

ISOTOPIC COMPOSITION OF STABLE CARBON AND CARBON
DIOXIDE CONCENTRATION OF ATMOSPHERE IN
STREAMBEDS NEAR TOMBSTONE, ARIZONA

by

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ABSTRACT

Gas samples were taken at approximately a meter deep about every 30 days for a year at three sites from ephemeral streambeds of the Walnut Gulch Watershed near Tombstone, Arizona. The streambeds are composed of sands and gravels of volcanic or granitic origin and free of vegetation. Two of the sites are underlain by a conglomeritic layer from 90 cm below streambed surface to some unknown depth. The data from these two sites had CO₂ concentration values ranging from .39% vol. to .02% vol. and $\delta^{13}\text{C}$ values ranging from -9.07‰ to -19.02‰. The third site has no evidence of a conglomeritic layer near the streambed surface. The CO₂ concentration values ranged from .94% vol. to .29% vol. and $\delta^{13}\text{C}$ values ranged from -17.53‰ to -20.75‰. All $\delta^{13}\text{C}$ values are with respect to PDB. Changes of CO₂ concentration and $\delta^{13}\text{C}$ values were related to flood events, physical characteristics of the streambed and banks, type of bank vegetation, season, and fractionation of ¹³C and ¹²C between gaseous CO₂ and bicarbonate. Atmospheric CO₂ contributed significantly to the streambed atmosphere following flood events; the relative importance of atmospheric CO₂ diminished as a function of the ease with which root-respired CO₂ recharged a site.

1. INTRODUCTION

Significance and Purpose of Study

Carbon-14 can be used to date samples of ground water. However, the carbon-14 date of a sample needs to be adjusted if the subsurface environment changed the initial $^{14}\text{C}/^{12}\text{C}$ ratio of the carbon content of the water as it traveled from the surface to the point of sampling. Various models have been proposed to correct for the alteration of modern carbon in ground water. Those of Ingerson and Pearson (1964); Mook (1976); Fontes and Garnier (1979); Reardon and Fritz (1978) and Wallick (1973) are among the best known. These models use the isotopic composition of the soil CO_2 in the area of recharge. The Ingerson and Pearson, Mook, and Fontes and Garnier models are sensitive to $\delta^{13}\text{C}$ ($\delta^{13}\text{C}$) values of soil CO_2 and of solid carbonate. Each model needs an accurate value for the $\delta^{13}\text{C}$ of the soil CO_2 in the areas of recharge.

Of interest for semi-arid climates is the $\delta^{13}\text{C}$ value of streambed atmosphere CO_2 because during runoff events, the transmission loss through the streambed is an important source of ground-water recharge. Ground-water

recharge by rain percolating through the soil to the water table is negligible for semi-arid climates according to Davidson (1973) and Wallace and Renard (1967). Thus, the value of $\delta^{13}\text{C}$ in the streambed is the critical value. I define the term streambed atmosphere to mean the gases that exist in the subsurface of a streambed. Parada (1981) used the terminology of soil gas in recharge areas instead of streambed atmosphere.

Parada's data (1981, 1983) indicated the arithmetic average for $\delta^{13}\text{C}$ of streambed atmosphere CO_2 at Tucson, Arizona during the months of April and June 1981, was -19.96% (per mil) vs. PDB; where PDB is a standard used for $\delta^{13}\text{C}$ measurements and stands for Cretaceous belemnite from the Pee Dee Formation in North Carolina. The arithmetic mean during November 1980, December 1980 and February 1981 was -20.86% . The difference between the largest and smallest value for April and June was 6.33% and for November, December and February was 4.67% .

I have investigated the yearly changes of CO_2 concentration and $\delta^{13}\text{C}$ value of streambed atmosphere in a climate similar to that of Tucson, Arizona. Data from this work are needed to help develop statistically valid distributions of the changes of CO_2 concentration and $\delta^{13}\text{C}$ value of streambed atmosphere for semi-arid climates similar to that of Tucson, Arizona. My data might be combined with Parada's (1981, 1983) data and applied to other semi-arid

basins. The fluctuation of CO_2 concentration and $\delta^{13}\text{C}$ value of the streambed atmosphere will determine the major sources that determine the $\delta^{13}\text{C}$ values. The knowledge of the major sources might refine isotopic models that use $\delta^{13}\text{C}$ values.

The Study Area

Location

The experiments described in this report were conducted in streambeds in the Walnut Gulch Experimental Watershed, at Tombstone, Arizona (Figure 1). The experimental watershed covers 150 square kilometers and is in the eastern portion of the Upper San Pedro River Valley. The watershed ranges in elevation from 1,950 meters at the upper end to 1,280 meters above sea level at the lowest gaging station. The main ephemeral stream is Walnut Gulch which enters the upper San Pedro River at Fairbank, Arizona.

Precipitation

The watershed receives a different type of rainfall in the summer than in the winter. Summer precipitation occurs as intense convective storms of small diameter during the months of July, August and September. This rainfall accounts for approximately two-thirds of the total annual precipitation. Its source is generally moist unstable air masses advancing into Arizona from the Gulf

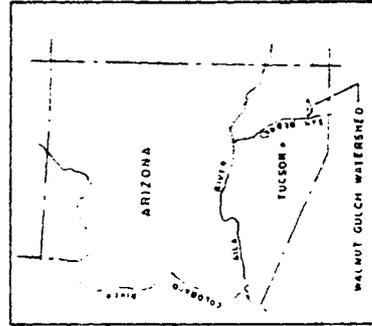
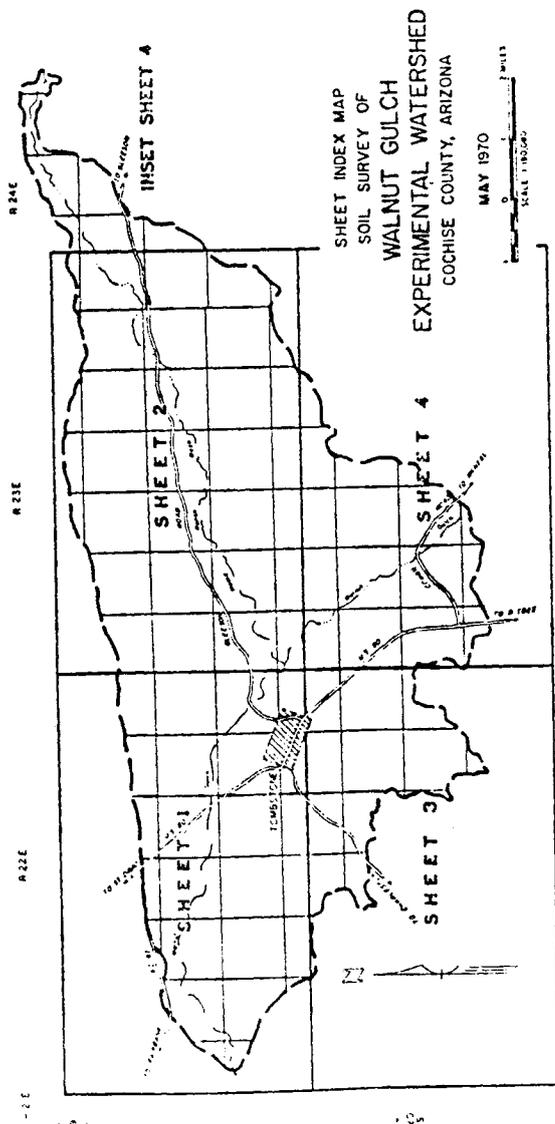


Figure 1. Location of Walnut Gulch Experimental Watershed (After Gelderman, 1970).

of Mexico. Figures 2 and 3 show isohyetal maps for two summer storms on the watershed.

Winter precipitation, falling during the months of December, January and February, accounts for most of the remaining one-third of the annual precipitation. Its source is cyclonic storms originating in the Pacific Ocean.

Osborn and Hickok (1968) reported a mean value of 28.50 cm of annual precipitation on the watershed from 1955 to 1966. Annual precipitation ranged from 18.03 cm to 36.07 cm.

Vegetation

The vegetation of the watershed is dominated by brush and grassland. Figure 4 shows the dominant vegetation at the three sites to be whitethorn (*Acacia constricta* var. *vernica*), creosote bush (*Larrea divaricata*) and tarbrush (*Flourensia cernua*). Renard, et al. (1962) reported vegetation along the channel banks can also be cottonwood, Arizona walnut and seep willow.

