The Isotopic Composition of Atmospheric

Carbon Monoxide

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The Isotopic Composition of Atmospheric

Carbon Monoxide*

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ABSTRACT

The concentration and the carbon and oxygen iso-
topic composition of atmospheric CO of the northern
hemisphere show regular seasonal variations. The iso-
topic pattern is different from that for CO from auto-
mobile engine combustion whether compared to combustion
in the same region as the air sample or to an estimated
world average. These results indicate that there are
several natural sources, one of which is much greater
than anthropogenic emissions. The most likely nature
of these sources are discussed and the production rates
estimated.

1. Introduction

In recent years, several investigations have revealed that carbon monoxide may have a more active and complicated role in nature than had generally been known. Swinnerton et al. [1] and Seiler and Junge [2] have discovered that the oceans may be a significant source of CO. Seiler and Junge [3] have shown that the tropopause is a sink for CO and Inman et al. [4] found that soils may also be a significant sink. Junge et al. [5] have discussed the global atmospheric budget of CO, assuming only anthropogenic and ocean water sources.

The abundance of the stable isotopes of CO might be a way of distinguishing CO from different origins and thus identifying the origins of atmospheric CO. Both carbon and oxygen have quite variable isotopic compositions in nature [6-8]. At almost every stage of any natural process involving these elements, there are isotopic fractionation effects. The combination of isotopic variations for two elements having different cycles might be of special diagnostic value.

A program of measuring the isotopic composition of CO in the atmosphere and from natural sources has been going on at Argonne since 1969. The atmospheric studies include two separate problems: (1) the determination of the global-average isotopic composition of CO emitted by internal combustion engines, and (2) the determination of the isotopic pattern of CO in the least polluted atmosphere (mostly in Illinois) at different seasons and, where possible, different latitudes and times of day.

2. Experimental Procedure

The atmospheric samples were collected in 87-liter aluminum cylinders which had been evacuated by a mechanical pump connected through a liquid N_2 trap. A cylinder was filled with air to a gauge pressure of 2-3 atm with one or two small rubber-diaphragm compressors, operated from a 12V automobile battery. These compressors produce less than 0.01 ppm CO.

The atmospheric samples were processed to convert CO to CO_2 and separate this CO_2 from all other constituents of air for precision isotopic analysis. The chemical and mass spectrometric analytical methods have been previously described in detail by Stevens and Krout [9]. To summarize this procedure, each sample is passed through a processing train that first removes moisture, atmospheric CO_2, N_2O, NO and NO_2, next oxidizes the CO to CO_2 with Schutze reagent (I_2O_5), then purifies the CO_2 of CO-origin by freezing with liquid N_2 and pumping, and finally manometrically measures the CO_2. In the oxidation of CO by I_2O_5 at room temperature, the original oxygen atom of CO is retained in the resulting CO_2, and the other oxygen atom in CO_2 (which is acquired from the I_2O_5 in the oxidation process) has the same isotopic composition for each sample. The method is quantitative in the yield of CO oxidized to CO_2, does not produce CO_2 from any other known atmospheric compounds containing carbon, and produces CO_2 of CO-origin free from impurities that could cause large errors in either the concentration or isotopic analysis.

The samples are isotopically analyzed for both carbon and oxygen by the usual high-precision technique using a modified Consolidated-Nier isotope-ratio mass spectrometer with a semiautomatic data-

collecting system. The oxygen isotopic abundances are given rela-
tive to the accepted oxygen isotopic reference - Standard Mean
Ocean Water (SMOW). To determine the absolute $^{18}O/^{16}O$ ratios of
the original atmospheric CO, CO was first quantitatively prepared
from SMOW by reaction with graphite at 1000°C; then this CO was
oxidized to CO_2 with I_2O_5 by the same method as was used for the
atmospheric samples. The CO_2 from both the SMOW and atmospheric CO
samples have one atom of oxygen designated $O^\dagger$, contributed by the
I_2O_5 with a constant isotopic abundance*; hence, the value of the
$^{18}O/^{16}O$ ratio in the original CO can be expressed as the per mil dif-
ference δR_{CO} relative to SMOW oxygen as

$$\delta R_{CO} = 2\left[\frac{(R_{COO^\dagger})_X}{(R_{COO^\dagger})_{SMOW}} - 1\right] \times 1000 \quad , \tag{1}$$

where $(R_{COO^\dagger})_X$ is the mass-46/mass-44 ratio of the CO_2 from oxida-
tion with I_2O_5 of the sample, and $(R_{COO^\dagger})_{SMOW}$ is the 46/44 ratio of
CO_2 prepared from oxidation (with I_2O_5) of CO prepared from SMOW H_2O.

The carbon results are given as per mil differences δR of the
$^{13}C/^{12}C$ ratio R, relative to PDB** carbon R_0, where

$$\delta R = \left(\frac{R}{R_0} - 1\right) \times 1000 - \Delta(^{18}O/^{16}O) \times 0.033 \quad . \tag{2}$$

The second term $[\Delta(^{18}O/^{16}O) \times 0.033]$ is the correction for the dif-
ference in the $^{17}O/^{16}O$ ratio between the sample CO_2 of CO-origin
and CO_2 prepared from PDB carbonate by the usual method using 100%

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*$O^\dagger$ = 5.8‰ relative to SMOW by comparison between $(R_{COO^\dagger})_{SMOW}$
  and $(R_{COO})_{PDB}$.

**The Peedee belemnite used as an isotopic standard for carbon.

H_3PO_4 where $\delta(^{18}O/^{16}O)$ is the difference in per mil of the $^{18}O/^{16}O$ ratio of the CO_2 sample relative to CO_2 prepared from PDB carbonate. However, since the $^{18}O/^{16}O$ ratio is measured relative to SMOW oxygen as described above, the ^{17}O correction term must take into account the difference in the $^{17}O/^{16}O$ ratio between CO_2 from PDB carbonate and $(COO^{\dagger})_{SMOW}$. In the $(COO^{\dagger})_{SMOW}$ molecule, the $^{18}O/^{16}O$ ratio of one oxygen atom from SMOW H_2O is -41‰ and the other (from the I_2O_5 oxidation) is -35.2‰ relative to CO_2 from PDB. Hence, the above expression becomes

$$\delta R = \left(\frac{R}{R_0} - 1\right) \times 1000 + 1.25 - \delta(^{18}O/^{16}O) \times 0.0165 \quad , \quad (3)$$

where $\delta(^{18}O/^{16}O)$ is the $^{18}O/^{16}O$ ratio difference of the CO relative to SMOW as determined in equation (1). The external error is estimated to be ±0.01 ppm for the CO concentration, ±0.3‰ for the $^{13}C/^{12}C$ ratio, and ±0.5‰ for the $^{18}O/^{16}O$ ratio.

Before July 1970 when the oxygen isotopic analyses were started, about 60 samples were collected and analyzed for CO concentration and the $^{13}C/^{12}C$ ratio. During the early part of this period, analysis with the Argonne 100-inch mass spectrometer showed that the CO_2 from the CO contained up to 1% N_2O. The results on these early samples were corrected on the basis of measurements of the N_2O/CO_2 ratio. In addition, some of the samples were purified by treatment with hot CuO. Meaningful values of the concentration and of $\delta(^{13}C/^{12}C)$ were obtained for about half of these samples and are plotted as solid or open squares in Fig. 4 in the section on atmospheric CO; the other half was unused because of known contamination with engine CO or because the sample was too small or was lost before the N_2O impurity was measured. In July 1970 the

molecular-sieve trap in the processing train was improved so that the amount of N_2O in the final CO_2 from atmospheric CO was less than 3×10^{-5} times the atmospheric N_2O concentration.

3. Urban Atmospheric Carbon Monoxide

Figure 1 shows the $\delta(^{13}C/^{12}C)$ and $\delta(^{18}O/^{16}O)$ ratios for CO in urban air collected for a number of major cities in the United States and Europe. The variable $^{13}C/^{12}C$ ratios reflect the variable $^{13}C/^{12}C$ ratio in petroleum. This is illustrated in the upper portion of Fig. 2, where the $\delta(^{13}C/^{12}C)$ values of the urban atmospheric CO are compared with the values for various petroleum sources. In these samples, taken so that the CO represented averages for many automobiles, the $^{13}C/^{12}C$ ratios in CO samples from San Francisco and Los Angeles had high values corresponding to the high values for California oil and low values for Chicago CO corresponding to low values for Texas sources [7].

The specific objective of the first part of this study is to determine the carbon isotopic composition of world-average engine CO in order to compare it with average atmospheric CO. Appendix I gives a detailed account of our method of estimating the $^{13}C/^{12}C$ ratio for both U.S.-average and world-average engine CO. The world-average value is found to be $\delta(^{13}C/^{12}C) = -27.4\%_o$. This is admittedly a crude estimate, but the error is probably not greater than $\pm0.3\%_o$. The average measured isotopic composition of oxygen in urban CO is $\delta(^{18}O/^{16}O) = 24.6\%_o$, which is $1.1\%_o$ higher than the value for atmospheric oxygen [14].

4. Data on Non-Urban Atmospheric CO

Figure 3 shows the isotopic patterns of surface atmospheric

CO for minimum pollution conditions at locations upwind from Chicago (solid points) and at several distant locations in the southern and northern hemispheres (crosses) in 1970 and 1971. The majority of the Illinois samples were collected about two miles west of Plainfield, Illinois, on days when the wind direction ranged from south to north-northwest. The nearest towns upwind from this location are 5-10 miles away and have populations of less than 1500. Other Illinois locations (and the corresponding wind directions) were rural sites near Buffalo Grove (NW to N) and Wilmington (SE to S). The Adler planetarium promontory on the Chicago lakefront, although not a rural location, was used on days when the winds ranged from north-east to southeast.

Figure 4 shows the seasonal variation of the concentration, and of the same oxygen and carbon isotopic abundance data as shown in Fig. 3 from August 1970 to the present time. In addition, samples collected before July 1970 (which were analyzed for only concentration and carbon isotopic abundance) are indicated as solid squares (night) or open squares (day) for Illinois rural locations.

The isotopic compositions of a few of the Illinois samples, $\delta(^{13}C/^{12}C) = =27.8$ to $-29.0\%_0$, $\delta(^{18}O/^{16}O) = +17$ to $+23\%_0$, show that 30-80% of their CO is from Illinois engine emissions, while the remainder is from CO whose oxygen isotopic composition is quite different from engine CO. In three of these cases, the concentration was proportionately higher and contamination with engine CO was suspected because of known proximity of automobiles. Except for these few cases, the isotopic variations indicate the contribution of local engine emissions is not significant.

In Figs. 5-11 the data are plotted for seven seasonal periods as follows: (a) the oxygen isotopic composition versus carbon isotopic composition, (b) the oxygen isotopic composition versus CO concentration, and (c) the carbon isotopic composition versus CO concentration. The periods are approximately as follows: Fig. 5 - early winter, Fig. 6 - late winter, Fig. 7 - spring, Fig. 8 - early summer, Fig. 9 - late summer, Fig. 10 - early autumn, and Fig. 11 - late autumn. The division of these seasonal periods was based on similarity of isotopic patterns.

5. Isotopic Fractionation Effects

The interpretation of these results must take into account the possible effects of isotopic fractionation and meteorological factors.

