	28
2433E	10/11 - 10/25	82	149.6	5.6	3.7	65	35
2439D	11/1 - 11/12	82	97.3	6.6	6.8	28	72
2439B	11/30 - 12/13	82	70.8	7.9	11.1	4	96
2440F	1/25 - 2/7	83	121.8	5.4	4.4	32	68
2444C	2/7 - 2/21	83	123.1	5.5	4.5	72	28
2445E	4/4 - 4/15	83	85.1	3.6	4.1	70	30
2448A	4/25 - 5/6	83	99.3	2.2	2.2	100	-
2448J	5/16 - 5/27	83	72.0	4.3	6.0	41	59
2450F	6/8 - 6/22	83	65	2.0	3.1	28	72
2453E	6/27 - 7/8	83	73	2.7	3.7	0	100
2456A	7/18 - 7/29	83	81.2	1.9	2.4	63	37
2458D	8/29 - 9/9	83	100.8	2.7	2.7	62	38
2459F	9/19 - 9/30	83	76.7	1.9	2.5	66	34
2452A	10/11 - 25	83	118.3	3.0	3.1	39	41
2459C	11/7 - 18	83	117.8	8.7	7.4	76	24

Table 5

Downtown Los Angeles

<u>UCLA No.</u>	<u>Date Collected</u>		$\mu\text{g}/\text{m}^3$			Carbon	
			<u>Total</u>	<u>C</u>	<u>%C</u>	<u>%Bio</u>	<u>%Fossil</u>
2428D	4/27 - 4/29	82	no data		10.1	57	43
2428G	5/18 - 5/31	82	68.1	11.8	17.3	88	12
2428H	6/7 - 6/18	82	74.5	9.4	12.6	0	100
2430B	6/28 - 7/9	82	61.9	15.0	24.2	0	100
2431B	7/19- 7/30	82	82.0	7.5	9.1	14	86
2433J	9/20 - 10/1	82	66.5	7.4	11.2	87	13
2440E	11/29 - 12/10	82	94.1	20.1	21.4	21	79
2438E	1/10 - 1/24	83	57.1	6.1	10.7	30	70
2444D	2/7 - 2/21	83	74.7	14.0	18.8	25	75
2448K	5/16 - 5/27	83	102.4	16.5	16.9	22	78
2450E	6/8 - 6/22	83	94	10.0	10.6	24	76
2453F	6/27 - 7/8	83	69	10	14.4	26	74
2456C	7/18 - 7/29	83	78.5	12.5	15.9	25	75
2457C	8/8 - 8/19	83	75.1	9.6	12.8	43	57
2458E	8/29 - 9/9	83	75.7	15.5	20.5	29	71
2459E	9/19 - 10/1	83	83.7	13.2	15.8	38	62
2452B	10/11 - 10/25	83	97	15.6	16.2	24	76
2459B	11/7 - 11/19	83	71.1	13.2	18.6	32	68

Table 6

El Monte

<u>UCLA No.</u>	<u>Date Collected</u>		$\mu\text{g}/\text{m}^3$			Carbon	
			<u>Total</u>	<u>C</u>	<u>%C</u>	<u>%Bio</u>	<u>%Fossil</u>
2427 A&B	3/25 - 4/9	82	82.4	10.9	13.4	84	16
2427 C,D&E	4/12 - 4/19	82	60.4	3.9	6.5	100	0
2427F	4/19 - 4/22	82	84.3	13.5	19.7	45	55
2428I	5/18 - 5/26	82	90.9	10.2	11.2	98	2
2428J	6/7 - 6/18	82	83.6	9.7	11.6	0	100
2430C	6/28 - 7/9	82	63.8	1.5	2.2	0	100
2431C	7/19 - 7/30	82	85.8	11.5	13.5	0	100
2433C	8/9 - 8/20	82	112.3	14.9	13.3	0	100
2464E	3/28 - 4/26	84	56.9	8.5	15.0	38	62
2445A	4/14 - 4/19	83	66.8	12.9	19.4	28	72
2445B	4/14 - 4/19	83	64.3	6.5	14.5	20	70
2464A	4/23 - 5/14	84	79.1	10.6	13.4	38	63
2451B	9/27 - 10/14	83	70.2	10.7	15.2	40	60
2451C	9/27 - 10/14	83	73.8	9.9	13.4	40	60
2451A	10/18 - 10/28	83	84.1	14.8	17.6	27	73
2451D	10/18 - 10/28	83	139.6	19.0	13.6	45	55
2449A	Brush		-	-	100	0	100
2449B	Large impactor		-	-	5.1	58	42
2449C	Small impactor		-	-	6.9	52	48
2449D	Precipitator		-	-	13.3	23	77

Table 7

Upland

<u>UCLA No.</u>	<u>Date Collected</u>		$\mu\text{g}/\text{m}^3$			Carbon	
			<u>Total</u>	<u>C</u>	<u>%C</u>	<u>%Bio</u>	<u>%Fossil</u>
2428K	5/18 - 5/31	82	90.7	11.9	13.1	17	83
2428L	6/7 - 6/18	82	94.3	11.6	12.3	22	78
2430D	6/28 - 7/9	82	60.9	3.4	5.6	0	100
2431D	7/19 - 7/30	82	95.2	9.6	10.1	7	93
2433A	8/9 - 8/20	82	120.5	19.3	16.0	9	91
2433H	9/20 - 10/1	82	74.8	9.0	12.1	65	35
2433G	10/11 - 10/22	82	101.7	9.2	9.0	95	5
2439A	12/6 - 12/17	82	82.4	14.2	17.3	0	100
2438F	1/10 - 1/21	83	61.2	6.9	11.2	72	28
2444A	2/8 - 2/21	83	72.3	9.8	13.5	26	74
2448H	5/16 - 5/27	83	106.5	16.9	15.9	17	83
2450G	6/8 - 6/21	83	110	15.0	13.6	16	84
2459A	11/7 - 11/18	83	73.7	12.0	16.3	45	55

Table 8

Chico

<u>UCLA No.</u>	<u>Date Collected</u>	<u>µg/m³</u>			<u>Carbon</u>	
		<u>Total</u>	<u>C</u>	<u>%C</u>	<u>%Bio</u>	<u>%Fossil</u>
2433F	9/21 - 10/7 82	28.0	5.0	17.7	79	21
2439G	10/28 - 11/10 82	42.9	14.7	34.1	75	25