Geology

Walnut Gulch has isolated mountain blocks which are separated by a broad alluvium-filled basin (Gilluly, 1956). High-angle reverse faults caused the high relief areas that comprise the Tombstone Hills to the southwest and the lower Dragoon Mountains to the northeast. Great thicknesses of sedimentary rocks (mostly limestone) dominate the outcrops

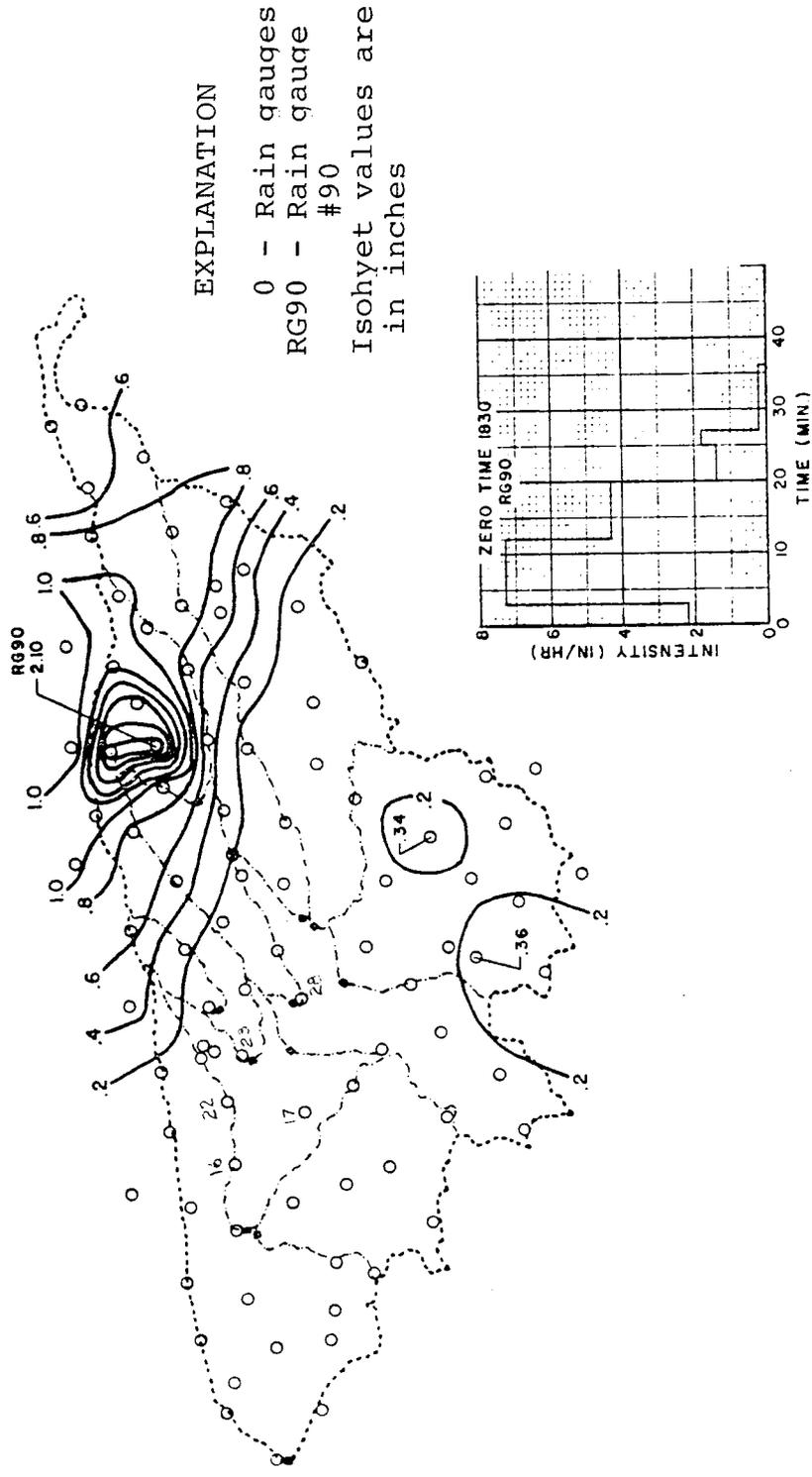


Figure 2. Isohyetal Map of Rainfall from the Storm of August 5, 1968, on the Walnut Gulch Watershed (From Renard, 1970).

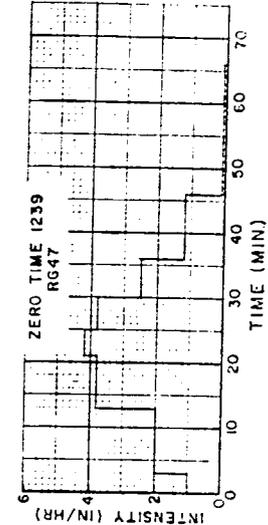
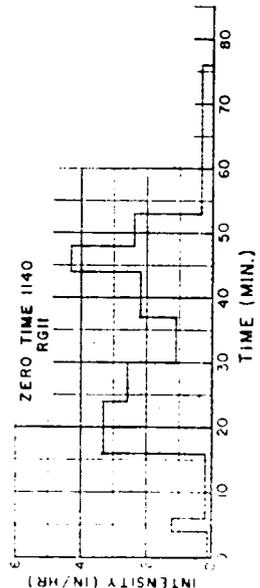
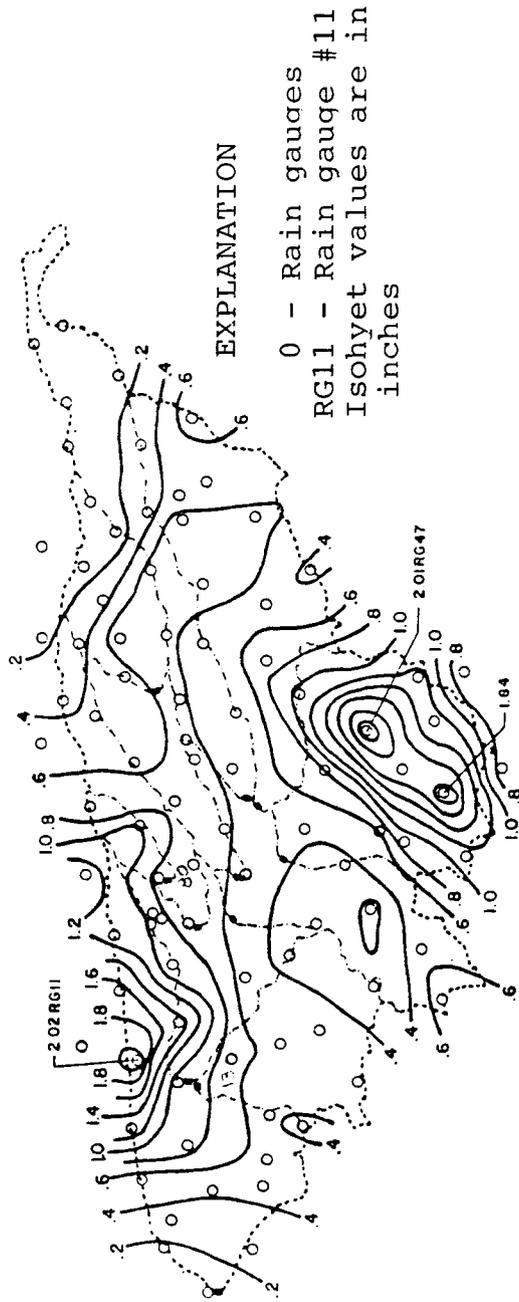


Figure 3. Isohyetal Map of Rainfall from the Storm of August 31, 1968, on the Walnut Gulch Watershed (From Renard, 1970).