The wide variations in both carbon and oxygen isotopic values imply a complicated model for atmospheric CO. In addition to mixtures of CO from multiple sources which may depend on season and latitude, there is the possibility of isotopic fractionation in the scavenging processes. Three scavenging processes have been proposed; bacterial consumption in soil [4] and photochemical reactions involving OH radical either in the troposphere [15] or stratosphere [3]. We have made several measurements of the isotopic fractionation effects in CO consumption by soil bacteria and find that this process favors the lighter isotopes of both carbon and oxygen. Reactions involving photochemically-produced radicals are probably diffusion limited, being very fast reactions with low concentrations of oxidant such as OH radical; thus, kinetic effects would be expected to be small. Further, isotopic fractionation for both diffusion and kinetic effects in most simple reactions favors the lighter isotope. A

decrease in CO concentration corresponding to a greater degree of scavenging should then be accompanied by an increase in the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios. The majority of samples showed the opposite effect for oxygen, with decreasing $^{18}O/^{16}O$ ratios with decreasing concentration for both long- and short-term variations. In most seasons, the $^{13}C/^{12}C$ ratio increased with a decrease in concentration, but the long-term seasonal trend was the same as for oxygen. In the summer and autumn, there were some samples with low CO concentrations and abnormally high values of both the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios indicating possible fractionation. Perhaps these were cases where scavenging by soil bacteria had been predominant.

Since fractionation of the $^{18}O/^{16}O$ ratio would be expected to be twice that of the $^{13}C/^{12}C$ ratio, the isotopic values for oxygen versus carbon would lie along a line with a slope of two. Examination of the data in Figs. 5-11 indicates that any such effect was small compared to variable mixtures of different isotopic species.

On the basis of these considerations, it would seem that isotopic fractionation in the scavenging process is of small importance compared to the variations from the mixing of isotopically different species.

6. Meteorological Effects

Meteorological factors such as wind speed and atmospheric stability are known to have an important influence on the concentration of pollutants in urban atmospheres in different seasons. Our samples were collected at ground level in country locations selected to be far upwind of cities and major highways. The sampling times were mostly 3-5 p.m. or 6-9 a.m. and were selected to be several hours

later than when the day and night time minimums of auto traffic would occur in the small country towns upwind of the sampling location.

The effects of meteorological factors are difficult to generalize. Most of the available data for seasonal variations of the atmospheric concentration of pollutants are for urban locations. The large midwestern cities of Chicago and St. Louis show higher 24-hour average concentrations of CO in the summer compared to the winter [28]. Colucci and Bergeman [29] have shown that in New York City and Los Angeles, the concentration is highest during seasons of lower than average wind speeds. For northern Illinois, the average surface wind speeds in the summer are about one-half of those in the winter [30] and, therefore, on the basis of the above data, the concentration of any locally emitted technological CO would be expected to be higher in summer than winter. The opposite was observed in our studies of atmospheric CO concentration in country locations between December and July. Data on seasonal variations of concentrations of pollutants in country are scarce. This is the first such study for CO. The concentration of SO_2 measured in country locations during 1937-1939 in England [31] showed seasonal variations which were proportional to the seasonal variations in power demand and residential heating [32]. Finally, the carbon isotopic values of most of our country air samples with higher than average CO concentrations during the period from December through July became asymototic to an isotopic composition which was very different from regional engine CO emission.

The conclusion is that the variation of the long-term minimum concentration of CO observed in our Illinois samples between winter and summer was not due to any meteorological influences involving technological emissions. As will be shown in the observed general trend in both the concentration and $^{18}O/^{16}O$ ratio was due to seasonal differences in production and scavenging rates of different varieties of CO.

Some of the short-term fluctuations of the CO concentration in our data were probably due to meteorological factors causing an increase in the concentration of CO from ground-level sources. The isotopic composition of these CO varieties rarely showed any contribution from regional engine emissions during the period between December and August.

Obvious meteorological influences were evident in our autumn data. The concentration became abnormally high during periods of atmospheric inversions. Also samples collected between 5-9 a.m. in 1970 showed on the average higher CO concentrations and $^{18}O/^{16}O$ values than those collected 3-5 p.m. This indicated there were surface emissions of CO which resulted in a higher ground level CO concentration during the hours of greater atmospheric stability. The isotope composition was variable and showed some contribution from regional engine CO, but there was a more dominant heavy-oxygen variety with an isotopic composition different from engine CO. This variety was most likely emitted from trees and plants and will be discussed in more detail in the section on autumn CO.

7. Varieties of Atmospheric CO and Model of Seasonal Patterns

An analysis of our data shown that atmospheric CO consists of several different isotopic varieties, the relative amounts of which

depend on the season and latitude. The determination of the iso-
topic characteristics of the pure species is complicated by the
fact that in all seasons atmospheric CO consists of mixtures of
two or more varieties.

The data shown in Figs. 5-11 indicate there were five varieties
of atmospheric CO, two with light oxygen and three with heavy oxy-
gen. These are summarized in Table 1 as characterized by either
the season occurrence or isotopic composition. The isotopic compo-
sitions of the different varieties are plotted in Fig. 12 in the
summary. These varieties do not necessarily correspond to separate
and distinct species in all cases - each of the heavier oxygen
varieties III, IV and V are possibly mixtures of more than one
heavy-oxygen species. Also, the same source may contribute to more
than one of the listed varieties.

Carbon monoxide with a light oxygen isotopic composition oc-
curred with variable carbon isotopic composition indicating the
possible existence of two species of CO with light oxygen (I and II
in Table 1). The heavier carbon variety predominated in Illinois
during the winter, going over to more variable and lighter carbon
in the summer. There is nothing obvious in the data to indicate
whether or not this variation represented different sources or some
carbon isotopic fractionation factor in the production process.

There were three isotopically different heavy oxygen varieties:
variety III occurred in small and variable amounts during the summer
of the northern midlatitudes; variety IV occurred abundantly during
the autumn in the northern midlatitudes; and variety V is the
heavy-oxygen variety which, relative to the concentration of the
light-oxygen varieties, occurred abundantly during the winter and

decreased in amount as the season progressed to summer. In general, the concentration of each of these heavy-oxygen varieties was quite variable.

The general seasonal characteristics of atmospheric CO for the northern hemisphere fit a pattern of a mixture of a relatively constant amount of 0.10-0.15 ppm of the light oxygen varieties mixing with variable amounts of heavy-oxygen varieties. The heavy-oxygen CO varied between 0.15-0.5 ppm in the winter and 0.02-0.3 ppm in the summer and was not the same isotopically in the different seasons. Figure 12 shows the general seasonal cycle of the isotopic composition of atmospheric CO in northern Illinois.

It has been suggested by McConnell et al. [19] that oxidation of CH_4 by photochemically produced OH radical might be an important source of atmospheric CO. The results of Weinstock [16] strongly support this suggestion and further show that the oxidation of CO by OH in the troposphere is highly likely as the scavenging mechanism for CO.

Our data (see section 7.2 - Source Strength of the Light Oxygen Varieties) suggest that the origin of the light oxygen varieties is in the atmosphere itself possibly from CH_4 or other organic constituents. If this CO is both produced by photochemically produced OH and scavenged by the same oxidation mechanism, then the concentration of these varieties would be independent of the amount of solar radiation and therefore shows no seasonal effects. Within a factor of two, this was the case. On the other hand, the atmospheric concentration of CO from sources whose global production rates are more or less constant (such as engine emissions and possible marine emissions) would be enhanced by the reduced solar radiation in the

northern-hemisphere winter - especially in the midlatitudes which are estimated to receive 25% of the amount during the summer [21]. The average atmospheric concentrations of the heavy-oxygen varieties in Illinois during the winter was 5-10 times greater than during the summer. The highly variable concentration of the heavy-oxygen varieties in all seasons indicates they are surface emissions. Surface emissions such as from technological and possibly marine and terrestrial biosphere sources would tend to produce more variable CO concentrations than a source in the atmosphere because of the non-uniform distribution of sources and the incomplete mixing of air masses within times shorter than several weeks.

7.1 Light-Oxygen Varieties (I and II) of Atmospheric CO

The major variety of atmospheric CO in the northern midlatitudes during the summer had a light-oxygen composition. In all other seasons, atmospheric CO showed a component of a light-oxygen variety which occurred with relatively constant concentration compared to the amount of heavy-oxygen varieties. The limited geographic data, shown in Fig. 3, indicate that the light-oxygen varieties were the dominant varieties all over the world. They were always the varieties which were predominant when the concentration was the lowest.

The carbon isotope abundance of the light-oxygen variety varied with the seasons in Illinois, having a high $^{13}C/^{12}C$ value in the winter and spring, and lower and more variable $^{13}C/^{12}C$ in the summer and autumn. There is nothing to indicate whether the variability of the carbon isotopic composition is the result of two different species with light-oxygen, isotopic variations in the source of the

carbon, or variations in isotopic fractionation in the production process.

Since there is no clear basis for distinguishing the light-oxygen varieties, we shall treat them as a composite variety even though the carbon isotopic composition is variable. There is a similarity in origin perhaps as the concentration was fairly constant during each season and was nearly the same in summer and winter, although somewhat higher in the spring (see discussion in section 7.7 - Atmospheric CO in the Spring).

7.2 Source Strength of the Light-Oxygen Variety of CO

The isotopic dilution method would be useful in estimating the source strength of the light-oxygen CO varieties in the northern hemisphere, if the average relative concentration of engine CO on a global basis can be determined and then treated as an internal isotopic standard. For accurate results, the isotopic dilution method requires a uniform mixture of the reference and the unknown species of CO, and it is evident from the geographic and time variations of the $^{18}O/^{16}O$ ratio and CO concentration that there is incomplete mixing of isotopically different species of atmospheric CO. Referring to Fig. 9, one-half of the days sampled in Illinois during July and August had low CO concentrations (0.12-0.20 ppm) and the lightest oxygen isotopic composition [average $\delta(^{18}O/^{16}O = 8‰]$ of all Illinois samples. These air masses must be the most representative of the average midlatitude atmosphere. It is reasonable to assume that the isotopic variations within this group of samples are due to small variable amounts of a heavy-oxygen variety mixing with a light-oxygen variety. While the source of the heavy-oxygen

variety is not know, an upper limit to the fraction of engine CO
in these samples can be estimated if these variations are con-
sidered as due to variable amounts of engine CO mixing with a light·
oxygen species of CO having a value of $\delta(^{18}O/^{16}O)_I$ = 5‰ which was
the oxygen isotopic composition of the lightest oxygen variety of
CO observed in the southern hemisphere and is assumed to be the
pure variety. Then the source strength of the unknown species of
CO Q_I is given by the isotopic dilution equation

$$Q_I = \frac{\delta(^{18}O/^{16}O)_{eng\ CO} - \delta(^{18}O/^{16}O)_{atm}}{\delta(^{18}O/^{16}O)_{atm} - \delta(^{18}O/^{16}O)_I} \tag{4}$$

$$X\ [f]\ X\ Q_{eng\ CO}\ ton/month \quad ,$$

where $\delta(^{18}O/^{16}O)_{atm}$ = 8‰. The factor f is introduced to take
account of any non-uniformity of the engine-CO concentration in
the hemisphere. Since engine-CO emissions are mostly located in
the midlatitudes, their concentration could have an average merid-
ional gradient which is dependent on the ratio of the residence
time of CO to the hemispheric mixing time. For a residence time
long compared with the hemispheric mixing time, there would be
uniform mixing of engine CO throughout the hemisphere. Then the
source strength Q_I of the predominant variety of CO in the northern
hemisphere summer must be at least five times that of engine CO*
or 1.5 X 10^{8} tons/month. This estimate is very likely too low for
two reasons. First, if the residence time is comparable to the
hemispheric mixing time, then the concentration of CO from a source
located in the midlatitudes such as engine CO would be higher than

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*2.8 X 10^{7} tons/month for July and August 1971, extrapolated from
gasoline-consumption data for 1965-1968 [10,18] and a CO/gasoline
ratio of 0.35 kg/l [18].

in the southern latitudes. Robinson and Robbins [18] observed an overall meridional concentration gradient in November and December 1967. The main source of the CO variety which produced this gradient was probably terrestrial plants and trees in the midlatitude regions and not engine CO (see section 7.5 - Heavy-Oxygen Variety of Atmospheric CO in the Autumn). Nevertheless, the results show a meridional concentration gradient from a non-uniform distribution of sources and a residence time less than or comparable to the hemisphere mixing time. Secondly, engine CO was assumed to be the only species of CO causing the variations in the $^{18}O/^{16}O$ ratio during the summer. There is evidence that this was not the case. The variations in the $^{18}O/^{16}O$ ratio versus concentration for the summertime Illinois samples shown in Fig. 9 suggest there is a source which is different from engine CO and produces a heavy-oxygen species of CO (see section 7.4 - Heavy-Oxygen Variety (III) of Atmospheric CO in the Summer).