Table 9

Lake Tahoe - various sites

<u>UCLA No.</u>	<u>Date Collected</u>		$\mu\text{g}/\text{m}^3$			Carbon	
			<u>Total</u>	<u>C</u>	<u>%C</u>	<u>%Bio</u>	<u>%Fossil</u>
2426 A&B	2/11 - 2/14	82	134.6	15.3	11.4	47	53
2426 C&D	2/29 - 3/4	82	81.9	6.2	7.6	47	53
2426 E	3/4 - 3/10	82	158.8	21.2	13.4	47	53
2426 F	3/10 - 3/16	82	43.3	8.0	20.7	47	53
2433 D	9/2 - 9/20	82	81.9	6.2	7.4	14	86
2456D	7/11 - 7/24	83	33.2	4.0	12.0	29	71
2450 B	7/25 - 8/2	83	26.6	4.6	17.4	80	20
2450 A	8/2 - 8/8	83	39.0	6.7	17.2	25	75
2457 A	8/8 - 8/22	83	15.1	2.8	18.3	57	43
2457 F	8/15 - 8/22	83	22.1	4.9	22.3	36	64
2458 F	8/22 - 9/6	83	29.3	4.9	16.7	50	50
2459 H	9/5 - 9/11	83	16.4	6.8	41.3	64	36
2459 I	9/13 - 9/19	83	25.5	5.0	19.5	42	58
2452 E	9/19 - 10/3	83	9.6	1.7	17.8	55	45
2452C	9/19 - 10/3	83	76.0	20.0	26.4	55	45

Table 10

Bakersfield

<u>UCLA No.</u>	<u>Date Collected</u>		$\mu\text{g}/\text{m}^3$			Carbon	
			<u>Total</u>	<u>C</u>	<u>%C</u>	<u>%Bio</u>	<u>%Fossil</u>
2438B	12/7 - 12/10	82	108.3	14.0	12.9	64	36
2438C	12/20 - 12/23	82	89.2	19.0	21.4	no data	
2438A	1/17 - 1/21	83	94.1	17.0	18.2	94	6
2438D	1/24 - 1/28	83	147.0	10.1	6.9	30	70
2444F	2/7 - 2/10	83	73.8	6.1	8.3	40	60
2444E	2/10 - 2/14	83	66.9	13.9	21.6	19	81
2448E	4/5 - 4/11	83	46.9	5.2	11.1	32	78
2453A	5/12 - 5/20	83	60	5.0	8.3	38	62
2453B	6/2 - 6/7	83	66	6.6	10.0	40	60
2453C	6/27 - 7/1	83	75	7.5	10.1	42	58
2453D	7/6 - 7/11	83	87	7.3	8.4	36	63
2458B	8/24 - 9/2	83	75.7	>6.3	> 8.3	52	48
2458A	9/20 - 9/26	83	83.2	2.2	2.6	73	27

Table 11

El Cajon

<u>UCLA No.</u>	<u>Date Collected</u>	$\mu\text{g}/\text{m}^3$			Carbon	
		<u>Total</u>	<u>C</u>	<u>%C</u>	<u>%Bio</u>	<u>%Fossil</u>
2439C	11/30 - 12/13 82	38.3	8.2	21.2	36	64
2438H	12/29/82-1/12/83	40.5	7.8	19.2	39	61
2438G	1/12 - 1/26 83	32.4	9.8	30.1	24	76
2445D	3/30 - 4/26 83	27.0	2.8	10.6	23	77
2448I	4/27 - 5/17 83	34.7	3.5	10.1	42	58
2448G	5/18 - 6/8 83	37.1	4.9	13.4	28	72
2450D	6/9 - 6/28 83	47	2.5	5.3	28	72
2456B	6/29 - 7/19 83	44	3.8	8.7	27	73
2450C	7/20 - 8/9 83	47	5.4	11.5	46	54
2457D	8/10 - 8/30 83	32.5	3.2	9.7	50	50
2459G	8/31 - 9/20 83	43.3	3.6	8.2	31	69
2452D	9/21 - 10/18 83	27.3	3.5	13.0	38	62

FIG. 1.

PACIFIC PALISADES : Total solids and total carbon (black) of particulates in air

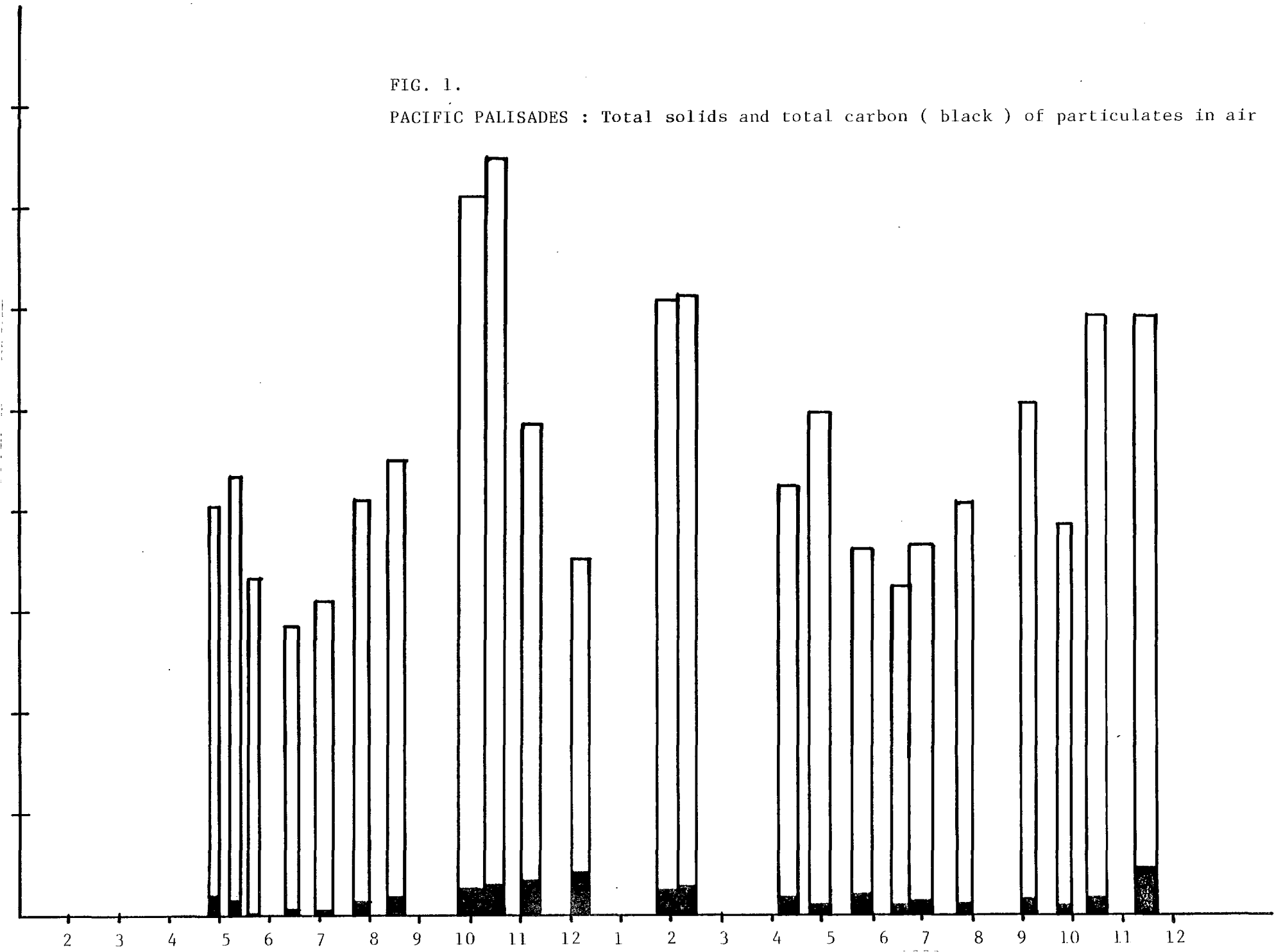


FIG.2.