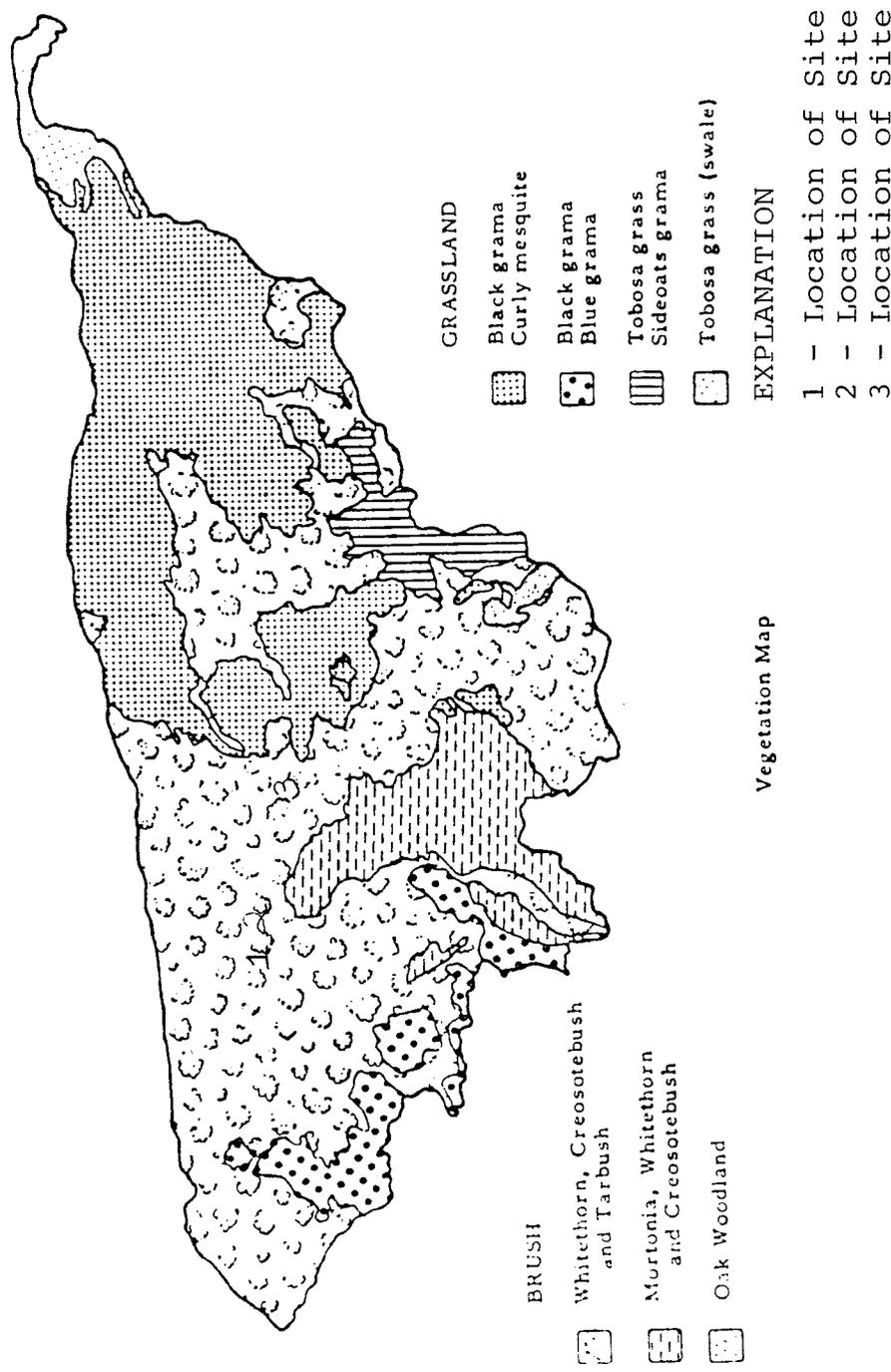


Figure 4. Distribution of Vegetation in the Walnut Gulch Watershed (From Renard, 1970).

in the Tombstone Hills. These sedimentary rocks are underlain by, and adjacent to, large igneous bodies of Tertiary age. The rocks in the lower Dragoon Mountains are Jurassic-Triassic (Figure 5).

Libby, Wallace and Spangler (1970) reported the rocks of the Walnut Gulch watershed range in age from Precambrian to Quaternary. Alluvium consists of sands and gravels. Calcium carbonate cements some of the alluvium to form caliche conglomerate.

Hydrology

Murphy, Lane and Diskin (1972) described the watershed as a youthful drainage system incised into a high foothills alluvial fan.

Local, perched aquifers created by alluvium-filled troughs lying on an undulating granodiorite plug were reported by Renard, et al. (1962). The undulating granodiorite plug is identified as the Schieffelin Granodiorite (Figure 5). A regional aquifer exists below the perched water tables.

Wallace and Cooper (1970) determined that some ground-water movement into the alluvial deposits of the experimental watershed occurs as underflow from the Dragoon Mountains. Spangler (1969) determined that the ground-water flow of Walnut Gulch moves west from the Dragoon Mountains and then northwest to the San Pedro River. The flow of ground water is due to two hydraulic gradients that

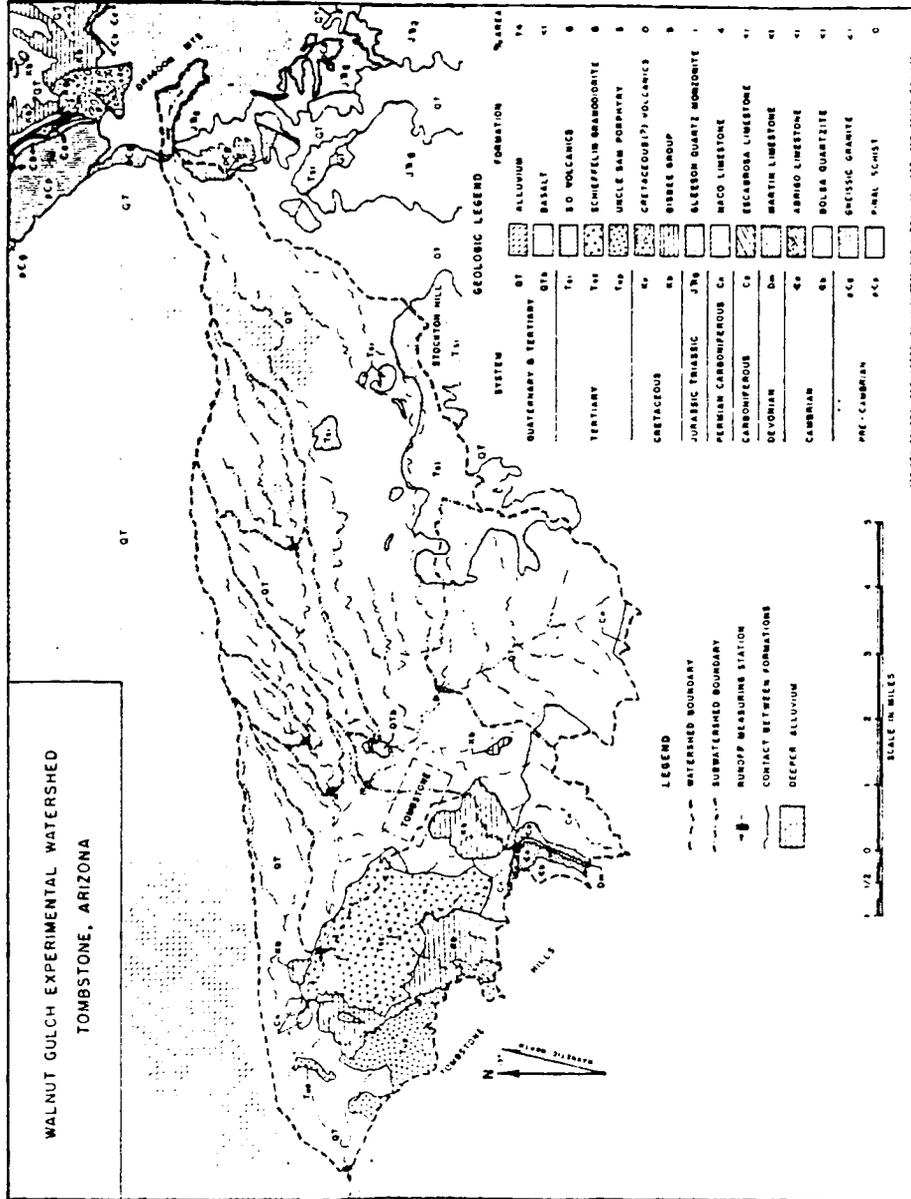


Figure 5. Geologic Map of the Walnut Gulch Watershed. (From Hanks, Wallace and Schreiber, 1981)

are relatively constant--a 2.5 to 3.0 percent gradient in the east region of the watershed and a .5 percent gradient extending from the central region to the San Pedro River. The two gradients are directly related to the impermeable bodies that underlie the Tombstone Hills which act as a barrier to deflect the ground-water flow pattern. Figure 6 is a contour map of the water-table.

