

RADIOCARBON MEASUREMENTS OF PARTICULATES IN SMOG

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ABSTRACT. In recent years in California, smog aerosols have been observed in metropolitan and rural areas. We wondered what the relative contribution is from sources such as fossil fuel combustion (eg, cars, factories) and emissions from trees and other plants. Pollution produced by fossil fuel combustion can be distinguished from biological sources using radioactive carbon. Carbon in fossil organic materials is radioactively dead whereas carbon in living plants contains ^{14}C . Smog particles were collected on clean glass or quartz fiber paper and analyzed in a small volume CO_2 proportional counter for ^{14}C content. Results are given for sampling locations at UCLA, El Monte, Riverside, and Lake Tahoe showing the relative contributions of fossil and modern carbon sources ranging from 0 to 74% and 26 to 100% respectively.

INTRODUCTION

A special aspect of the carbon cycle in nature involves the presence of carbon-containing particles in smog aerosols. Generally, the carbonaceous portion of smog consists mainly of a gaseous phase and ca 3% particulates (Grosjean and Friedlander, 1975). Even though the latter contribution is relatively small, it causes much air pollution and visibility problems affecting eg, air traffic.

Smog largely occurs in areas where the downward air motion of the Hadley cell produces, mainly in the summer, high pressure areas near 30° N or S latitude. As these high pressure cells are associated with little wind, temperature inversions often develop, placing warm over cool air near the surface of the earth. This condition causes the trapping of atmospheric pollutants below the inversion layer.

At the same time, photochemical reactions operate due to strong insolation. Nitrogen oxides formed give rise to

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ozone which, in turn, oxidizes hydrocarbons to such irritants as aldehydes, peroxides, or epoxides. Briefly summarized, some of the principal chemical reactions are: (Varney and McCormac, 1971)

- 1) $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$
- 2) $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$
- 3) $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ (where M is a third body)
- 4) $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
- 5) $\text{O}_3 + \text{hydrocarbons} \rightarrow \text{aldehydes, peroxides, and epoxides}$

This combination of meteorologic and chemical processes will produce smog with its attendant particulates.

In recent years, appreciable concentrations of smog reaching from ca 32°N to 42°N latitude, have been observed in previously unaffected rural or semi-rural areas of California. The need arose to determine if smog drifts in from large metropolitan centers or if trees and other plants contribute enough organic substances (eg, terpenes and pollen) to become an alternate source of air pollution (Sandberg, Basso, and Okin, 1978; Bufalini, 1979; Miller, Pitts, and Winer, 1979; Sandberg, Basso, and Okin, 1979; Currie et al, 1983). This question can be answered by analyzing aerosol particles for their ^{14}C content. Biospheric origin manifests itself in ^{14}C concentrations in the recent biosphere. On the other hand, fossil origin is indicated by the absence of ^{14}C , which because of its half-life of 5730 ± 30 years, has long ceased to exist in measurable quantities in fossil fuels formed millions of years ago.

SAMPLE COLLECTION

In 1978, personnel from the State of California Air Resources Board began collecting particulates, using first air samplers containing chemically isotopically clean glass filters and later quartz paper. The latter does not melt in the intense heat of the combustion process causing cracking of the Vycor-tubes in which the sample burning is accomplished. Both glass and quartz filter papers were checked for contaminating organic compounds by heating blanks. No measurable gas or activity was found.

At the outset of the sampling program, three stations were set up in southern California: at UCLA, El Monte, and Riverside. Since westerly breezes blow smog mainly toward

Riverside and beyond, it was thought that the lowest air contamination might exist at UCLA increasing in severity toward El Monte and Riverside (fig 1). In 1982, several other stations such as Lake Tahoe and more in the greater Los Angeles area were added to this ongoing program of particulate analysis.