DOWNTOWN LOS ANGELES : Total solids and total carbon (black) of particulates in air

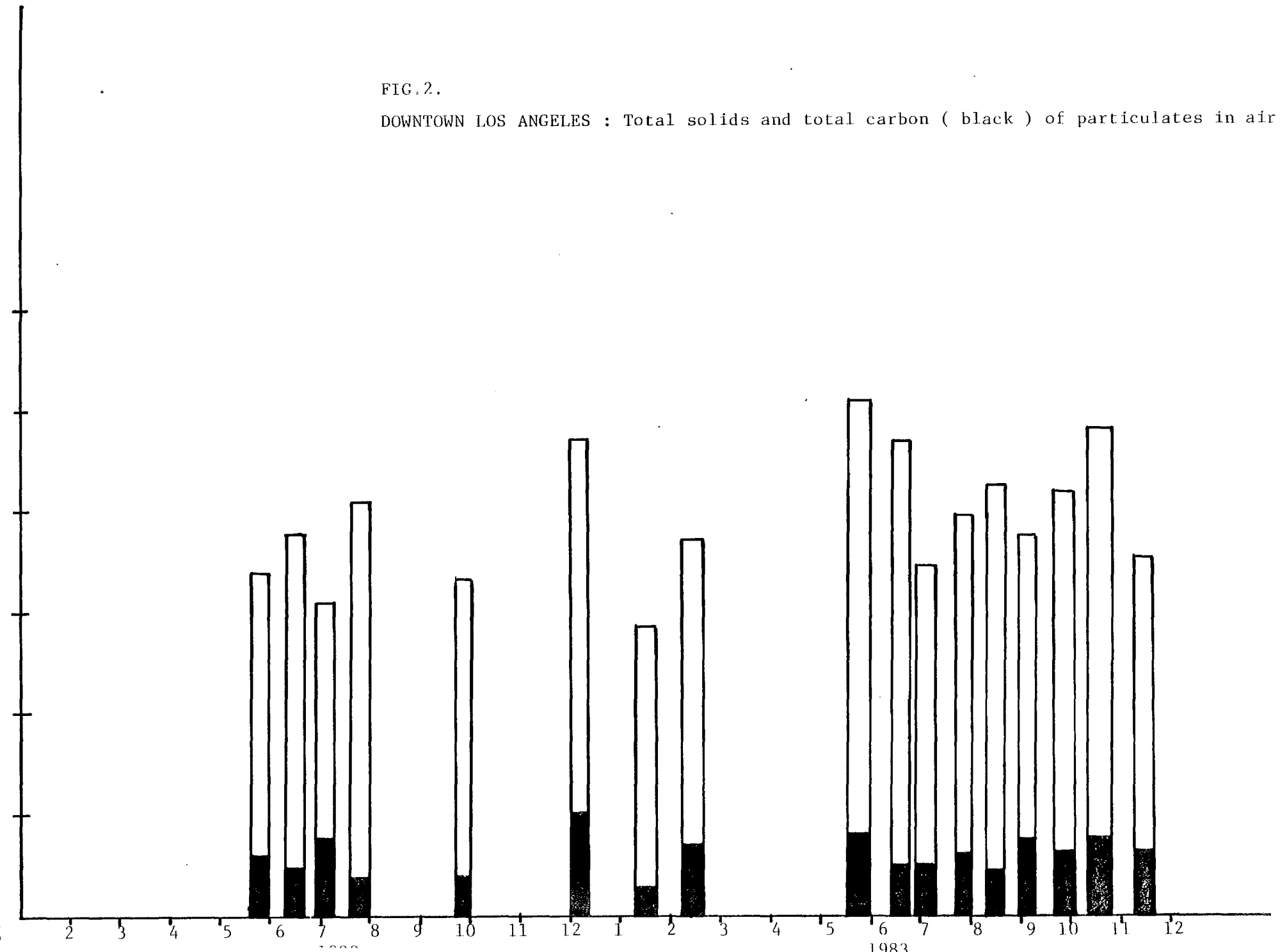


FIG.3.

EL MONTE : Total solids and total carbon (black) of particulates in air

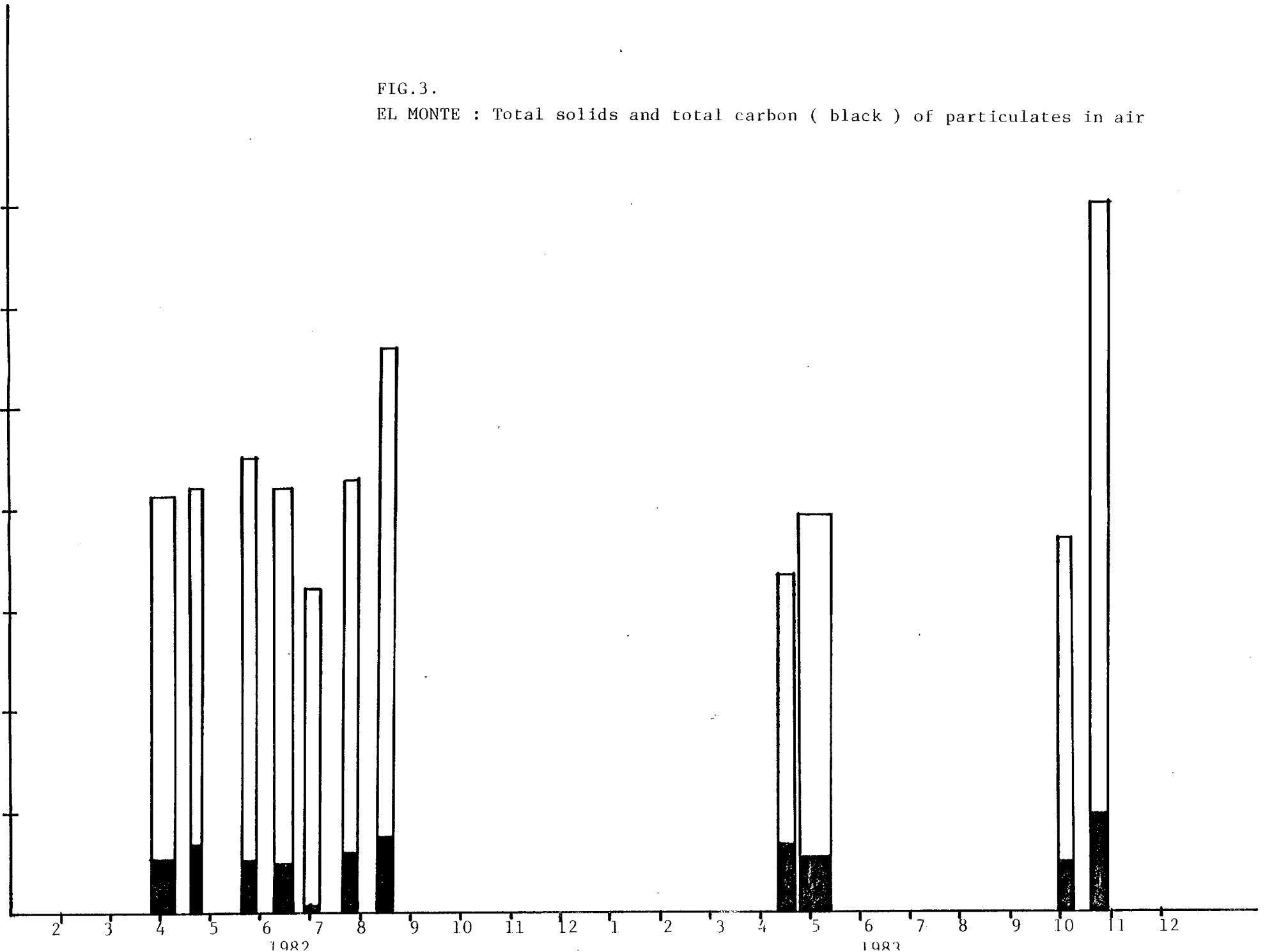


FIG.4.