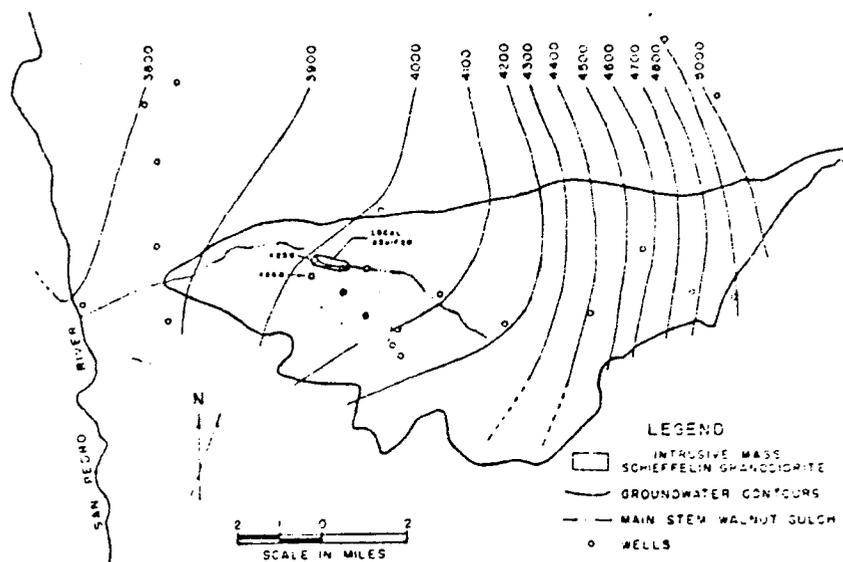


Figure 6. Ground Water Elevations of the Walnut Gulch Watershed (From Renard, Keppel, Hickey and Wallace, 1964).

Ground water elevations are in feet above mean sea level.

Recharge to the ground water is primarily a result of transmission loss in the ephemeral streams according to Keppel and Renard (1962) and Wallace and Renard (1967). Direct recharge through the desert floor by precipitation

was considered negligible by Qashu and Evans (1967) and Wallace and Renard (1967). Wallace and Renard (1967) added that infiltration in the smaller tributaries is limited, primarily because of the infrequency of the runoff events.

Transmission Losses

Several factors influence the transmission loss in ephemeral streams. Matlock (1965) showed that while a flow occurred, infiltration decreased with time owing to the sealing effects of fine sediments suspended in the flow. Murphy, Lane and Diskin (1972) listed the following major factors that influence transmission loss:

1. Nature (type and configuration) and volume of alluvium beneath the channel;
2. Available porosity and specific yield of that alluvium;
3. Antecedent moisture conditions;
4. Hydraulic conductivity of the streambed.

Keppel and Renard (1962) also listed peak discharge at the upstream gaging station, duration of flow and the width of the channel as possible factors.

Wallace and Renard (1967) studied transmission losses in Walnut Gulch from flume 2 to flume 1 (Figure 7). A loss of 1.2651×10^4 cubic meters (m^3) per kilometer (km) was recorded from runoff on August 10, 1963. The maximum recorded loss was $3.8212 \times 10^4 m^3$ per km. Keppel and

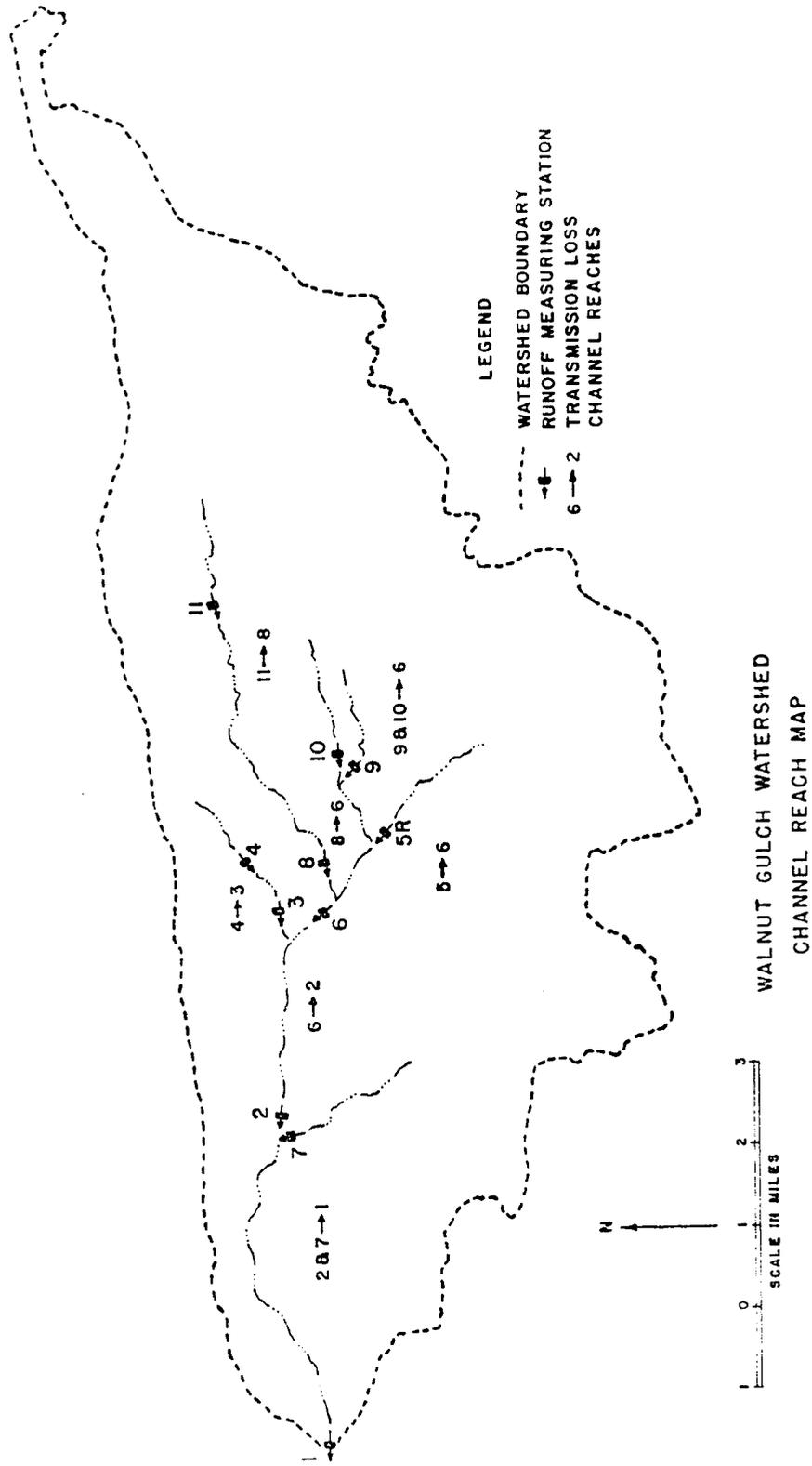


Figure 7. Instrumented Channel Reaches on the Walnut Gulch Watershed for which Transmission Losses can be Evaluated. (From Renard, 1970)

Renard (1962) calculated the maximum loss to be $6.1139 \times 10^4 \text{ m}^3$ per km under ideal conditions.

Keppel and Renard (1962) studied transmission losses from flume 5 to flume 2 (Figure 7) and recorded a loss of $1.9168 \times 10^4 \text{ m}^3$ per km. The computed maximum is $2.3002 \times 10^4 \text{ m}^3$ per km.

Murphy, Lane and Diskin (1972) studied transmission losses for the drainage area to flume 8 (see Figure 7). The maximum loss recorded was $1.5208 \times 10^4 \text{ m}^3$ per km.

Sampling Sites

Location

Three sites in the Walnut Gulch watershed were used to obtain air samples from streambed sediments. Site 1 was 51.6 m upstream from flume 8. Site 2 was at the streambed wells identified as 1A on watershed maps. Site 3 was 7.6 m downstream from the point where the city of Tombstone discharges effluent into Walnut Gulch. Site 3 was placed near the effluent discharge "stream" to reflect possible effects of effluent discharge on the CO_2 concentration and $\delta^{13}\text{C}$ values. The sampling pipes at sites 3 and 2 were reimplemented several times because flows in Walnut Gulch or school children removed them from the streambed. Figure 7 shows the location of the sampling sites.

The location of Site 1 is $110^\circ 02' 35''$ longitude, $31^\circ 43' 24''$ latitude. The location of Site 2 is $110^\circ 03'$

57" longitude, 31° 43' 55" latitude. The location of Site 3 is 110° 04' 12" longitude, 31° 43' 52" latitude.