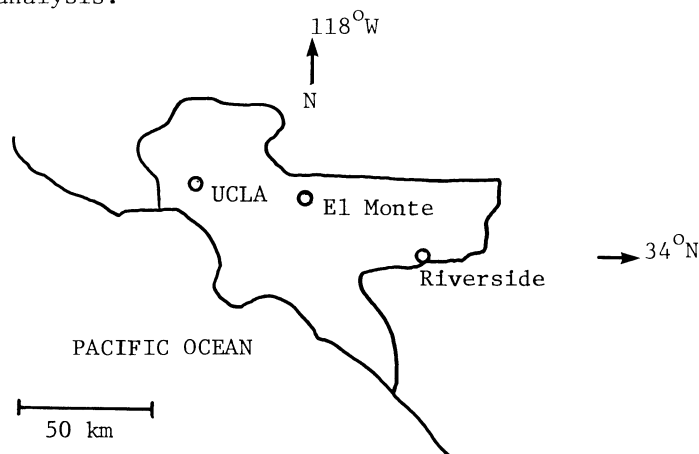


Fig 1. The area shown is the air basin of metropolitan Los Angeles. The surrounding region is mountainous or hilly except for the Pacific coastline. Winds during most of the year are from the west. During the winter Santa Ana winds occur which blow from the desert areas east of Los Angeles toward the ocean. The wind velocity precludes then any accumulation of smog over Los Angeles.

RADIOISOTOPIC ASSAY

As aerosol particles occur in relatively small quantities, a special low-level counting system had to be designed, constructed, and tested, based on previous experience with CO_2 proportional counters. Typically, aerosol phases contain only ca $100\mu\text{g}$ of organic material in lm^3 of air. Thus, a small 200mL copper proportional counter was built which needs only 100mg of carbon for filling, obtainable often within 1-3 days on the inert particulate filters. This unit was placed inside an anti-coincidence guard assembly which is, in turn, protected from ambient environmental radiation by a 7.5 ton radioactively clean steel shield. The elec-

tronics unit consists of 3 anti-coincidence and 3 coincidence channels powered by ultrastable high voltage supplies. Three standard are used: 1) by international convention, 95% of the count rate of NBS oxalic acid (1.88cpm), 2) CO_2 derived from marble as primary source (0.87cpm), and 3) a CO_2 gas sample derived from a deck plank of the funerary boat of Sesostris III, historically dated to 1800 B C (0.63cpm). The latter standard is used to assure that the equipment performs accurately.

Depending on the filter loading which varies from ca 0.5 to 2.9g one or more filters are placed into an isotopically clean Vycor-quartz tube and burned in a stream of analytically pure oxygen. The resulting CO_2 is purified by washing in silver nitrate and chromic acid solutions. Any CO is converted to CO_2 by copper oxide at 500° . Finally, all electronegative impurities such as O_2 or NO_2 which interfere with proportional counting are removed by passage over clean elementary copper at 500° . Subsequently, these clean CO_2 samples are stored for one month in high-pressure steel cylinders to allow all radon to decay. Typically, samples are then counted for about 2000 minutes to a standard deviation of 2%.

RESULTS

Table 1 lists the data for particulates by percentage of fossil fuel and by inference of recent biospheric contributions. In addition to the ^{14}C measurements, a series of $^{13}\text{C}/^{12}\text{C}$ stable isotope measurements were made to ascertain that there was no inclusion of carbonate-dust in the particulate samples. The range of $\delta^{13}\text{C}$ determinations is from -26.30% to -29.72% with respect to the PDB standard. Since carbonate-derived CO_2 has a $\delta^{13}\text{C}$ near zero no inorganic contamination is present.