UPLAND : Total solids and total carbon (black) of particulates in air

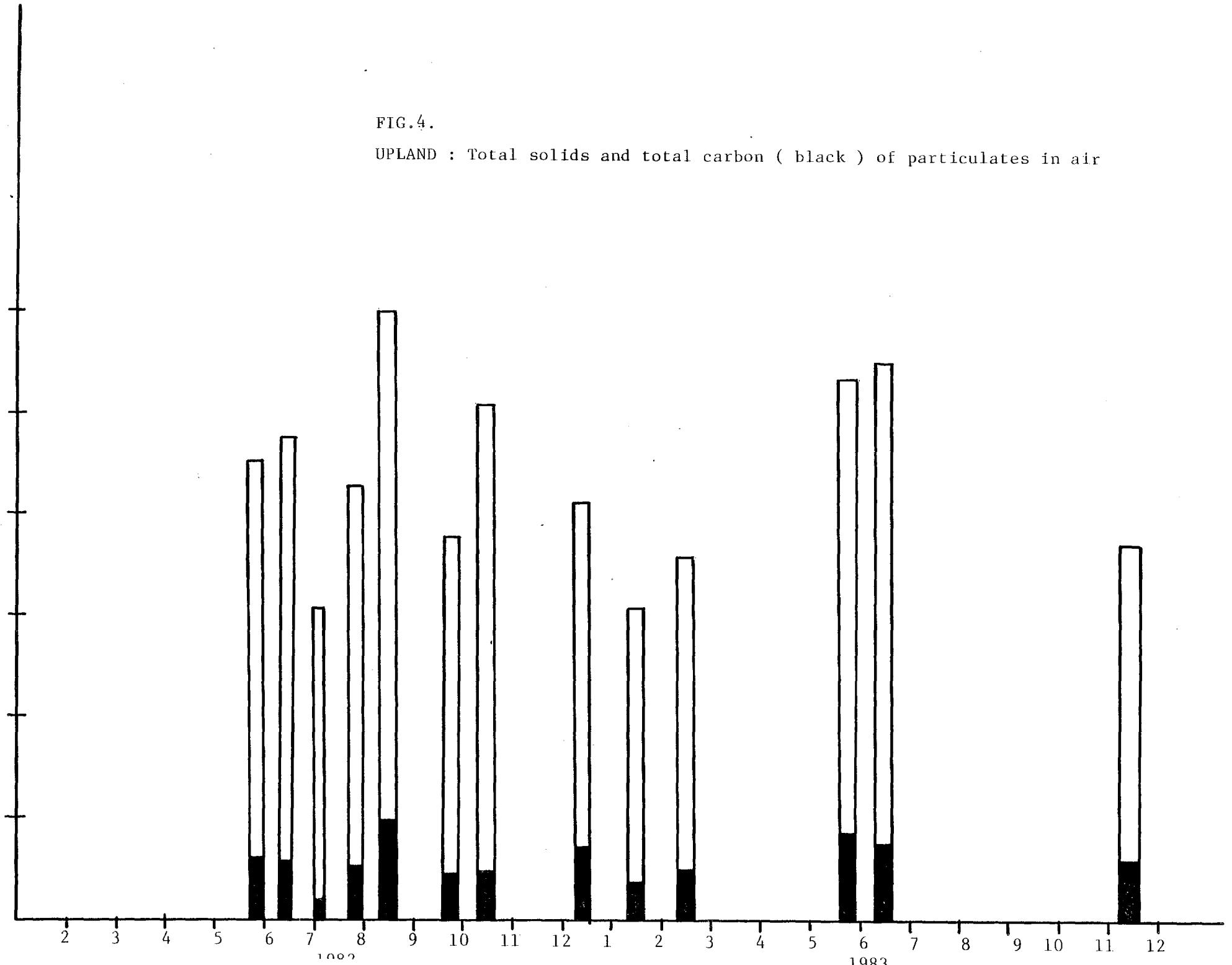


FIG.5.

CHICO: Total solids and total carbon (black) of particulates in air

2 3 4 5 6 7 8 9 10 11 12

1982

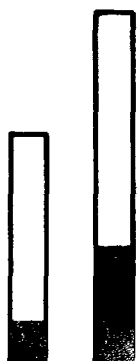


FIG. 6.