If the isotopic-dilution calculation is adjusted using a factor of two for the non-uniformity of the meridional concentration of engine CO, the production rate of the light-oxygen species is at least 3×10^8 tons/month during July and August. We believe that this is a very conservative estimate. The rate could be much greater depending on the production rates of other natural sources during the summer with a heavy-oxygen isotopic composition.

7.3 Nature of the Source of the Light-Oxygen CO Variety

This predominant variety must be of natural origin since engine CO constitutes 88% of known anthropogenic emissions. If this CO were produced by surface emissions such as the oceans, lakes, trees,

etc., the rate would have to be greater than 1 std cc/hour/m^2. This is 1-2 orders of magnitude too much to be accounted for by any known surface sources in the biosphere. Junge et al. [5] estimated that the supersaturation of CO in ocean waters produced 0.05 std cc/hour/m^2. We have found CO in lakes and rivers in amounts equal to or less than in ocean water, depending on the degree of pollution. Some species of trees and plants emitted CO, but the amounts were much too low to account for such a rate. Also, the oxygen isotopic compositions of all these surface-emitting species were 10-15‰ higher than those of the light-oxygen variety. Thus, this predominant source is most likely produced directly in the atmosphere.

Recently McConnell et al. [19] have suggested oxidation of CH_4 by OH as an important source of atmospheric CO. Little is known about the sources and geographical and seasonal variations of atmospheric CH_4. Estimates of total global emission rates of CH_4 from biological activity in paddy fields, swamp lands, and tropical regions are 3.1 - 14 X 10^8 tons/year [18,20]. Since oxidation of CH_4 would be dependent on photochemical production of OH, there would be a seasonal variation in the rate of formation of CO. Taking into account the seasonal and meridional variation of the daily solar radiation intensity [21], our estimate of 3 X 10^8 tons/month in the summer would integrate to 2.7 X 10^9 tons/year for the northern hemisphere assuming a constant concentration of CH_4. This is comparable to the highest estimated global CH_4 production rate.

Very little information about the carbon isotopic composition of atmospheric CH_4 is available. Craig [6] obtained $\delta(^{13}C/^{12}C)$ = -40.3 and -10.7‰ for two samples, but had reservations about the

purity and absence of fractionation in the samples. Bainbridge et al. [22] obtained -39‰. Our values for the CO species with the lightest oxygen varied between -31 and -22‰ with no correlation between the carbon and oxygen isotopic abundances. This could indicate that there are two sources of CO with a light oxygen abundance, one of which may be atmospheric CH_4 with $\delta(^{13}C/^{12}C)$ as low as -39‰. The other possibility is that the carbon isotopic abundance of atmospheric CH_4 is variable, but this seems unlikely because the residence time for CH_4 [18] is significantly longer than hemispheric mixing times. In view of the limited data on atmospheric CH_4, one cannot be sure whether or not atmospheric CH_4 is the principal source of atmospheric CO.

7.4 Heavy-Oxygen Variety (III) of Atmospheric CO in the Summer

In previous sections, it has been pointed out that the heavy-oxygen variety of CO occurring during the summer in Illinois appeared to be emitted from the surface and had an oxygen isotopic abundance which is significantly different from engine CO. Carbon monoxide from marine sources [1,2] is undoubtedly a constituent. Wilks [23] has observed CO release from bagged tree branches as well as from cut green plant structures. Swinnerton et al. [24] have reported that rain water is supersaturated with CO. We have confirmed these sources of CO and find that the $^{18}O/^{16}O$ ratio for these species of CO is greater than $\delta(^{18}O/^{16}O) = 16$‰. Thus, this variety of heavy-oxygen CO may consist of a mixture of several species of CO including engine CO. All of these are minor constituents of the summer atmospheric CO. It is planned to discuss these species of CO in more detail in a later report.

7.5 Heavy-Oxygen Variety (IV) of Atmospheric CO in the Autumn

The increase in the $^{18}O/^{16}O$ ratio in September and October for
Illinois samples and the simultaneous increase in concentration is
most likely related to the end of terrestrial plant life in the
autumn.

Increased atmospheric stability and lower wind speeds in this
season would result in higher concentrations of any CO from ground
emissions. The contribution of the light-oxygen species was still
very noticeable until the end of November. The heavy-oxygen variety
was considerably different from world-average engine CO and espe-
cially Illinois engine CO indicating a different and large CO source.
It has been suggested by Loewus and Delwiche [25] and Katz [26] that
CO emissions may possibly accompany the degradation of chlorophyll
in plants and trees. There is a definite diurnal effect which can
be attributed to the effect of atmospheric stability on the concen-
tration of surface emissions. Samples collected in the early
morning (5-7 a.m.) showed higher CO concentrations and higher $^{18}O/^{16}O$
values than those collected in the late afternoon (3-5 p.m.).
November 1970 showed a decrease in concentration corresponding to
either dispersion of this CO throughout the northern hemisphere or
the effects of the scavenging process. In late October 1970, there
occurred an eight-day peak in the CO concentration; the maximum of
nearly 1 ppm coincided with an atmospheric subsidence. The fact
that the carbon isotopic abundance at that time was 3-5‰ higher
than regional engine CO indicates that these were due to surface
emissions which consisted mostly of non-engine CO. Samples col-
lected in regions of large forests (Sioux Narrows, Ontario and
Alleghany State Park, New York) in the autumn showed both high CO

concentrations and high $\delta(^{13}C/^{12}C)$ values, the same as the general trend of atmospheric CO in the autumn in Illinois.

The amount of this seasonal CO production of variety IV in the northern hemisphere is estimated at 2-5 X 10^8 tons emitted over 1-1/2 months.

7.6 Heavy-Oxygen Variety (V) of Atmospheric CO in the Winter

Except for the October maximum, the average monthly CO concentration had a maximum of 0.35 ppm in December and then decreased gradually during January and February to 0.24 ppm in March. The make-up of this CO is not certain. Undoubtedly it consists partially of a light oxygen variety similar to the dominant variety in the summer.

The isotopic abundance of the dominant heavy-oxygen variety indicates a large contribution from engine emissions. We have discussed briefly in an earlier section the possibility of the reduced solar radiation in the winter decreasing the scavenging rate for CO and consequently increasing the concentration of a source with a constant emission rate. The concentration of CO from engine emissions, which are principally localized in the northern midlatitudes, could be enhanced by a factor of as much as eight times the average hemispheric concentration because of the combined effect of the reduced solar radiation and a non-uniform meridional distribution. Carbon monoxide from the combustion of fuel for residential heating which Robinson and Robbins [18] have estimated to be 4% of total annual anthropogenic sources would be enhanced in the winter in the northern midlatitudes both by a large seasonal factor of 4-5 and by the same effects of non-uniform distribution and reduced

scavenging rate as engine emissions. We estimate that atmospheric CO in the winter in the northern midlatitudes could consist of as much as 10% from residential heating and 50% from total anthropogenic sources, even though the average contribution of the latter to total technological sources throughout the northern hemisphere is less than 10%. The measured average oxygen isotopic composition of CO at this time was in agreement with such a mixture. However, the $^{13}C/^{12}C$ ratio was 1-2‰ higher than would be expected for such a distribution. Other possible constituents would include marine CO and residual amounts of the autumnal emissions not yet fully scavenged, both of which may account for the higher $^{13}C/^{12}C$ ratio.

7.7 Atmospheric CO in the Spring

The CO occurring in the spring consists of a mixture of a light-oxygen heavy-carbon variety similar to variety II occurring in the winter and a mixture of heavy-oxygen varieties intermediate between the winter and summer heavy-oxygen varieties (V and III, respectively).

The total CO concentration varied between 0.2-0.4 ppm, the same range as during the winter. However, the concentration of the light-oxygen variety was about 0.15 ppm or 1-1/2-2 times as much as in the winter with the concentration of the heavy-oxygen varieties correspondingly lower. This decrease in the concentration of the heavy-oxygen varieties is consistent with an increase in the scavenging rate from increasing solar radiation in this season. The cause of the increase in the concentration of the light-oxygen variety to a value higher than the value either in the winter or summer is not understood. We have suggested that this variety is related to variety I, the light-carbon light-oxygen variety, and that the source

or sources of these varieties are in the atmosphere itself and consist of methane and possibly other organic compounds. At this state in our understanding of these sources, it is only possible to speculate on what factors could cause the higher concentration of variety II. Some of these speculations are: 1) the change of air masses in midcontinental U.S. in this season, with lower frequency occurrence of polar-continental air and higher frequency of tropical-marine air compared with winter, may result in a higher concentration of any marine organic compound which might be the precursor of this CO variety, 2) the start of the growing season with the possibility of an increase in plant expirations of organic substances, or 3) the increase in the amount of atmospheric water with higher temperatures which may alter the production rate of CO from methane in the mechanism suggested by McConnell et al. [19].

8. Atmospheric CO in the Southern Hemisphere

The atmospheric CO concentrations for Tonga Islands and American Samoa in August were higher than those for Australia in May. This is in agreement with the corresponding seasonal differences observed for Illinois. These very limited data, if compared with those for the northern hemisphere during the same season, confirm the findings of Robinson and Robbins [18] and Seiler and Junge [3] that the concentration is lower in the southern hemisphere than in the northern hemisphere. The very high concentration (0.75 ppm) obtained near San Paulo in May is analogous to the high concentrations in Illinois in the autumn. The $^{18}O/^{16}O$ ratio is lower than the values observed in Illinois. It is also considerably lower than the $^{18}O/^{16}O$ ratio in urban atmospheric CO indicating that

pollution sources were not the major source of the high CO concentration. The difference in the $^{18}O/^{16}O$ ratio between the samples from American Samoa and Tonga Islands of about 6‰ may be due to the presence of some heavy-oxygen variety, possibly marine CO, emitted in the region of American Samoa.

9. Residence Time

The conclusion (based on evidence from isotopic compositions) that natural emissions of CO are many times the amount of engine CO emissions implies that the residence time is shorter than had been indicated previously by Junge et al. [5] and Dimitriades and Whisman [27]. The residence time of CO in the summer is less than 1.0 month if we use our estimate of at least 3×10^8 tons/month for the production rate of the predominant species of CO in the northern-hemisphere summer and an average concentration of 0.12 ppm for this species. Weinstock [15] has calculated a value of 0.1 year based on the concentration of ^{14}CO in the atmospheric CO collected at Buffalo, New York, between January and March. This result supports our estimate of an upper limit of the residence time. Furthermore, if the scavenging process is inversely proportional to the amount of solar radiation, as indicated by our data, then the summer residence time based on Weinstock's winter value is about 10 days. The production rate of the predominant light-oxygen species in the summer would then have to be 8×10^8 tons/month. We have indicated that the production rate based on isotopic dilution by engine CO could be as much as this.

