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 irri-
tants as aldehydes, peroxides, or epoxides. Briefly summar-
ized, some of the principal chemical reactions are:
(Varney and McCormac, 1971)

1) $N_2 + 2O_2 \rightarrow 2NO_2$

2) $NO_2 + hv \rightarrow NO + O$

3) $O + O_2 + M \rightarrow O_3 + M$ (where M is a third body)

4) $NO + O_3 \rightarrow NO_2 + O_2$

5) $O_3 + hydrocarbons \rightarrow$ 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 Cali-
fornia. The need arose to determine if smog drifts in from
large metropolitan centers or if trees and other plants con-
tribute 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 mani-
fests 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 accomp-
lished. 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 par-
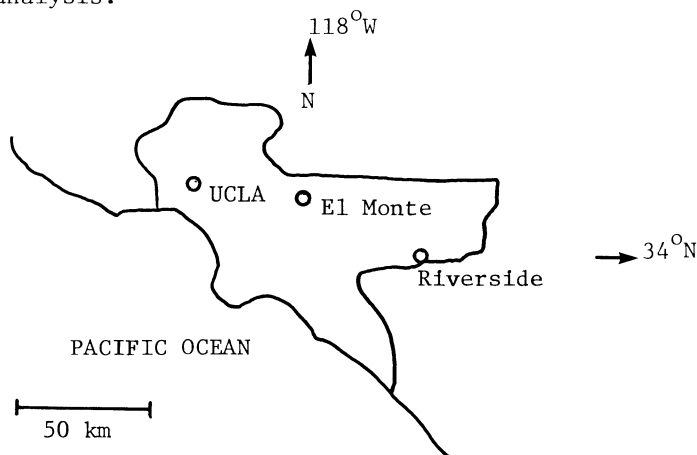ticulate analysis.

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 quanti-
ties, 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 con-
tain only ca 100µg of organic material in 1m^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 $^{13}C/^{12}C$ stable isotope measurements were made to ascertain that there was no inclusion of carbonate-dust in the particulate samples. The range of $\delta^{13}C$ determinations is from -26.30% to -29.72% with respect to the PDB standard. Since carbonate-derived CO_2 has a $\delta^{13}C$ 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 ± 2
2209B	8/16-18/78	0.949	74 ± 2
2209C	8/21-24/78	0.759	59 ± 2
2427A,B	3/25-26 and 4/7-9/82	0.506	16 ± 2
2427C,D,E	4/12-19/82	0.877	0 ± 2
2427F	4/19-22/82	0.526	55 ± 2

From Riverside

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

From Lake Tahoe

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

*Based on $^{14}CO_2$ 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 varia-
tion in the composition of particulates in the Los Angeles
air basin, eg, UCLA 2209B is composed of almost 75% of fos-
sil 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.

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