LAKE TAHOE : Total solids and total carbon (black) of particulates in air

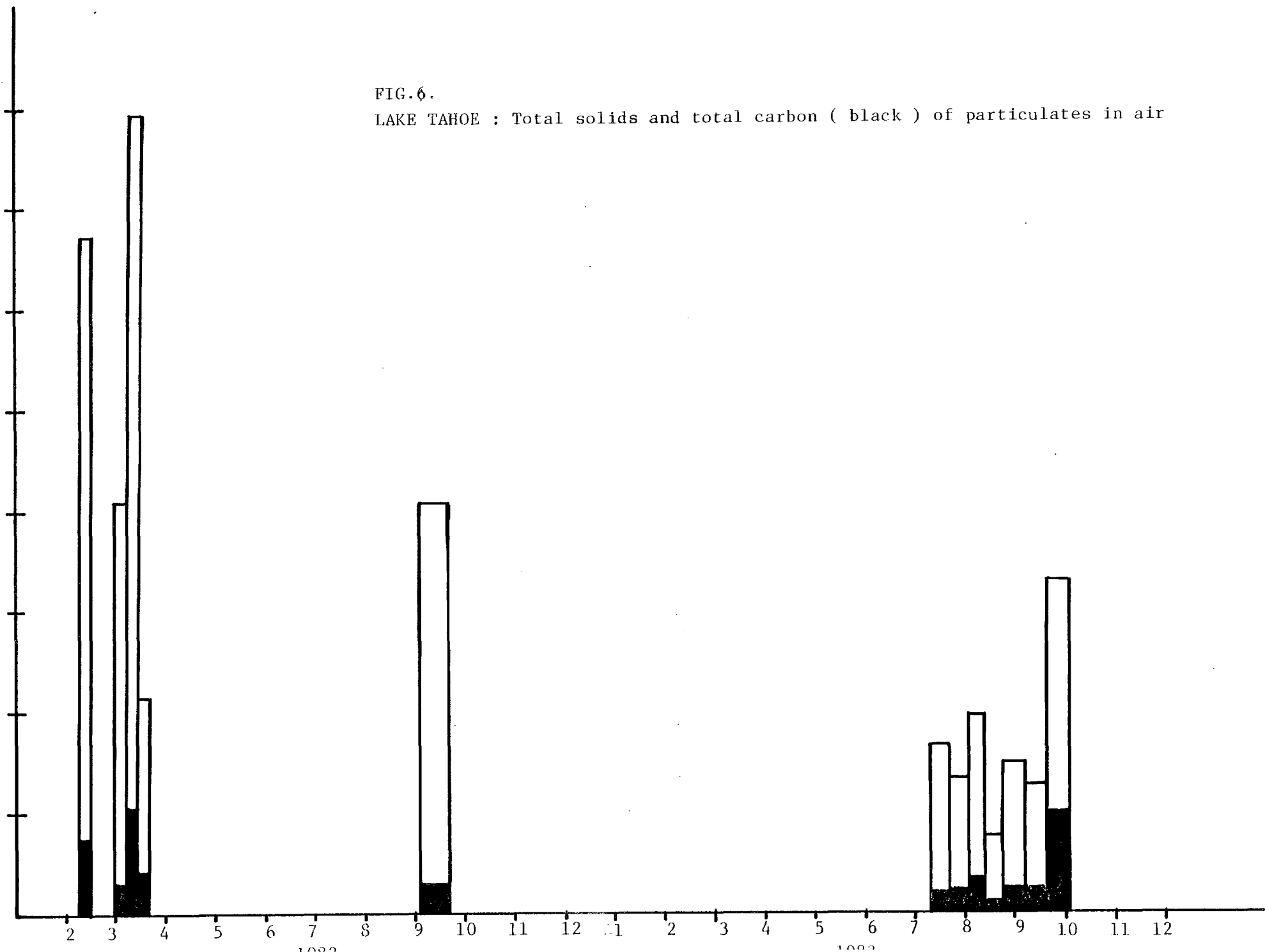


FIG. 7.

BAKERSFIELD : Total solids and total carbon (black) of particulates in air

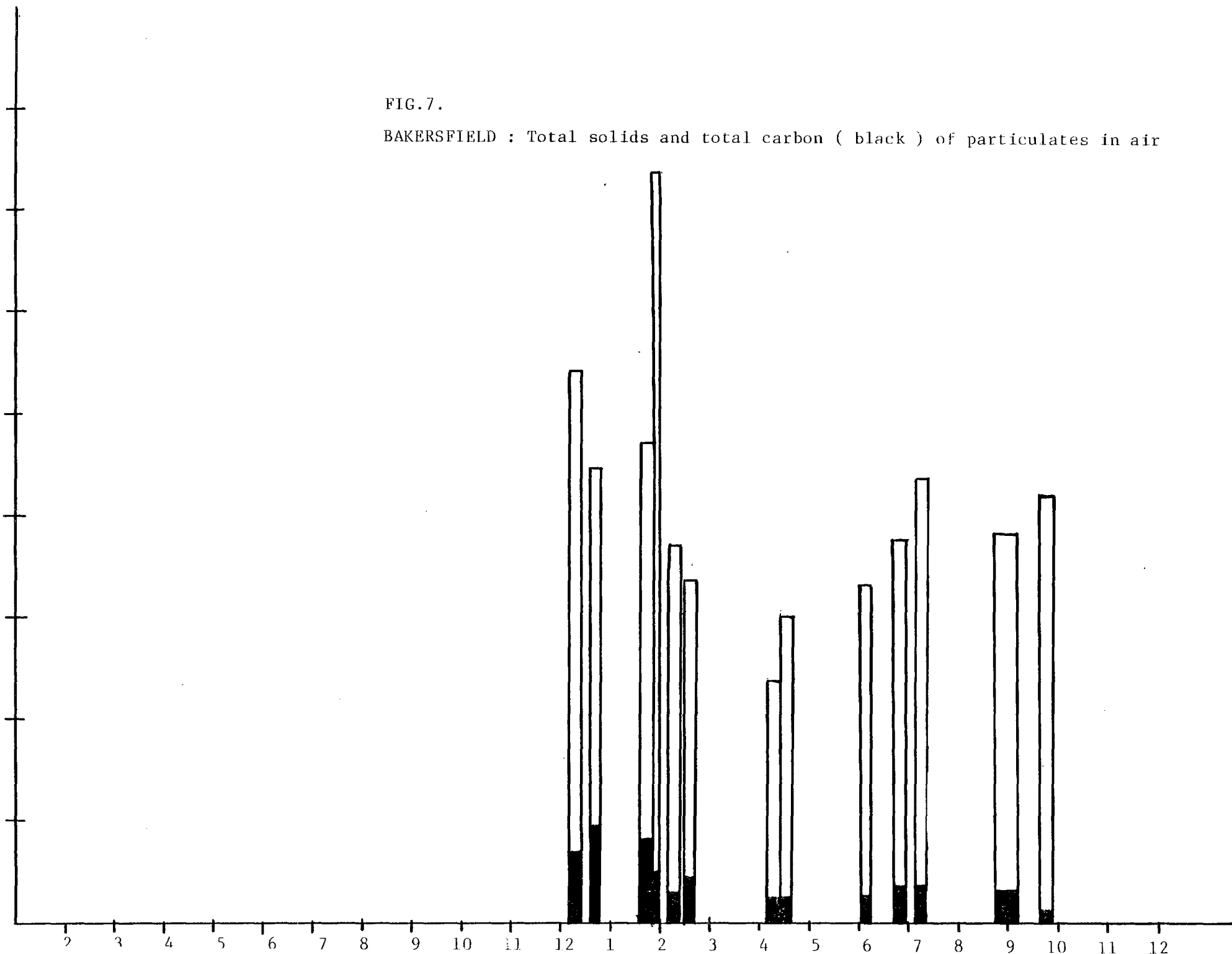


FIG.8.