10. Summary

The seasonal variation of the isotopic composition of

atmospheric CO in northern Illinois is summarized in Fig. 12. The
following conclusions are drawn from the results of this study:

(1) Varieties of atmospheric CO with a low $^{18}O/^{16}O$ ratio
dominate during the northern hemisphere summer and are similar to
atmospheric CO seen in the limited number of samples collected in
the southern hemisphere where technological sources are many times
smaller than in the northern hemisphere. It is deduced that this
form is produced year round and originates from the atmosphere itself.
The variability of the carbon isotopic composition indicates the
possibility of two types of sources. Oxidation of atmospheric
methane is a suggested source of the light carbon species of this
variety and oxidation of the other organic constituents of the atmo-
sphere from either marine or terrestrial origin may account for the
heavy carbon species. More investigation is needed to resolve the
origins of these species of CO. In the northern hemisphere, the
production rate is estimated to be > 3 X 10^9 tons/year as compared
to 2.7 X 10^8 tons/year from man-made sources.

(2) A large burst in concentration of a heavy oxygen variety
of CO is seen in the autumn, quite probably derived from the degrada-
tion of plant life chlorophyll at that time of the year. The total
amount emitted in the northern hemisphere over a 1-1/2-month period
is estimated at about 2-5 X 10^8 tons.

(3) Another major variety with a heavy oxygen composition
occurs during the winter and spring in the northern midlatitudes and
may be a mixture of CO from several different sources. Anthropogenic
emissions from engines and residential heating could be significant
constituents of this variety. The atmospheric concentrations of
these sources would be enhanced during the winter of the northern

midlatitudes by the combined effects of a seasonal slowing-down of any scavenging process dependent on solar radiation, the localization of emissions in the northern midlatitudes, and the increased seasonal emissions of heating fuels. The magnitude of the production rate of this collective species including the anthropogenic emissions is estimated to be in the range of $3-6 \times 10^7$ tons/month during the winter.

(4) There appears to be a small variable amount of a heavy-oxygen variety of CO occurring during the summer in the northern midlatitudes. This would include any anthropogenic emissions, but the oxygen isotopic values indicate they are not a major constituent of this variety.

The isotopic composition of the atmospheric CO in all seasons is more variable than can be explained by assuming various mixtures of only two isotopic species. Assuming there is no problem in the analytical procedure, there has to be some other factor causing the wide variations of both the carbon and oxygen isotopic compositions. Possible factors are: (1) isotopic fractionation of the production and scavenging processes, (2) the existence of three or more isotopcially different species, and/or (3) variations in the isotopic composition of the carbon and oxygen in the CO from the source. A more detailed treatment of these data can be made. In addition, the results of an unfinished study of the isotopic composition of CO from fresh and marine waters, trees and plants, and rain may help to decipher the atmospheric data.

The limited geographic and seasonal sampling of the atmosphere hampers the interpretation of these results. The complete description of atmospheric CO becomes very complicated because of geographic and

seasonal variations of the production rates of the several sources as well as the scavenging processes. Regular sampling of the atmosphere in several locations, including regions of the trade winds and of the westerlies in each hemisphere, would provide the data for a better understanding of this complex subject.

Appendix I Estimation of Carbon Isotopic Abundance of World-
Average Engine CO

Two methods have been used to determine U.S.-average engine
CO, which is 50% of the world's emissions. One method is to com-
bine the regional 1968 automobile registrations [10] with the
corresponding regional isotopic abundances of engine CO. The U.S.
was divided into three sections (western, midwestern and eastern)
and the measured isotopic compositions of CO for Los Angeles,
Chicago and New York City were taken as representative of the
respective regions. The resulting average is $\delta(^{13}C/^{12}C) = -27.4‰$.
The second method combines the quantity of petroleum produced in
each state [11] with the $^{13}C/^{12}C$ ratios for the corresponding oil
fields [7]. The data in Fig. 2 indicate that isotopic fractiona-
tion in going from crude oil to engine CO is very small. The U.S.-
average composition of engine CO then was found to be $\delta(^{13}C/^{12}C) =$
$-27‰$. The agreement between the two methods is surprising in view
of the broad assumptions made in the computations, especially
since the spread of $^{13}C/^{12}C$ ratios is ten times the difference be-
tween the results of the two methods.

Only meager data on the $^{13}C/^{12}C$ ratio are available for the
other principal regions of the world. The world-average is esti-
mated from the 1968 automobile registrations of the U.S., Europe
and the U.S.S.R. [12], which represent 90% of the world automobiles.
The average value for London and Paris urban CO is probably quite
representative for the $^{13}C/^{12}C$ ratio of European engine CO. There
is a published value $\delta(^{13}C/^{12}C) = -29‰$ for average petroleum from

the Volgograd region of the U.S.S.R. [13]. The world-average for engine CO is found to be $\delta(^{13}C/^{12}C) = -27.4‰$. This is admittedly a crude estimate, but the error is probably not greater than $\pm 0.3‰$

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Figure Captions

Figure 1 -- The isotopic composition of carbon and oxygen in CO of urban air.

Figure 2 -- Comparison between the isotopic compositions of carbon in CO of urban air (present work), petroleum from different sources by Silverman and Epstein [7] and Alekseev et al. [13], and natural sources by Craig [6].

Figure 3 -- The isotopic composition of carbon and oxygen in CO in non-urban air.

Figure 4 -- Seasonal variations in atmospheric CO: (a) concentration, (b) $\delta(^{18}O/^{16}O)$, and (c) $\delta(^{13}C/^{12}C)$. The collection sites and times are indicated.

Figure 5 -- Non-urban atmospheric carbon monoxide in the period December 4 to January 18. In this plot and in Figs. 6-11 (a) is $\delta(^{18}O/^{16}O)$ versus $\delta(^{13}C/^{12}C)$, (b) is $\delta(^{18}O/^{16}O)$ versus CO concentration, and (c) is $\delta(^{13}C/^{12}C)$ versus CO concentration. In all figures, the isotopic composition of world-average engine CO is shown - in (a) as an open square, and in (b) and (c) as a dashed line. All solid lines in all figures represent mixing curves between different varieties as indicated by the data. Dotted lines represent theoretical mixing curves of the light-oxygen variety with variable amounts of engine CO.

The data are plotted with open and closed circles as day and night Illinois collections resp. in 1971, open and closed triangles as day and night in Illinois in 1970, open and closed inverted triangles in Illinois in 1969, winged circles as collections made in Illinois by airplane at 4000-5000 ft and crosses as collections in non-Illinois locations as noted below:

1. Northwestern United States
2. Northeast Coast, Oahu, Hawaii
3. Matsue, Japan
4. Brittany, France
5. Sioux Narrows, Ontario
6. Caroline, New York
7. Atlantic Ocean, 74°W - 29°N
8. Caribbean, 78°W - 12°N
9. Pacific Ocean, 140°W - 24°N
10. Pt. Reyes, California
11. Big Sur, California
12. Parguera, Puerto Rico
13. Sugar Loaf Key, Florida
14. Yanchep Beach, Australia
15. Ely, Minnesota
16. Cotia, Brazil
17. Horseshoe Lake, Mississippi River
18. Pago Pago, American Samoa
19. Tonga Island
20. Allegany State Park, New York
21. Eastern Iowa
22. LaCrosse, Wisconsin

The southern hemisphere samples are plotted six months out of phase with the actual collection dates.

Figure 6 -- Non-urban atmospheric carbon monoxide in the period January 19 to February 27. The format is the same as in Fig. 5.

Figure 7 -- Non-urban atmospheric carbon monoxide in the period March 4 to June 2. The format is the same as in Fig. 5

Figure 8 -- Non-urban atmospheric carbon monoxide in the period June 5 to July 7. The format is the same as in Fig. 5.

Figure 9 -- Non-urban atmospheric carbon monoxide in the period July 8 to September 14. The format is the same as in Fig. 5.

Figure 10 -- Non-urban atmospheric carbon monoxide in the period September 15 to October 13. The format is the same as in Fig. 5.

Figure 11 -- Non-urban atmospheric carbon monoxide in the period October 17 to December 10. The format is the same as in Fig. 5.

Figure 12 -- The seasonal isotopic composition of atmospheric CO in northern Illinois. The dashed line indicates the seasonal cycle of the average isotopic composition of atmospheric CO. The estimated isotopic composition of the five varieties of atmospheric CO are shown by the numbered circles.

Table 1 - Varieties of Atmospheric CO

Variety	$\delta(^{18}O/^{16}O)$ ‰	$\delta(^{13}C/^{12}C)$ ‰	Principal Seasonal or Meridional Occurrence	Probable Sources	Estimated Production Rate in Northern Hemisphere
I	5	-30	Major species occurring during summer in northern midlatitudes.	Atmospheric CH_4 (?)	$> 3 \times 10^9$ tons/year
II	5	-24	Occurs in varying amounts with I in northern midlatitudes. Most abundant in winter and spring. Also occurs in marine air of low northern latitudes.	Unknown	
III	16-18	∿-28	Lesser abundant heavy-oxygen variety occurring during summer in northern midlatitudes.	Unknown	$\cong 5 \times 10^7$ tons/month during summer
IV	26-33	-26 - -22	Major variety occurring during autumn in northern midlatitudes.	Degradation of chlorophyll.	$2-5 \times 10^8$ tons during autumn
V	20-25	∿-27	Major variety occurring during winter and spring in northern midlatitudes.	Consists partially of anthropogenic emissions. Other species unknown.	$3-6 \times 10^7$ tons/month during winter

Figure 1

Figure 2

Figure 3

Fig. 2. Seasonal Variations in Atmospheric Carbon Monoxide during 1969-1971: (a) concentration, (b) $\delta(^{18}O/^{16}O)$, (c) $\delta(^{13}C/^{12}C)$. The collection sites and times are indicated above.