Description of Sites

The streambed at site 1 is variable in width, but is approximately 10 meters wide at the sampling site. Hills north and south of the streambed form the banks and support desert vegetation. The streambed is essentially free of vegetation. The sampling pipe was imbedded to a depth of one meter and located approximately four meters south of the north bank. The streambed material consists of gravels and sands. The gravels and sands are mainly quartzitic and volcanic. It was suspected that some carbonate material existed in the streambed because of the presence of calcareous soils in the uplands. Samples of the streambed were reacted with phosphoric acid and measurement of the CO_2 evolved showed approximately 4.0×10^{-2} grams of calcium carbonate per 1.0 gram of streambed.

The streambed at site 2 is 20 to 25 meters in width and is free of vegetation. The south bank rises vertically for approximately 3 meters and exposes roots of large desert bushes. The north bank slopes gently, supports a sparse amount of desert vegetation and has carbonate conglomerate as a base. The sampling pipe was imbedded to a depth of .9 m and located four meters from the south bank. The streambed material consists of sands and gravels that are loosely cemented by carbonate. The

sands and gravels are mainly quartzitic and volcanic. A layer of carbonate conglomerate exists in the streambed from a depth of .6 m and continues downward to at least .9 m. The carbonate conglomerate made it very difficult to drive the sampling pipe deeper than .9 m.

The streambed at site 3 is 20 to 25 meters wide and is essentially free of vegetation. The south bank is level and supports a dense growth of desert vegetation due to the effluent stream. The effluent stream runs approximately parallel to the south bank and is approximately 3 m from the south bank. The north bank slopes gently and supports desert vegetation. The streambed material consists of sands and gravels that are loosely cemented by carbonate. The sands and gravels are mainly quartzitic and volcanic. A layer of carbonate conglomerate exists in the streambed from a depth of .8 m and continues downward to at least 1.0 m. The sampling pipe was imbedded to a depth of 1 m and located 3 m north of the effluent stream.

2. SAMPLING METHOD AND ANALYTICAL TECHNIQUES

Sampling Method

Sampling was accomplished by the same method used by Parada (1981). Hollow pipes 1.5 m long with an outer diameter of 12.70 mm were driven into the streambed. The hole for each pipe was started by driving a 19.05 mm outer diameter iron rod 80 cm into the streambed. Once the pipes were in place, they were left alone unless subsequent stream flow or vandals ripped them out.

The pipes were far enough from the banks to sample only the atmosphere in the sediments of the streambed, not the soil atmosphere under the normal desert-shrub vegetation. The bottom of the pipe (Figure 8) was perforated to allow the atmosphere from the sediments of the streambed to pass up the pipe when suction was applied at the upper end.

Streambed atmosphere was collected in evacuated, one-liter flasks. The sampling system is shown in Figure 8, except that two evacuated flasks were connected to the fitting, rather than one as shown on the figure.

At first, water was poured on the streambed around the pipe to reduce the possibility of air leaking down channels along the pipe (Galimov, 1966). The metering

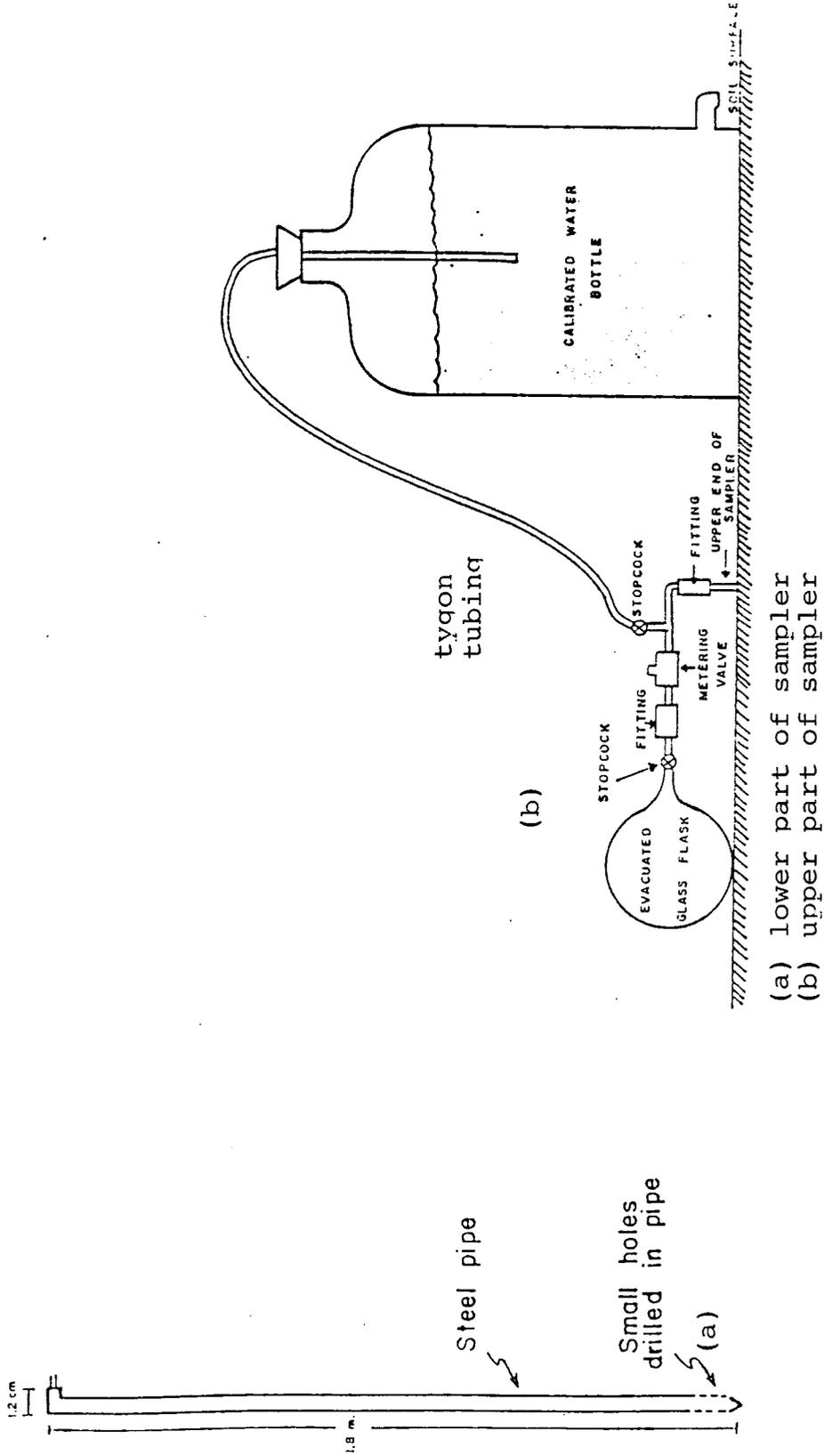


Figure 8. Streambed Atmosphere Sampler.
(After Parada, 1981)

valve and stopcock to the flask were closed, while the stopcock to the water bottle was open. The outlet of the water bottle was opened slightly to cause a suction on the rest of the system as the water drained. Two liters of water were drained to fill the tubing with streambed atmosphere. Then the stopcock to the water bottle was closed, the stopcock to both flasks were opened and the fine metering valve was opened to allow a controlled flow to the flasks. This controlled flow prevented fractionation. The fitting was a Cajon-tee^c which allowed two flasks to be attached at the same time. One flask served as duplicate for the experiments. Because the flasks previously had been evacuated, streambed atmosphere flowed into them. The flask stopcocks were left open for 15 minutes.

Several samples of air above the streambed were taken at Walnut Gulch in an evacuated, five-liter flask. Air entered the flask for 15 minutes to insure no fractionation occurred. These samples were analysed for CO₂ concentration and $\delta^{13}\text{C}$ values to compare with the CO₂ concentration and $\delta^{13}\text{C}$ values of the streambed atmosphere.

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Analytical Techniques

Sample Analysis for Total CO₂

The CO₂ concentrations of the samples were determined by a Varian Model 3700 Gas Chromatograph equipped with a thermal conductivity detector. The column used to separate different gases was a .32 cm outside diameter stainless steel tube, 200 cm long and filled with poropak Q 100-120 mesh. Flow rate was approximately 30 ml/minute. Temperatures at which runs were made were: column temperature, 40°C; thermal conductivity detector, 120°C; filament in detector, 180°C. Retention time of CO₂ was about 1.9 minutes.

The concentration of CO₂ in a sample was calculated by comparing the area of its peak to the area of the peak of the CO₂ standard. The standard was 495 ppm, ± 5%, CO₂ gas in a nitrogen-balance gas. The area of a peak was calculated automatically by a HP 3380A Hewlett-Packard Integrator. The areas were unitless. Details concerning the calculation of CO₂ concentration are given in Appendix A of Parada (1981) except my standard gas had a composition of 0.0495 ± 5% vol. CO₂ with N₂ gas occupying the rest of the volume (accuracy of analysis ± 2%).