TABLE 1. Carbon Composition of Total Suspended Particles

From UCLA

UCLA no	Collection date	Weight sample(g)	Fossil fuel contribution(%)*
2210B	9/26/78	1.752	65 ± 2
2210C	9/29/78	1.657	60 ± 2

From El Monte

2209A	8/11-15/78	0.784	66 $\pm$ 2
2209B	8/16-18/78	0.949	74 $\pm$ 2
2209C	8/21-24/78	0.759	59 $\pm$ 2
2427A,B	3/25-26 and 4/7-9/82	0.506	16 $\pm$ 2
2427C,D,E	4/12-19/82	0.877	0 $\pm$ 2
2427F	4/19-22/82	0.526	55 $\pm$ 2

From Riverside

2211A	9/29/78	2.670	58 $\pm$ 2
2211B	10/3/78	2.708	59 $\pm$ 2
2211C	10/6/78	1.246	66 $\pm$ 2
2211E	10/13/78	2.880	55 $\pm$ 2

From Lake Tahoe

2426A,B	2/11-14/82	0.593	53 $\pm$ 2
2426C,D	2/24-3/4/82	0.879	53 $\pm$ 2
2426E	3/4-10/82	1.146	53 $\pm$ 2
2426F	3/10-16/82	0.450	53 $\pm$ 2

*Based on $^{14}\text{CO}_2$ concentration of +35% for 1978 and +25% for 1982 in troposphere above 95% of the count rate of NBS oxalic acid (Berger, ms in preparation).

DISCUSSION

The initial data show that there is considerable variation in the composition of particulates in the Los Angeles air basin, eg, UCLA 2209B is composed of almost 75% of fossil carbon due to anthropogenic emissions. On the other hand, UCLA-2427CDE contains only recent biospheric material. Could it be that this latter sample is made up entirely of pollen from a nearby tree? If so, the choice of sampling location is very critical. Yet on the whole, except for two samples, all data show a clear preponderance of fossil over recent biospheric carbon. This is even true for a High Sierra resort such as Lake Tahoe during February-March 1982.

All these determinations compare well with appropriate measurements obtained by Currie, Klouda, and Cooper (1980) and Currie et al (1983). However, the variations in the data call for more detailed studies linking location, meteorology, and seasonal factors. Such a program of research is now being continued at UCLA.

ACKNOWLEDGMENTS

This study was supported by the State of California Air Resources Board. Our gratitude is extended to D Sullivan, D McJunkin, I Kaplan, and D Winter, whose cooperation has been invaluable. This is publication no 2347 of the Institute of Geophysics and Planetary Physics, UCLA.

REFERENCES

- Bufalini, J J, 1979, Factors in summer ozone production from the San Francisco air basin: *Science*, v 203, p 81.
- Currie, L A, Klouda, G A, Continetti, R E, Kaplan, I R, Wong, W W, Dzubay, T G, and Stevens, R K, 1983, On the origin of carbonaceous particles in American cities: results of radiocarbon "dating" and chemical characterization, in Stuiver, M and Kra, R S, eds, Internatl ^{14}C conf, 11th, *Proc: Radiocarbon*, v 25.
- Currie, L A, Klouda, G A, and Cooper, J A, 1980, Miniradio-carbon measurements, chemical selectivity, and the impact of man on environmental pollution and climate, in Stuiver, M and Kra, R S, eds, Internatl ^{14}C conf, 10th, *Proc: Radiocarbon*, v 22, no 2, p 349-362.
- Grosjean, D and Friedlander, S K, 1975, Gas and particle distribution factors for organics and other pollutants in the Los Angeles atmosphere: *Jour Air Pollution Control Assoc*, v 25, p 1038-1044.
- Miller, P R, Pitts, J N, and Winer, A M, 1979, Factors in summer ozone production in the San Francisco air basin: *Science*, v 203, p 81-82.
- Sandberg, J S, Basson, M J, and Okin, B A, 1978, Winter rain and summer ozone: a predictive relationship: *Science*, v 200, p 1051-1054.
- _____, 1979, Factors in summer ozone production in the San Francisco air basin: *Science*, v 203, p 82-83.
- Varney, R and McCormac, B M, 1971, Atmospheric pollutants, in McCormac, B M, ed, *Introduction to the scientific study of atmospheric pollution*: Dordrecht, Reidel Pub Co, p 8-52.