Figure 4
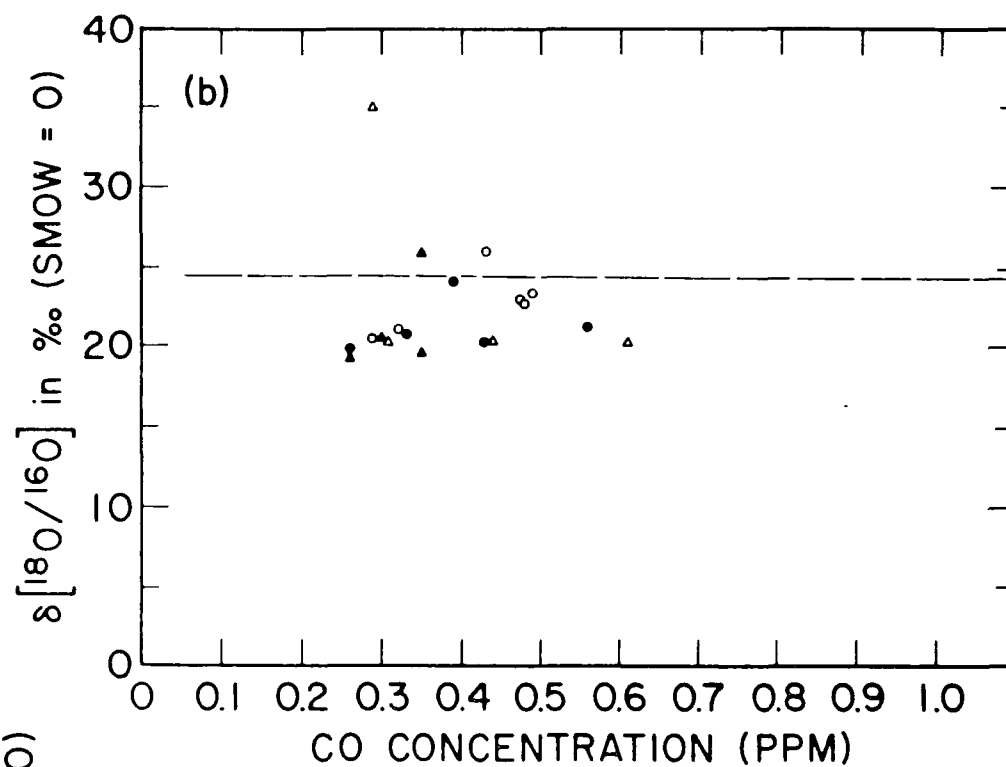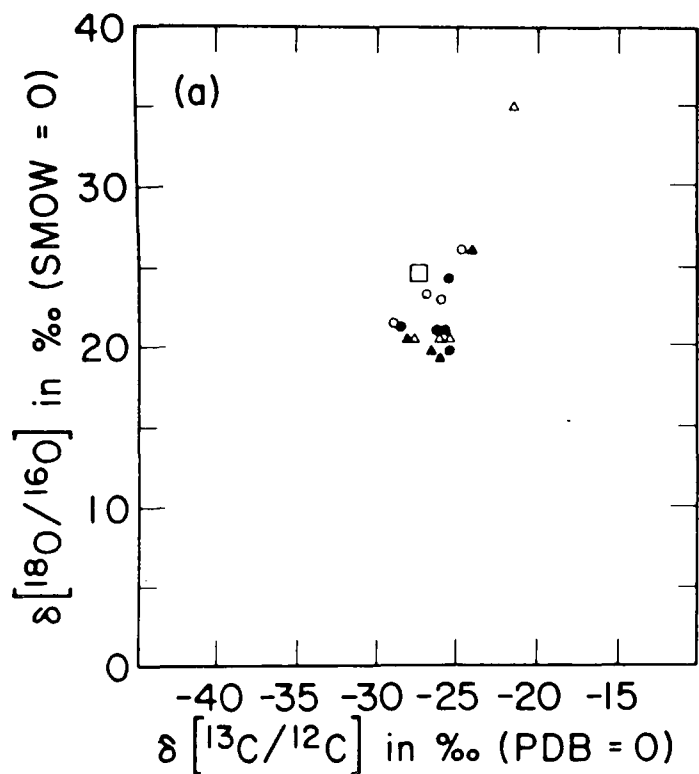
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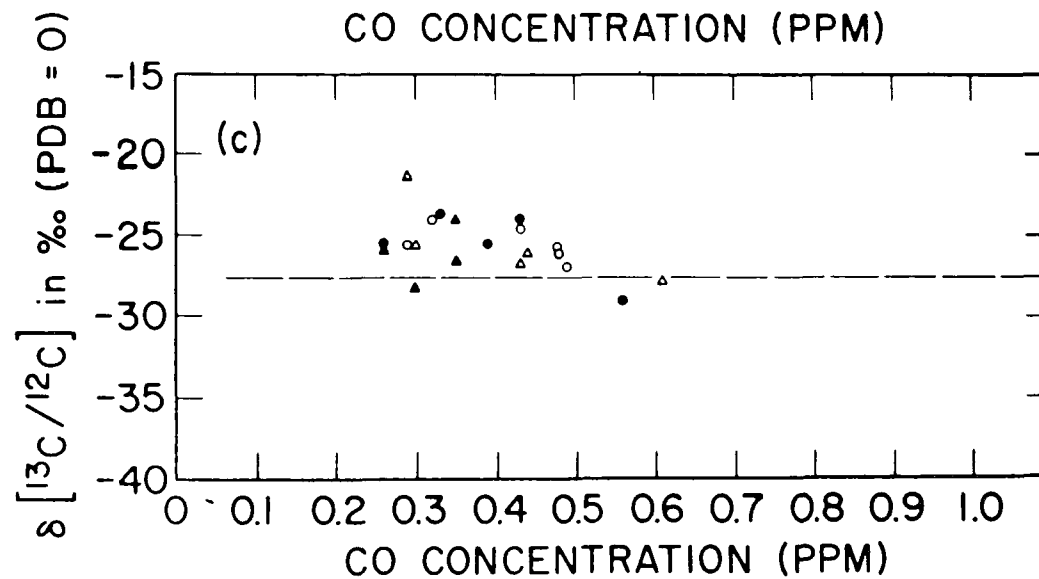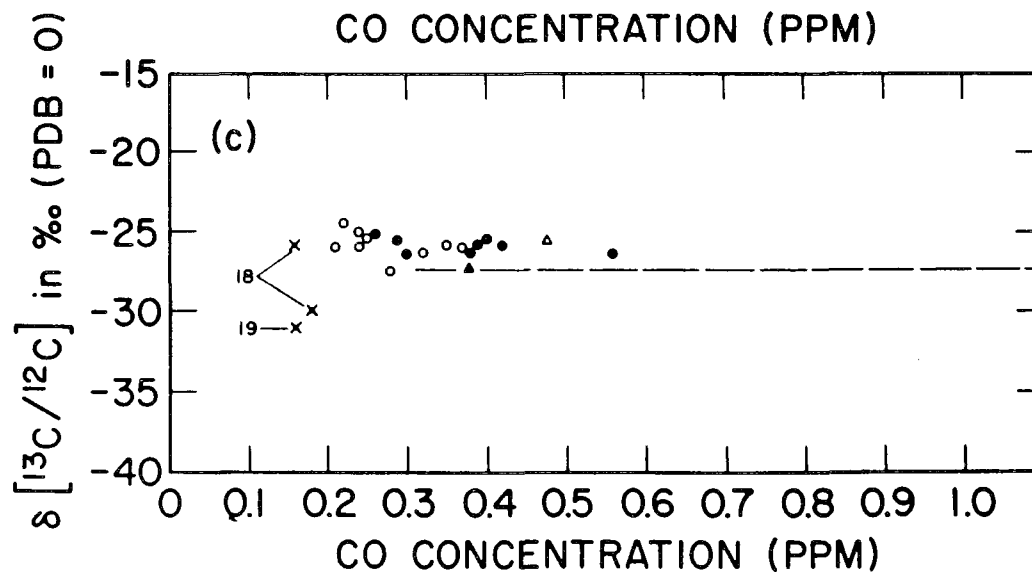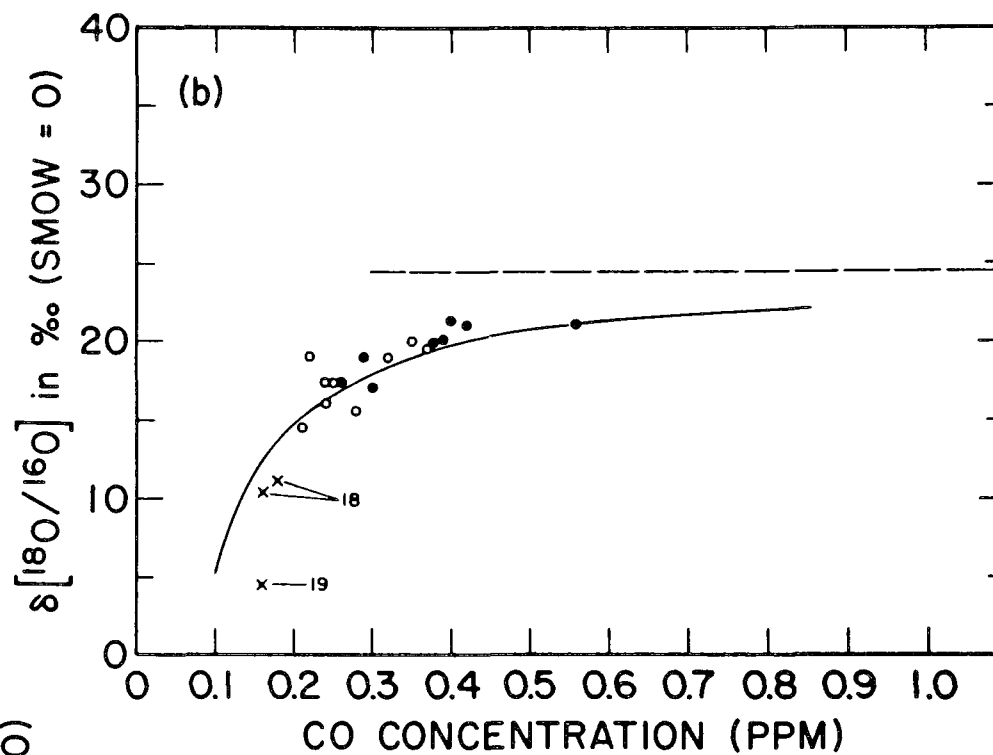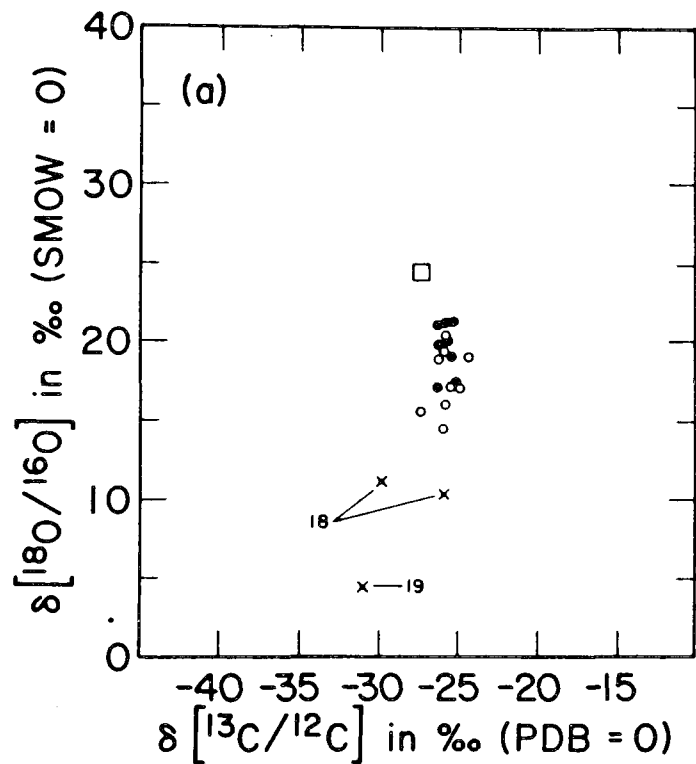
LATE WINTER