Samples were injected by a gas sampling valve with a 1 cm³ loop. This kind of valve allowed a fixed volume of sample to be injected into the column almost instantly. A gauge showed the pressure of sample gas in the sample

loop. Each sample was analysed two or more times. The standard deviation of the samples was always less than 5% of the mean value.

Separation of CO₂ from Other Gases

A vacuum line was used to separate CO₂ from the other gases in the sample flask (Figure 9). The streambed atmosphere passed through a cold-alcohol trap (-80°C) and then through a liquid nitrogen (LN₂) trap (-195°C). Water vapor was collected in the first trap and CO₂ in the second trap. The CO₂ collected in the second trap was transferred to an evacuated sample vial by closing off the vacuum line from the vacuum, placing a LN₂ bath on the sample vial, opening the sample vial and taking the LN₂ bath off the CO₂ trap. This procedure caused the CO₂ to vaporize from the CO₂ trap and condense in the sample vial.

A fine-metering valve controlled the flow of streambed atmosphere from a flask to the vacuum line to prevent fractionation.

Purification of CO₂

After CO₂ was separated from most other gases present in the sample flasks, it was then passed through a preparatory gas chromatograph to separate the CO₂ from any N₂O. N₂O freezes out with CO₂ in a LN₂ trap and therefore needs to be separated from the CO₂ because N₂O has the same masses as CO₂ (44, 45, 46) and similar properties. N₂O

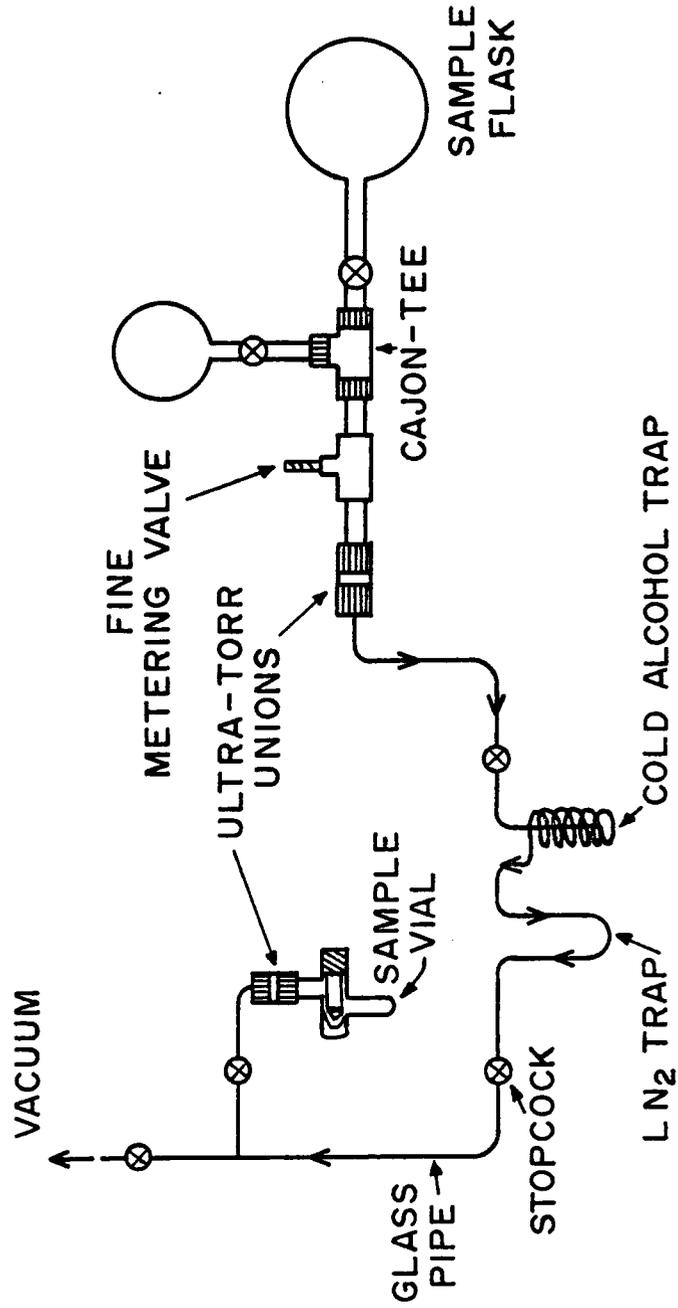


Figure 9. CO₂ Purification Line.

mixed with CO₂ in the mass spectrometer causes $\delta^{13}\text{C}$ values to be lighter than pure CO₂ (Craig and Keeling, 1963). The machine was a HP 775 Hewlett-Packard Preparative Gas Chromatograph. The column used was 6.35 mm outside diameter stainless-steel tubing, 9.144 m long filled with Porapak Q 80-100 mesh. Runs were made under the following conditions: column at room temperature; thermal conductivity detector, 40°C; buffer zone heater, 40°C; manifold heater, off. Retention time for CO₂ was approximately 20 minutes.

A trap was used to hold the sample gas for injection (Figure 10). The trap was copper tubing, 30.48 cm long and 6.35 mm outside diameter. The sample vial was connected by an ultra-torr union^c. The trap and volume leading up to the sample vial valve was evacuated. The valve to the vacuum was closed, the trap immersed in a liquid-nitrogen bath and the sample vial valve opened to collect the sample gas in the trap. After two minutes, the sample vial valve was closed, valve A closed, and the liquid-nitrogen bath was taken off. The trap warmed to room temperature and then the carrier-gas valves to the sample trap were opened. Pressurized-carrier gas was allowed to sweep the trap to carry the sample gas into the gas chromatograph by means of an inject switch. The intent of this procedure was to introduce the sample gas as a "slug." The head pressure of the column was 40 psi.

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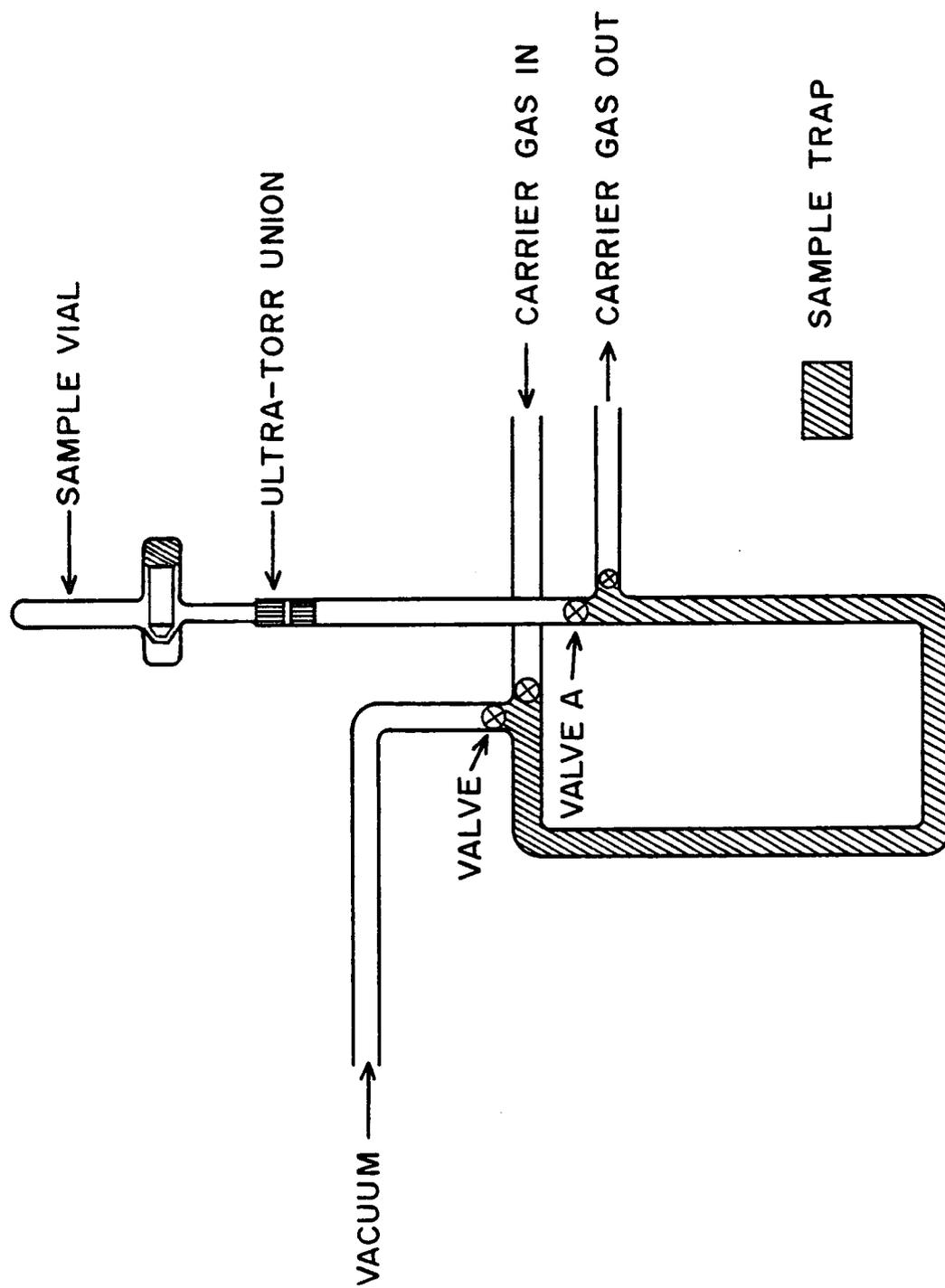


Figure 10. CO₂ Trap for Purification of CO₂.