EL CAJON : Total solids and total carbon (black) of particulates in air

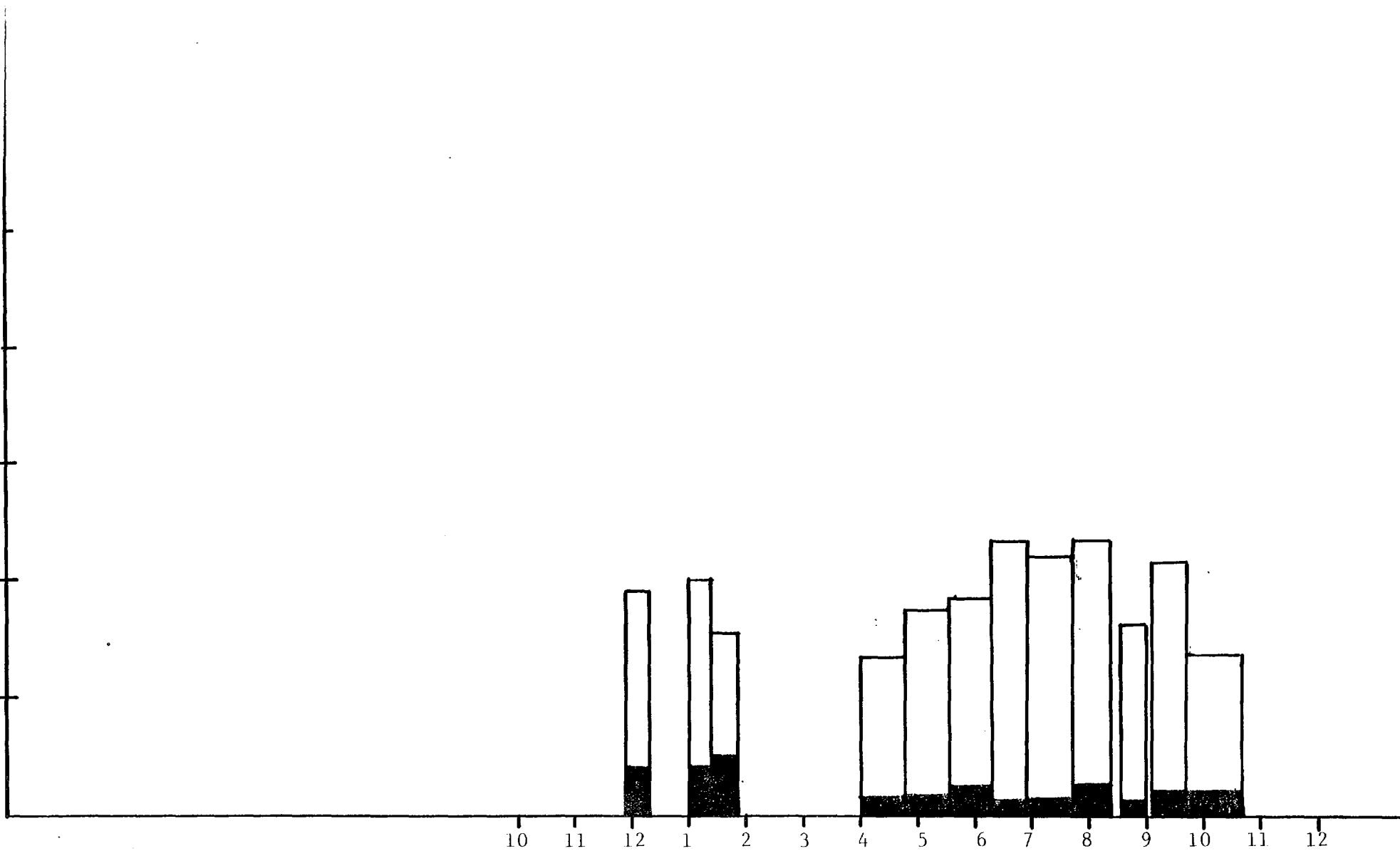