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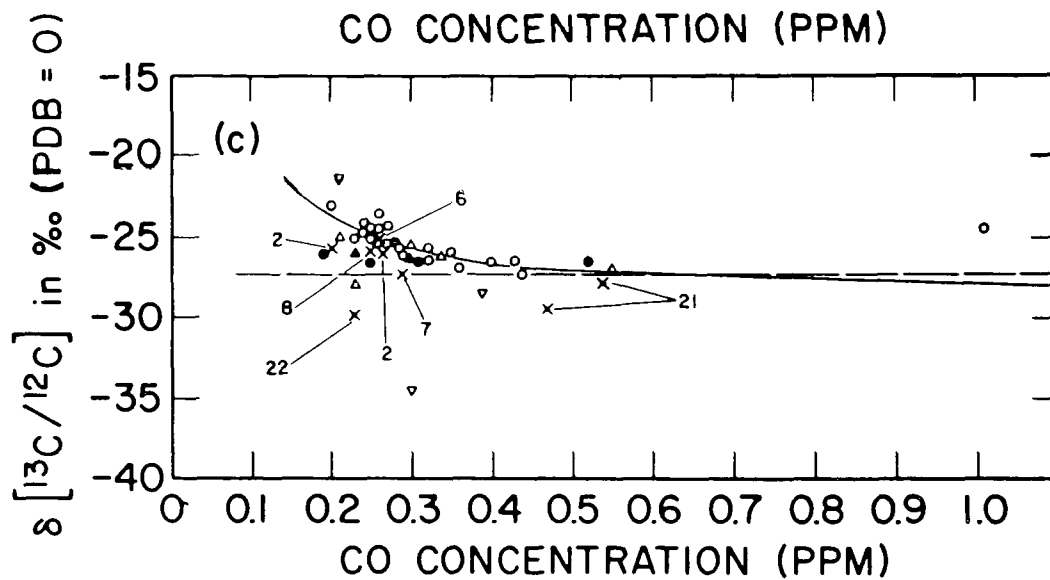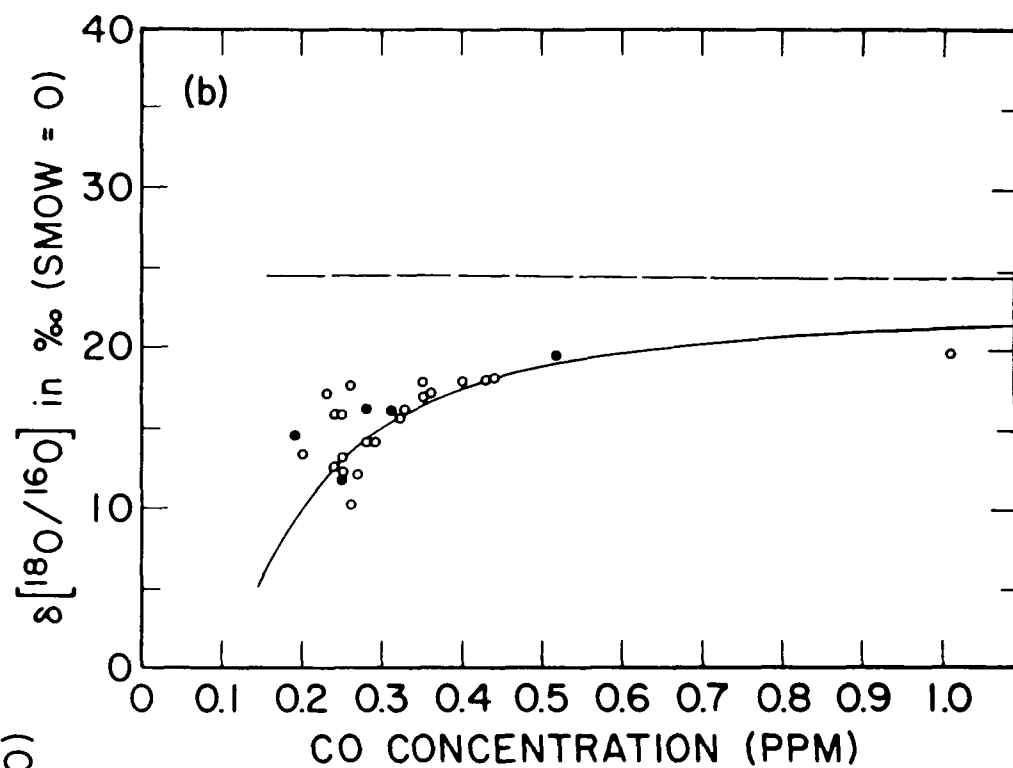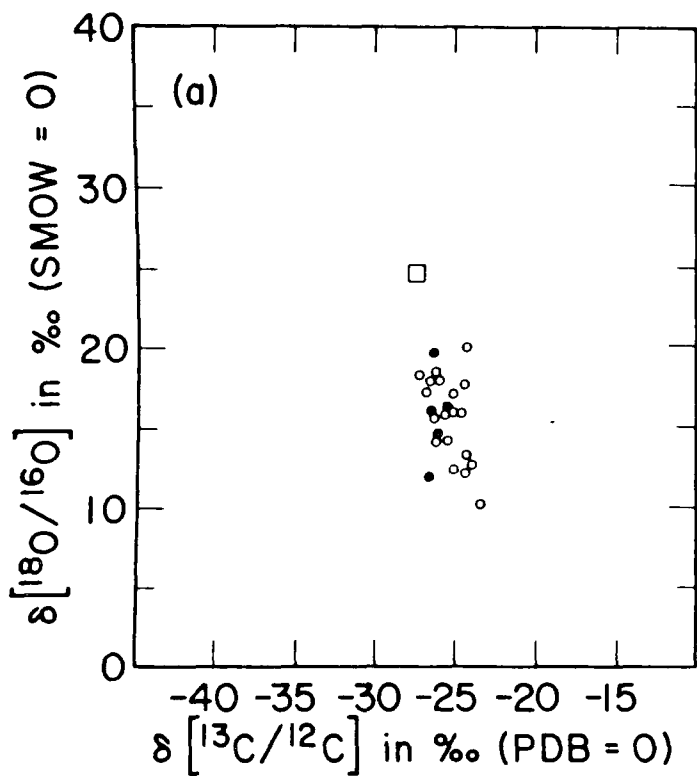
SPRING