The CO_2 was collected automatically in a glass trap that was immersed in a LN_2 bath. The glass trap had been previously swept by carrier gas. The CO_2 peak was detected and at that point the gas chromatograph switched the carrier gas from bypassing the glass trap to entering the glass trap. In this manner, the CO_2 was collected in the glass trap as the carrier gas swept through. When the peak for CO_2 was finished, the system again bypassed the glass trap. A standard mixture of CO_2 and N_2O showed the N_2O peak to start about four minutes after the finish of the CO_2 peak. A standard of CO_2 showed the system did not cause fractionation.

The CO_2 was transferred back to the sample vial in another laboratory and then was ready to run on the mass spectrometer.

Sample Analysis for $\delta^{13}\text{C}$ Value

A mass spectrometer was used to determine the ion current ratio of mass 46 and mass 45 of the sample CO_2 as compared to a CO_2 reference gas. The mass spectrometer was a V. G. Micromass Model 602C Isotope Ratio Mass Spectrometer. It is equipped with a dual inlet system which allows rapid comparison of the sample gas with a reference gas.

A microcomputer in the Isotope Geochemistry Laboratory of the University of Arizona calculated $\delta^{13}\text{C}$ values from the ion current ratio of mass 45/mass 44 and

mass 46/(mass 44 + mass 45). Appendix B of Parada (1981) details the calculations performed by the microcomputer.

Fractionation Test

The analytical technique for CO₂ separation from other gases and CO₂ purification was checked for fractionation. A known standard of CO₂ was run through each analytical technique. The $\delta^{13}\text{C}$ of the standard before and after a run is shown in Table 1. No significant fractionation occurred in either of the two techniques.

Table 1. Fractionation Test Results of Laboratory Standard for CO₂ Separation and CO₂ Purification.

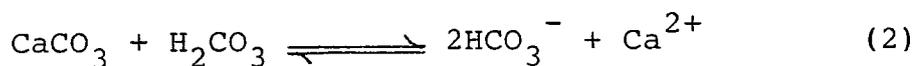
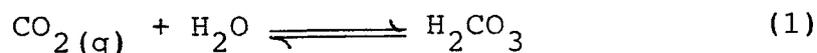
| | |
|------------------------------|---|
| CO ₂ separation | $\delta^{13}\text{C}$ before separation = |
| | -42.19% w.r.t. PDB |
| | $\delta^{13}\text{C}$ after separation = |
| | -42.29% w.r.t. PDB |
| CO ₂ purification | $\delta^{13}\text{C}$ before purification = |
| | -42.15% w.r.t. PDB |
| | $\delta^{13}\text{C}$ after purification = |
| | -42.24% w.r.t. PDB |

3. FACTORS AFFECTING CO₂ CONCENTRATION AND $\delta^{13}\text{C}$ VALUES

Carbonate Chemistry

Calcium carbonate (CaCO₃) exists in the streambed at each site. Carbonate is disseminated as small particles and quite possibly as coating on streambed particles at site 1. The uplands of site 1 have calcareous soils and are the source of CaCO₃ particles for site 1. Carbonate fills streambed pore space and loosely cements streambed particles at sites 2 and 3. Carbonate conglomerate exists approximately 70 cm below the streambed surface at site 2 and site 3.

Precipitation and dissolution of CaCO₃ affects the CO₂ concentration and $\delta^{13}\text{C}$ value of streambed atmosphere at each site. The chemical reactions:



show CO₂ gas is absorbed when equation 2 proceeds to the right (dissolution) and CO₂ gas is released when equation 2 goes to the left. Fractionation occurs in the carbon isotope exchange between bicarbonate and CO₂ gas. The equilibrium $\delta^{13}\text{C}$ value of gaseous CO₂ and HCO₃⁻ is dependent upon temperature (Mook, Bommerson, and Staverman,

1974), pH and the initial $\delta^{13}\text{C}$ values of the gaseous CO_2 and HCO_3^- (Dueser and Degens, 1967).

Fractionation of carbon isotopes between gaseous CO_2 and bicarbonate fluctuates with changing temperature. The temperature of streambed moisture at a meter depth in highly permeable streambed material at Tombstone, Arizona could be expected to fluctuate greatly within a year.

The streambed moisture could be cooled to a temperature near 0°C during the coldest part of winter by precipitation and mountain runoff infiltrating the streambed. A reasonable temperature for precipitation and mountain runoff during the coldest part of winter is 2°C . The freezing of streambed moisture during the night would also cool the streambed moisture.

The temperature of streambed moisture at a meter depth can be raised to an elevated but undetermined temperature during the hottest part of summer. Surface particles of the streambed are heated to temperatures in excess of 100°C at midday during the summer. The surface particles are so hot that almost all water present even in thin films would vaporize. Some of the water vapor would respond to a vapor pressure gradient and move deeper into the streambed, condense and therefore add heat to surrounding water films. Stream flows could be expected to have a temperature range of 20°C to 25°C . The combined effect of stream flows and condensation of water vapor would tend

to keep streambed moisture at a meter depth in a temperature range of 20°C to 25°C and possibly higher.

Samples of streambed conglomerate that were a combination of carbonate clasts and carbonate cement were taken at site 2 and site 3 and were analyzed for $\delta^{13}\text{C}$. The results are shown in Table 2.

Table 2. Isotopic Composition of Carbonate Cement Mixed with Carbonate Clasts at Sites 2 and 3, Walnut Gulch, Arizona.

| Site No. | $\delta^{13}\text{C}$ (‰ wrt PDB) | Mean $\delta^{13}\text{C}$ Value (‰ wrt PDB) |
|----------------------------------|-----------------------------------|--|
| 2 | -1.94 | -1.97 |
| | -2.01 | |
| 3 | -2.72 | -2.70 |
| | -2.68 | |
| Typical Caliche in Tucson Basin* | | -3.5 |

*Wallick, 1973

The conglomerate samples were broken with a hammer while in a cloth bag and then sifted through 60-mesh screen. One-tenth gram samples of the sifted samples were heated under vacuum at 500°C ± 10°C for two hours to decompose organic matter. The isotopic composition of the CaCO_3 particles was not altered. The samples were put into reaction vessels that had side arms filled with 95% phosphoric acid as suggested by McCrea (1950). The reaction vessels were evacuated for one hour, tipped to allow the acid to react with the 0.1 gram sample and then left overnight.

The CO_2 produced was analysed for its $\delta^{13}\text{C}$ by a mass spectrometer.

Treated Sewage Effluent

Treated sewage effluent is discharged continuously into the streambed of Walnut Gulch at approximately 7.6 m upstream from site 3. The location of site 3 was chosen to determine the effect, if any, of moisture and organic material of the effluent on the concentration and isotopic composition of streambed CO_2 . The average rate of effluent discharge is approximately 61,000 gallons per day ($231 \text{ m}^3/\text{day}$) (Fernandez, 1983).

Effluent might significantly affect the $\delta^{13}\text{C}$ value and CO_2 concentration of the streambed atmosphere. Effluent keeps the streambed moist in the immediate vicinity. The moisture promotes decomposition of organic matter by microorganisms (Beck, 1968). Also, the $\delta^{13}\text{C}$ value of the organic matter carried out in the effluent and the CO_2 produced by the decay of the effluent organic matter are factors of interest.