Figure 9

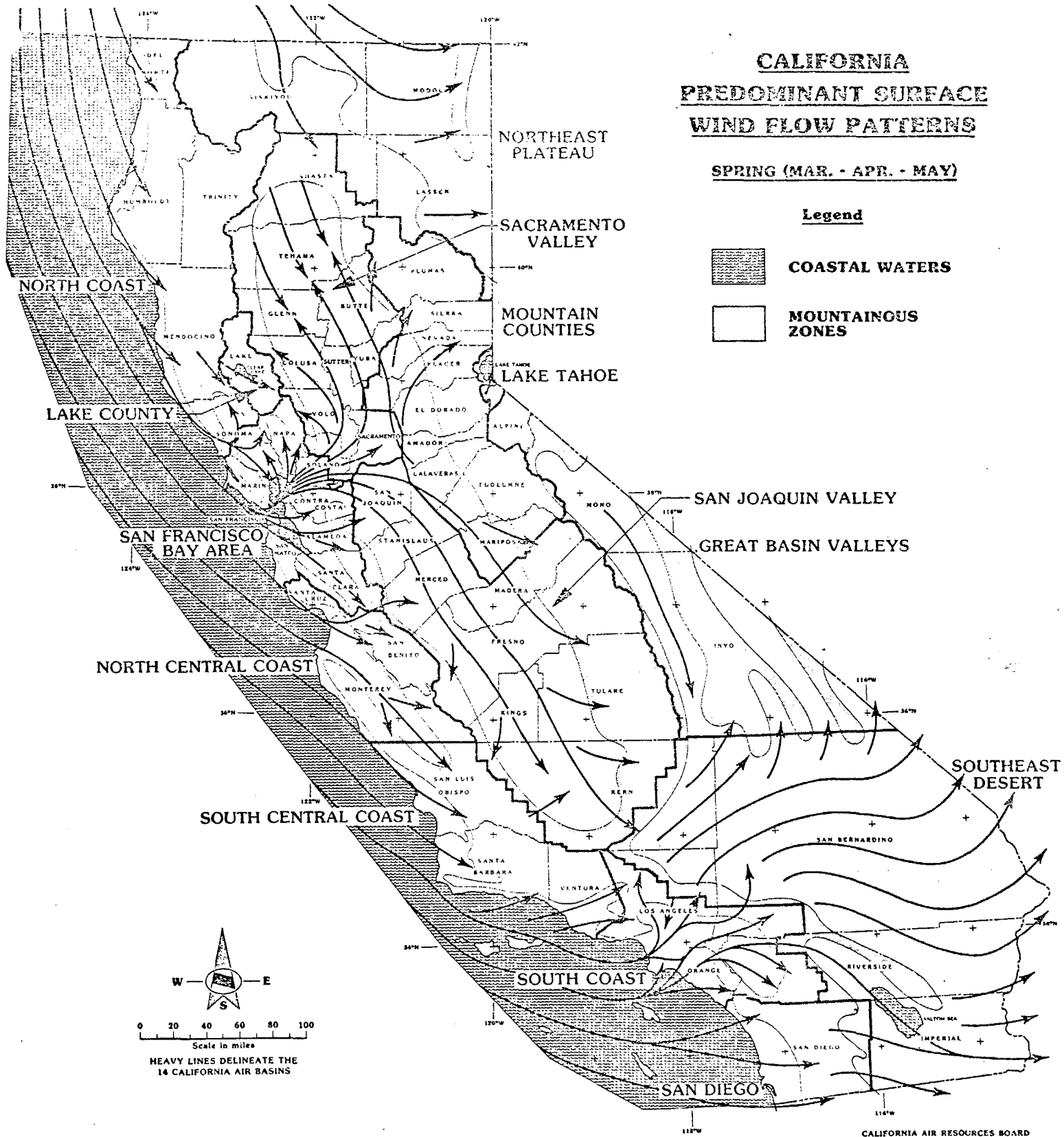
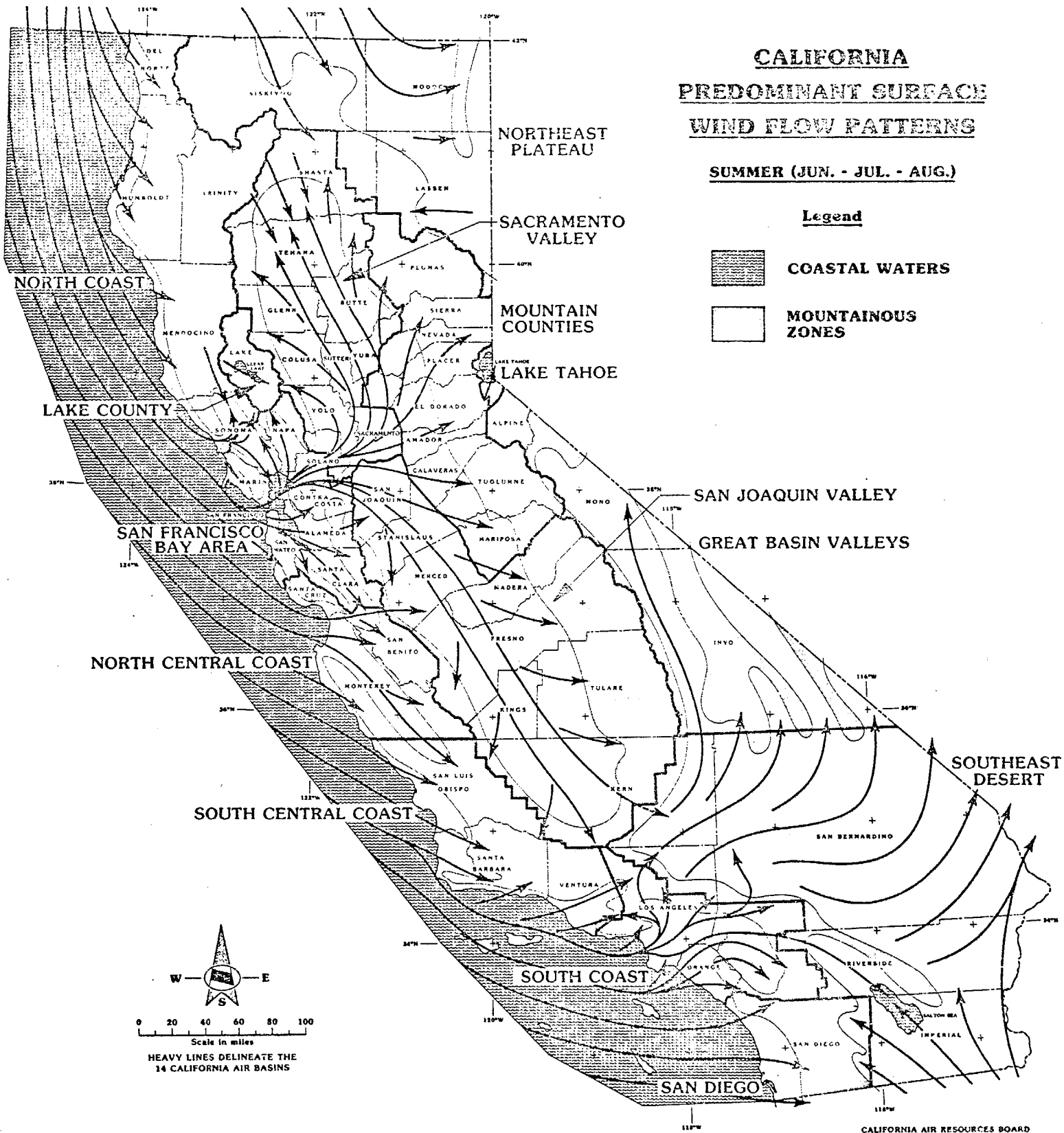