Figure 7
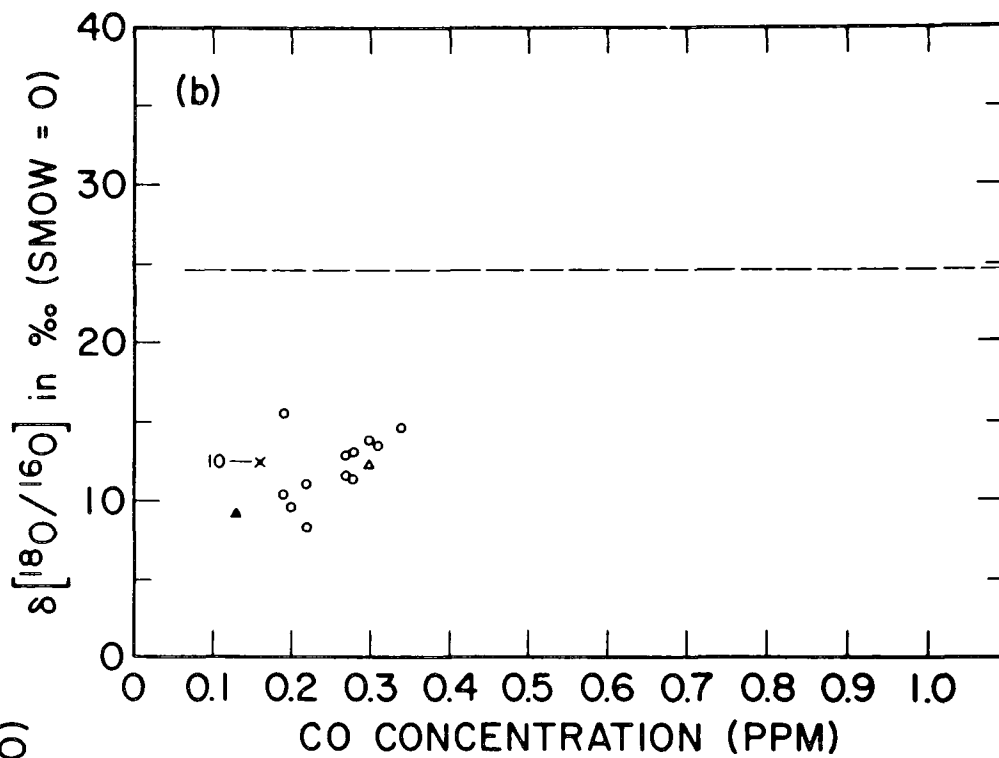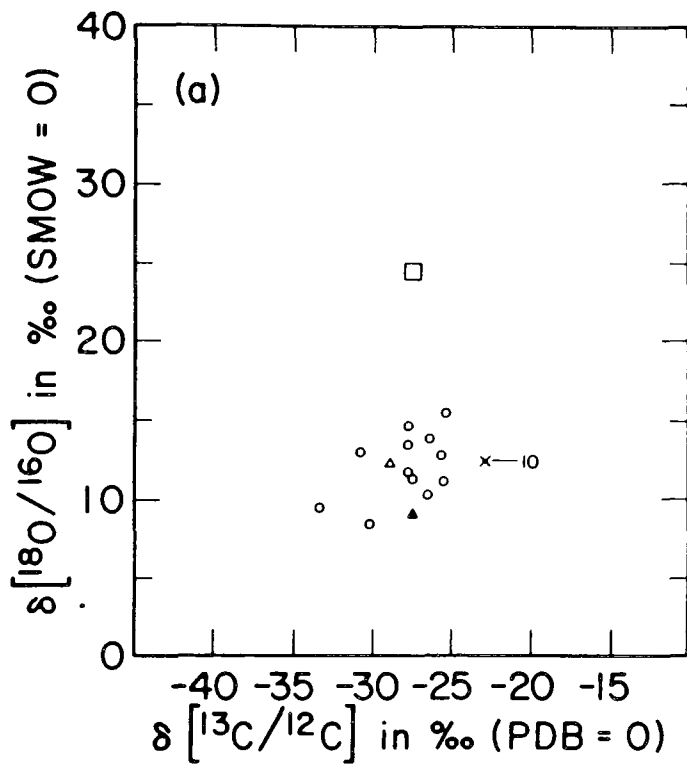
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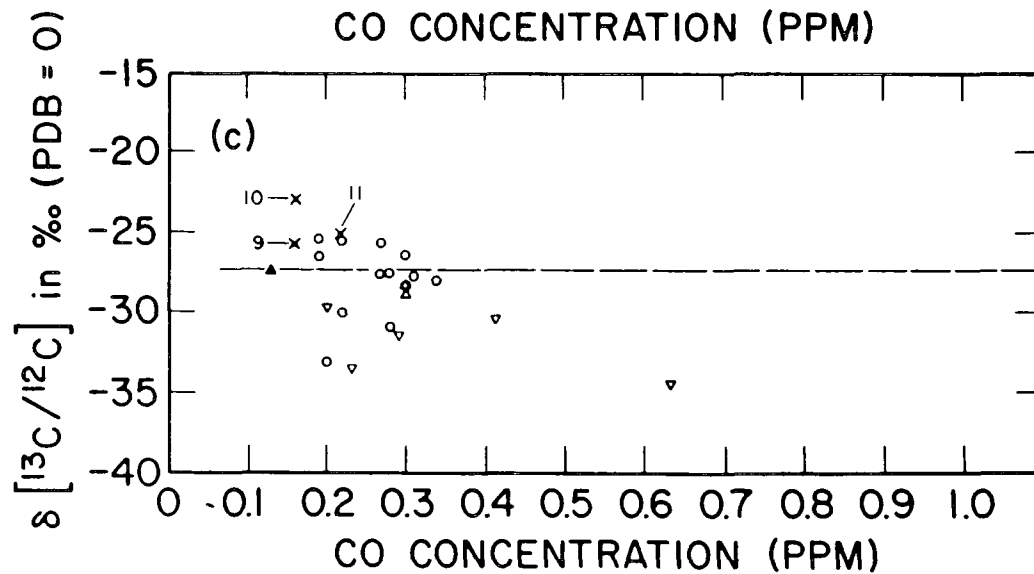
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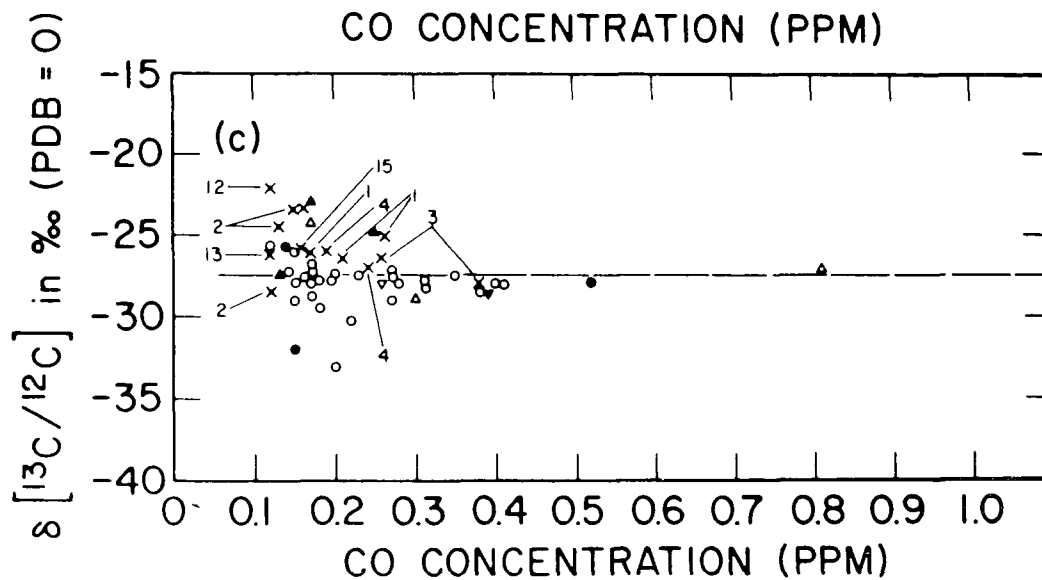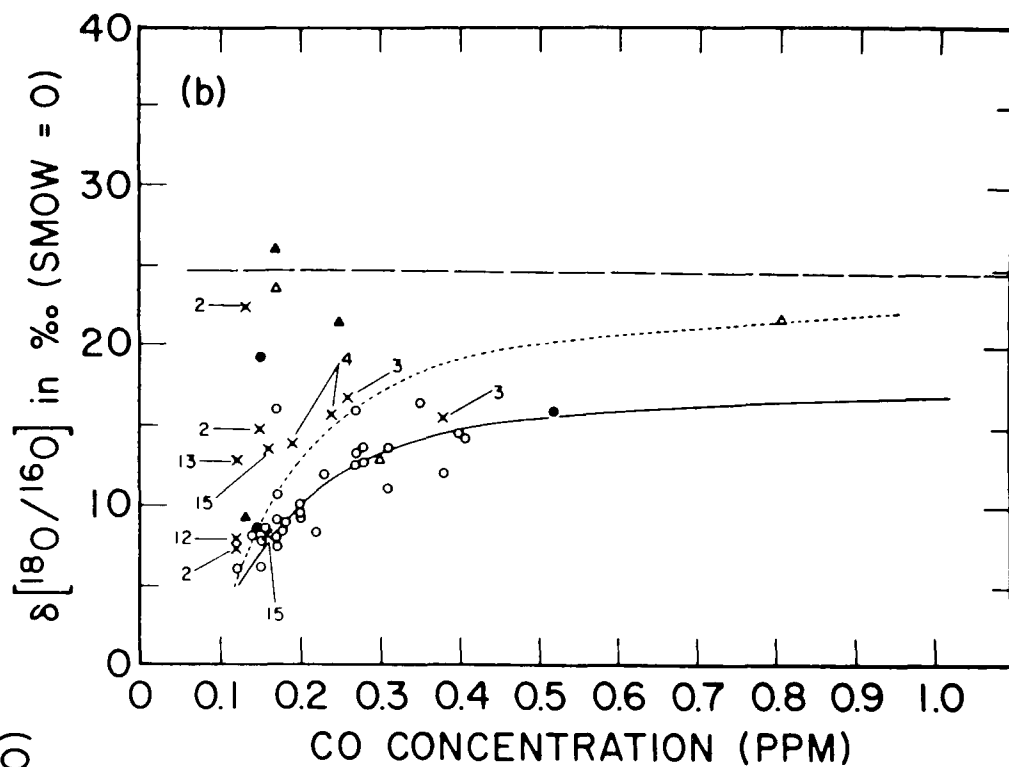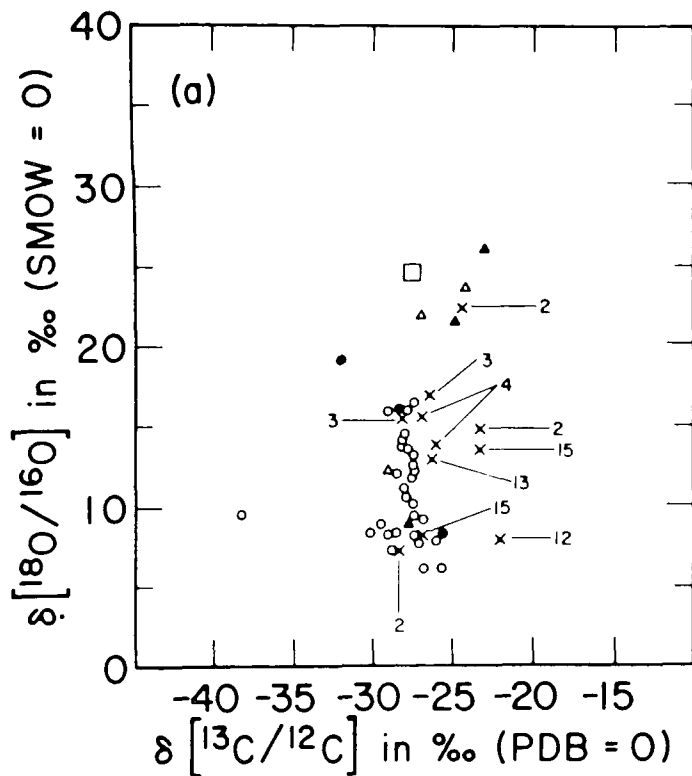