Figure 10



CALIFORNIA AIR RESOURCES BOARD
TECHNICAL SERVICES DIVISION 7/83

Figure 11

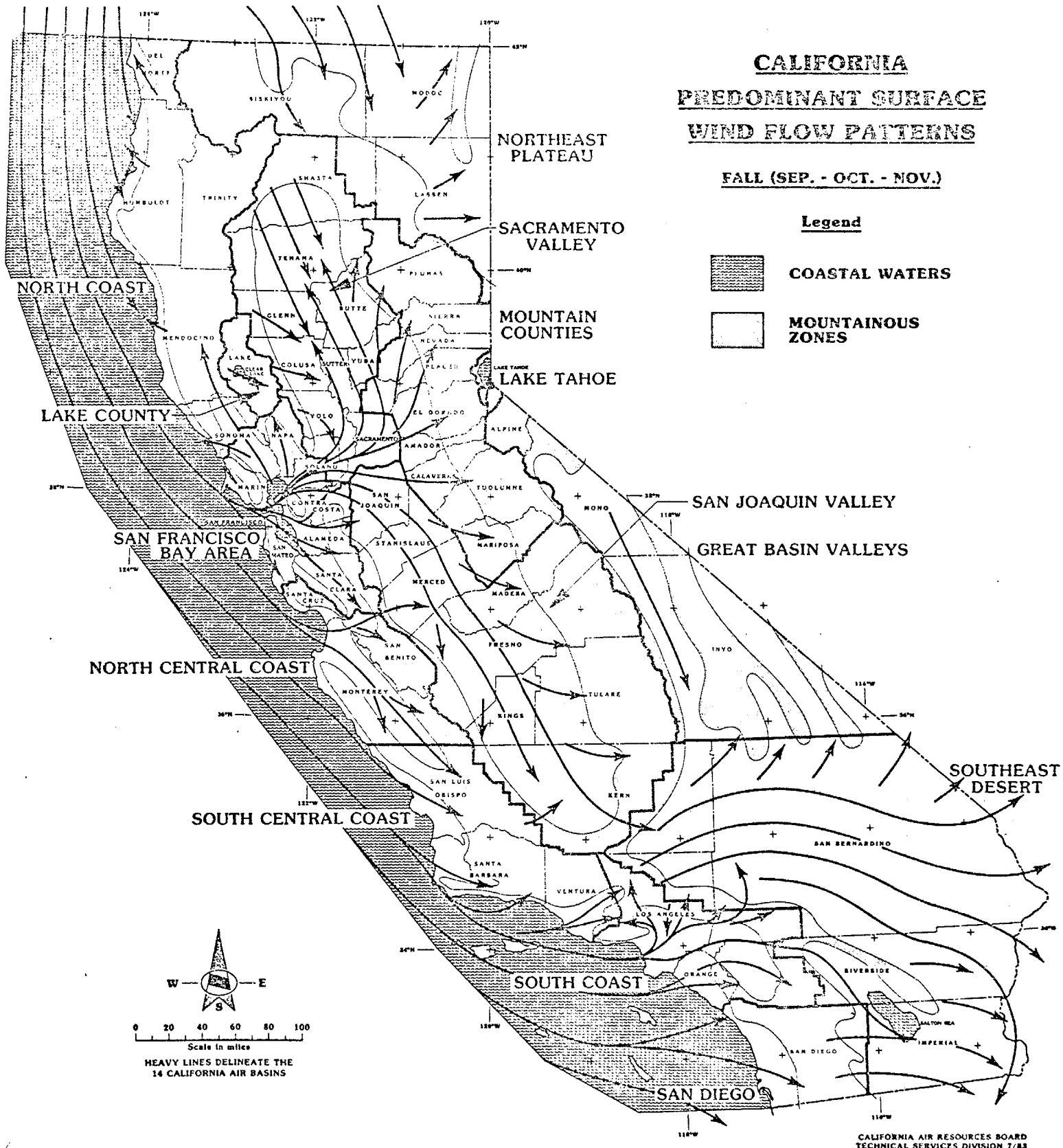
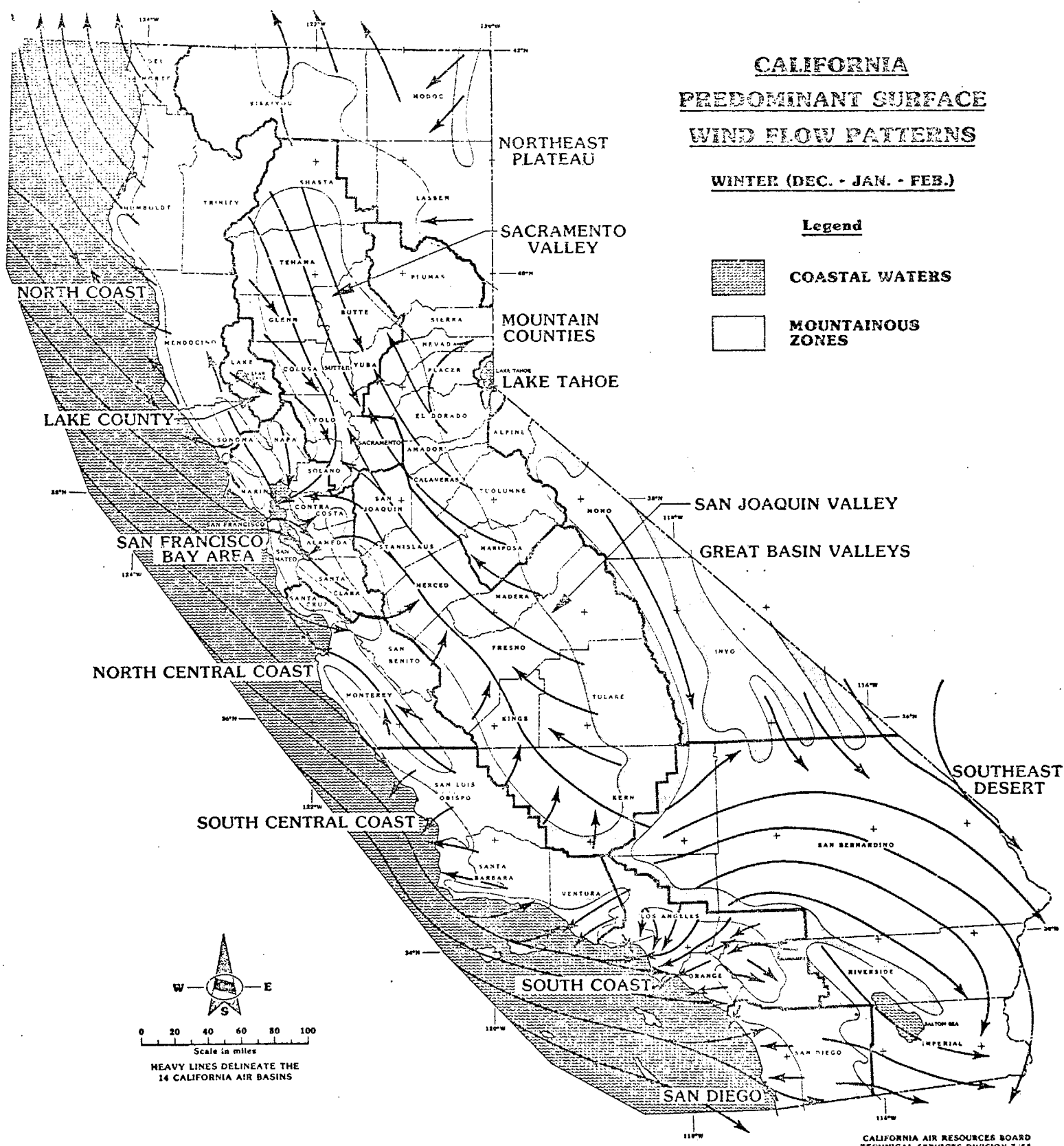


Figure 12



CALIFORNIA AIR RESOURCES BOARD
TECHNICAL SERVICES DIVISION 7.68

References

- B.R.Appel, Y.Tokiwa, J.Hsu, E.L.K.Kothny, E.Hahn and J.J.Wesolowski,
Visibility reduction as related to aerosol constituents,
CARB Final Report, Contract No. A 1-081-32, October 1983
- R.Berger, Radiocarbon content of the troposphere, Radiocarbon, in press.
- R.Berger, Direct bone dating in a small CO₂ counter, Radiocarbon 25, 655-659(1983).
- R.Berger, R.M.Johnson and J.R.Holmes, Radiocarbon measurements of
particulates in smog, Radiocarbon 25, 615-620(1983).
- J.J.Bufalini, Factors in summer ozone production in the San Francisco
air basin, Science 203, 81(1979).
- I.Levin, K.O.Munnich and W.Wiess, The effect of anthropogenic CO₂ on the
distribution of ¹⁴C in the atmosphere, Radiocarbon 22, 379 (1980).
- L.P.Lodge, Sr., G.S.Bien and H.E.Suess, The carbon-14 content of urban
airborne particulate matter, Internat.J.Air Pollution 2, 309-312(1960).
- P.R.Miller, J.N.Pitts, Jr. and A.M.Winer, Factors in summer ozone production
in the San Francisco air basin, Science 203, 81(1979).
- J.S.Sandberg, M.J.Basso and B.A.Okin, Winter rain and summer ozone: a predictive
relationship, Science 200, 1051(1978).
- J.S.Sandberg, M.J.Basso and B.A.Okin, Factors in summer ozone production in
the San Francisco air basin, Science 203, 82(1979).

Publication

The following preliminary publication has appeared
in print :

"Radiocarbon measurements of particulates in smog!"
Rainer Berger, R.M. Johnson and J.R. Holmes in
RADIOCARBON 25, No.2, p. 615-620 (1983).

Glossary of Terms

Biospheric carbon	Carbon derived from modern living things
Carbon-13 or ^{13}C	Stable isotope of carbon
Carbon-14 or ^{14}C	Unstable or radioactive isotope of carbon
C-3 pathway	A particular biochemical metabolic pathway used by leafy plants
Fossil carbon	Carbon of fossil fuels such as coal or natural gas of geologic age
PDB Standard	An international reference standard used to compare carbon-13 concentrations
°/oo or per mil	Parts per thousand
Proportional counter	A radiation detector which registers the magnitude of radioactive disintegrations depending on the voltage applied to the counter
Radiocarbon	Radioactive carbon, carbon-14 or ^{14}C
Radon	A radioactive daughter product generated during uranium-series decay
Troposphere	The air compartment between the surface of the earth and the tropopause located at approximately 40,000 feet of altitude
TSP	Total suspended particles in air