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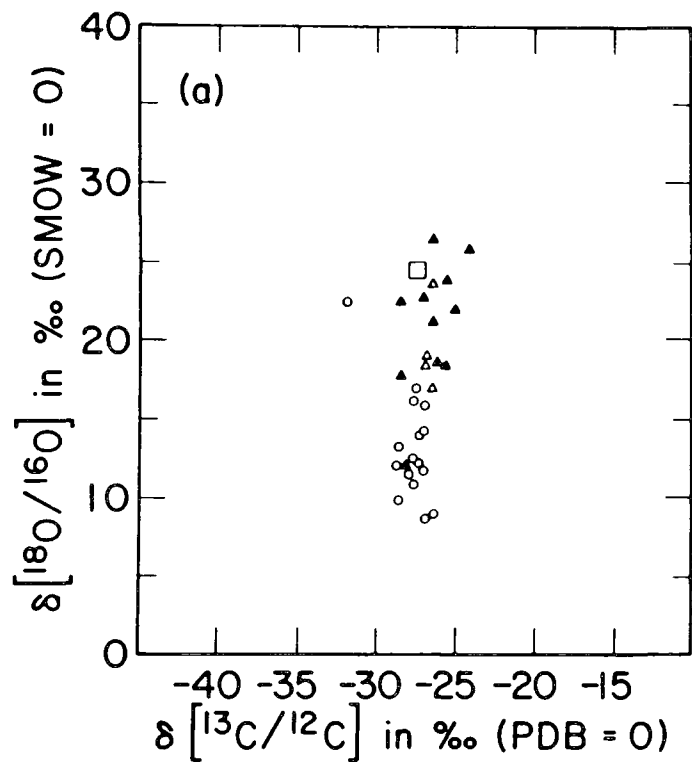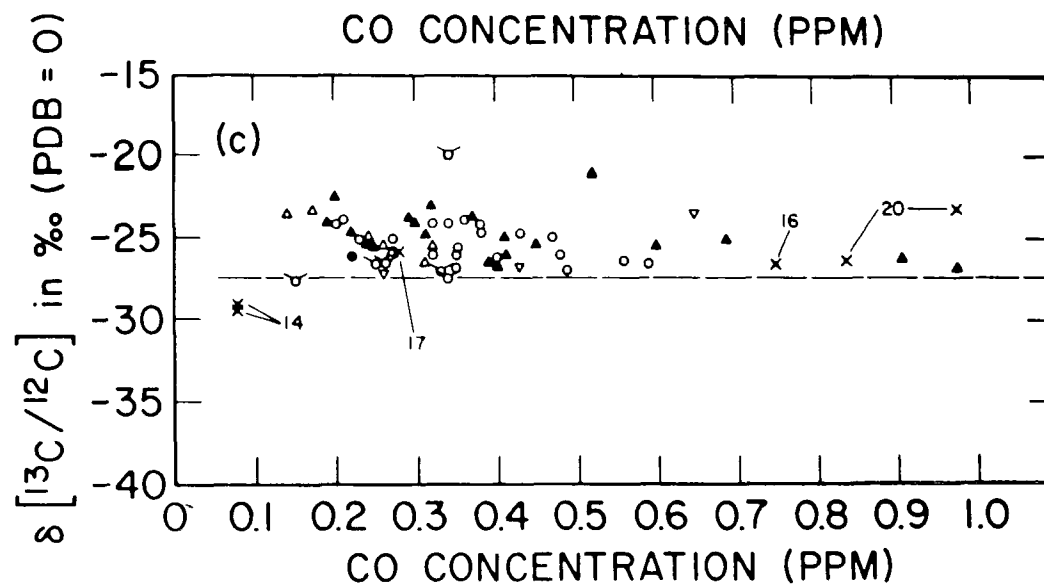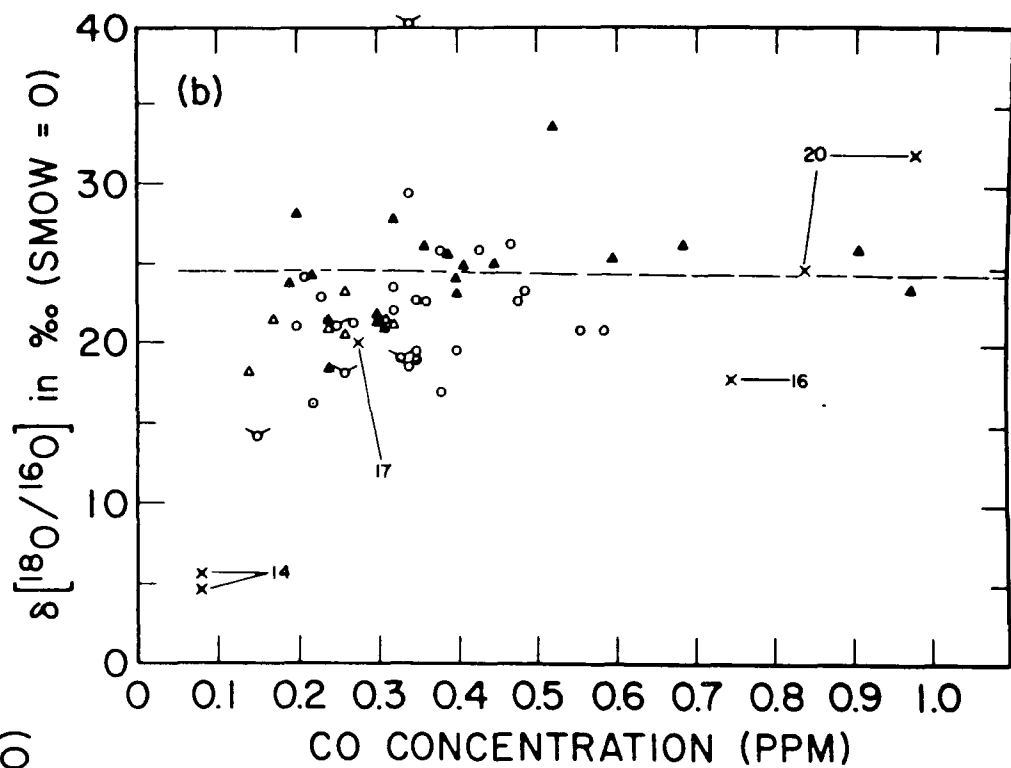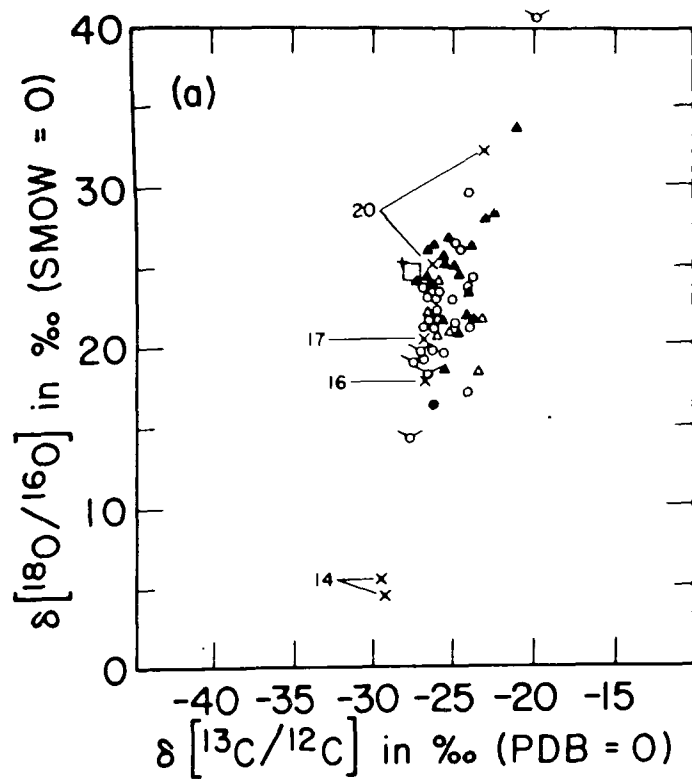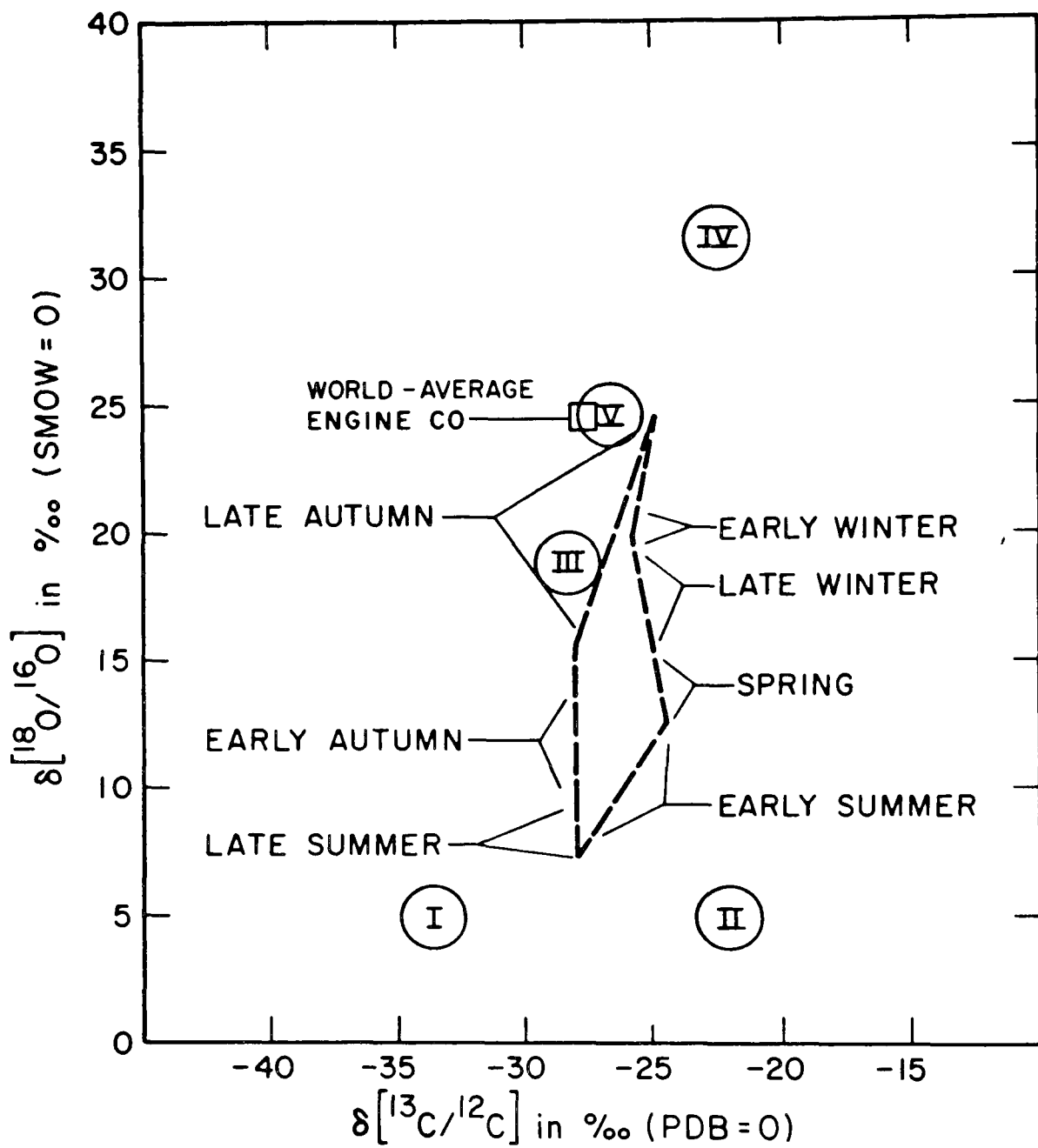Figure 9
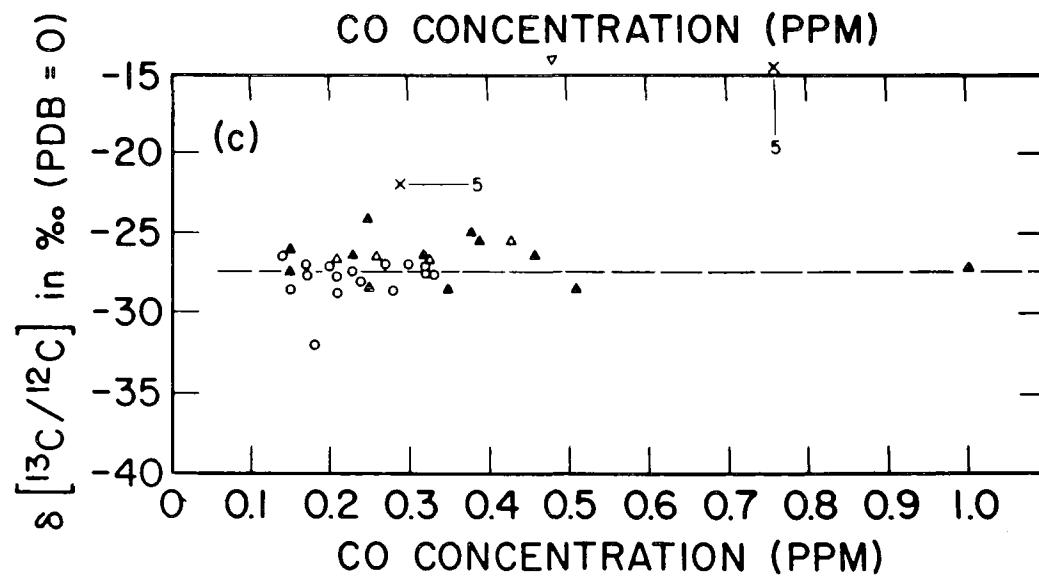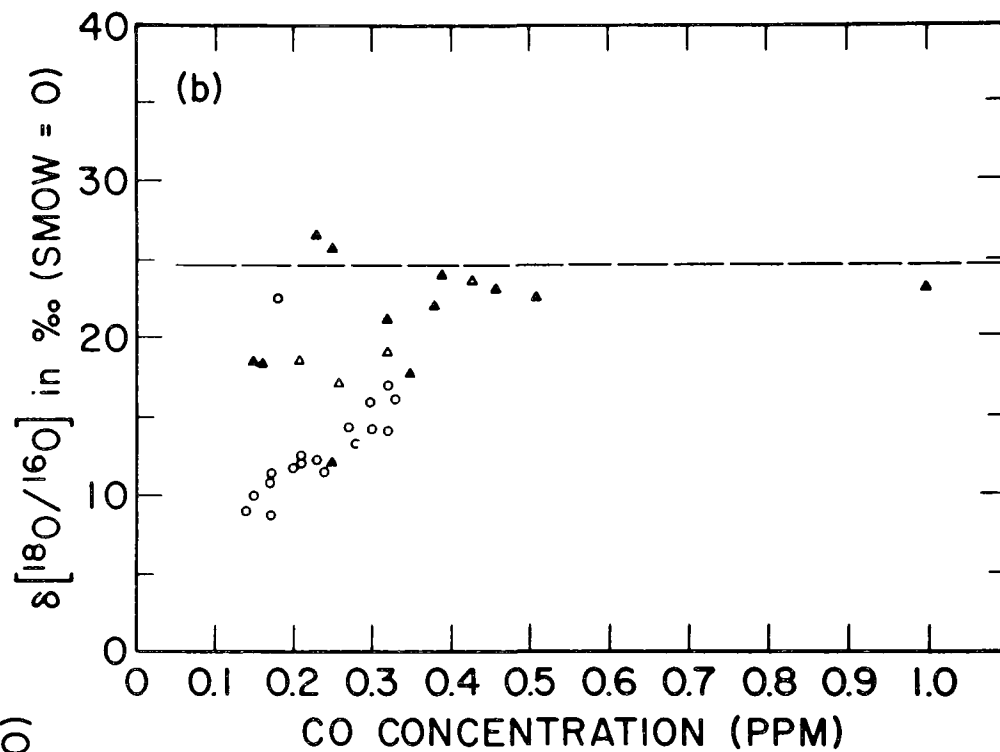
EARLY AUTUMN

Figure 10

LATE AUTUMN

Figure 11

Figure 12