Treated effluent was randomly sampled and analysed for biological oxygen demand (B.O.D.) and other factors. The results of the analyses that are of interest are shown in Table 3. The effluent probably has a pH of 7.5 to 8.0 by the time it reaches the streambed (Krauskopf, 1979) and the pH is stabilized due to the $\text{CaCO}_3/\text{Ca}(\text{HCO}_3)_2/\text{HCO}_3^-$ system which acts as a buffer (Miotke, 1974). The B.O.D. values

indicate the amount of organic matter carried in the effluent. A sample calculation shows how many kg/day of organic matter is discharged in the treated sewage effluent (Fernandez, 1983):

$$5 \text{ mg/l} \times 61,000 \text{ gal/day} \times 11/0.2642 \text{ gal} \times 1 \text{ kg}/10^6 \text{ mg} =$$

$$1.15 \text{ kg/day} \quad (3)$$

Five mg/l is assumed to be a representative 5-day B.O.D. value of Table 3. 1.15 kg/day is not a significant amount of organic matter considering it is distributed along 275 to 366 meters of the effluent stream.

Table 3. Analyses of the Treated Sewage Effluent that is Discharged to Walnut Gulch at approximately 7.6 m Upstream from Site 3.*

| <u>Date</u> | <u>pH</u> | <u>5-Day B.O.D. (mg/l)</u> |
|-------------|-----------|----------------------------|
| 05/19/82 | 6.82 | 3.3 |
| 07/29/82 | 6.87 | 1.8 |
| 08/04/82 | 7.09 | 3.8 |
| 09/30/82 | 7.11 | 3.4 |
| 10/30/82 | 6.52 | 0.9 |
| 11/29/82 | 6.85 | 2.4 |
| 12/31/82 | 7.22 | 22.0 |
| 01/30/83 | 6.32 | 6.8 |
| 02/26/83 | 6.49 | 3.0 |
| 03/31/83 | 5.88 | 5.7 |
| 04/30/83 | 6.15 | 3.1 |
| 05/18/83 | 7.44 | 3.7 |
| 06/14/83 | 6.55 | 4.0 |

* Analyses performed by Smith & Smith Environmental Consultants, Environmental Laboratory, 429 South San Francisco, Flagstaff, Arizona, 86001.

Streambed samples were taken at site 3 and 50 meters downstream from site 3 to analyze for percent organic

matter (% O.M.) according to the Walkley-Black Method (Methods of Soil Analysis, 1965). The samples were taken approximately 2.5 m from the effluent stream toward the center of the streambed. The samples were moist from the effluent spreading out under the streambed surface. The results are shown in Table 4.

Table 4. Analyses of Organic Matter (% O.M.) in Samples from Walnut Gulch Streambed from Site 3 and 50 Meters Downstream from Site 3. Samples Collected 7/5/82.

| <u>Location</u> | <u>No.</u> | <u>Depth of Collection</u> | <u>% # O.M.</u> |
|-----------------------------|------------|----------------------------|-----------------|
| Site 3 | 1 | 30 cm | 0.22 |
| Site 3 | dup. of 1 | 30 cm | 0.28 |
| Site 3 | 2 | 60 cm | 0.22 |
| Site 3 | dup. of 2 | 60 cm | 0.28 |
| 50 m downstream from Site 3 | 3 | 35 cm | 0.31 |
| 50 m downstream from Site 3 | dup. of 3 | 35 cm | 0.34 |
| 50 m downstream from Site 3 | 4 | 60 cm | 0.33 |
| 50 m downstream from Site 3 | dup. of 4 | 60 cm | 0.34 |

The percent organic matter measurements show that either the effluent contained a negligible amount of organic matter to begin with, or microorganisms have reduced the organic matter almost completely by the time the effluent reached the sampling points, or streambed material prevented suspended organic matter from penetrating the streambed to 30 cm (Schmutz-Decke effect). The physical

appearance of the surface of the streambed material does not support the idea that a significant amount of organic matter was being collected by the Schmutz-Decke effect. Therefore, it seems the effluent will be most important as a source of moisture rather than as a source of organic matter.

Plant Activity

Plants affect the $\delta^{13}\text{C}$ and CO_2 concentration of streambed atmosphere by respiring CO_2 from their roots (Park and Epstein, 1960). The P_{CO_2} around roots is greater than the P_{CO_2} of the streambed. This concentration gradient causes root-respired CO_2 to infiltrate the streambed by molecular diffusion (DeJong and Schappert, 1972). The gas movement obeys gas diffusion laws in porous media. Gas movement might also result from mass flow caused by changes of moisture content, temperature gradients and barometric pressure changes (Reardon, Allison and Fritz, 1979). Mass flow of soil gas obeys the laws of fluid mass flow in porous media. Plant activity determines the amount of CO_2 respired by the roots and is directly related to soil moisture and temperature, except when soil moisture approaches saturation or when temperature increases excessively.

The dominant plants of the sites were analyzed for their $\delta^{13}\text{C}$ value. The results are shown in Table 5 and indicate the vegetation to be a potential source of CO_2 with $\delta^{13}\text{C}$ values in the range of -24.28‰ to -26.43‰. The $\delta^{13}\text{C}$ of the CO_2 respired by the plant root is very similar

Table 5. Photosynthetic Pathway and Identification of the Dominant Vegetation at the Three Sampling Sites. (1), (2)

| Scientific Name | Common Name | Photosynthetic Pathway | $\delta^{13}\text{C}$ (3) (‰ PDB) |
|---------------------------------|-------------------|------------------------|--------------------------------------|
| <i>Flourensia cernua</i> | american tar-bush | C ₃ | -26.43 |
| <i>Acacia neovernicosa</i> | viscid acacia | C ₃ | -24.28 |
| <i>Larrea tridentata</i> | creosote bush | C ₃ | -25.45 |
| <i>Rhus microphylla</i> * | | C ₃ | -24.57 |
| <i>Bacharis sarathroides</i> ** | desert broom | C ₃ | -25.44 |

* Minor but not insignificant part of vegetation at site 1.

** Plant grows on streambed banks.

Minor but not insignificant part of vegetation at each site. Plant grows in the streambed and on the streambed banks.

(1) Analyses for $\delta^{13}\text{C}$ values performed by Lisa Warnecke and Steve Leavitt of the Isotope Geochemistry Laboratory, University of Arizona.

(2) Identification of plants performed by Rodney Engard, Executive Director, Tucson Botanical Gardens, Tucson, Arizona.

(3) Standard used to calculate $\delta^{13}\text{C}$ values has Delta 13C (NBS20-PDB) = -1.06‰.

to the $\delta^{13}\text{C}$ of the plant except for plants that have Crassulacean Acid Metabolism (CAM) (Deines, 1980; Troughton, 1972; Smith, 1971; Park and Epstein, 1960). Bender (1968), Smith and Epstein (1971) and Troughton (1971, 1972) found variations in carbon isotope fractionation by various species of plants that were attributed to different carbon fixation pathways. Plants can be classified according to carbon fixation pathway. Plants that have a CAM pathway such as prickly pear, saguaro and cholla, are virtually absent from the environs of the three sampling sites.

Microorganisms

Microorganisms respire CO_2 when they decay organic matter (Beck, 1968). The $\delta^{13}\text{C}$ of the respired CO_2 should closely match the $\delta^{13}\text{C}$ of the decaying matter (Deines, 1980; Galimov, 1966; Lerman, 1972; Rightmire and Hanshaw, 1973). Decaying matter at the three sites should be heavily dominated by whitethorn, creosote bush and tarbush. The $\delta^{13}\text{C}$ values of these plants are shown in Table 5.

Beck (1968) researched the living conditions and metabolism of microorganisms. He determined that microorganisms evolve large amounts of CO_2 under favorable conditions and stop growing when soil CO_2 concentration rises above 10% or oxygen concentration decreases to an extreme. They grow best when the field capacity of the soil is between 50% and 80%. The lowest field capacity where microorganism activity can be expected is 5%. The

population and activity of microorganisms decreases as soil moisture decreases. Thus, microorganism activity will decrease during the drought periods of fall and early summer at Walnut Gulch. The cold temperatures of winter will also decrease microorganism activity.

Microorganisms that exist in water film surrounding inorganic soil particles continue to cause chemical solution activity during relatively dry periods. These water films are a popular environment for microorganisms and are the place where limestone surfaces are most actively dissolved even during dry periods (Miotke, 1974).

Channel Flow

Channel flow acts as a flushing agent of the gases in a streambed by dissolving gases and filling pore space. As a flow recedes into the streambed, atmosphere will follow to fill pore space. This process makes it possible for streambed atmosphere to reach the $\delta^{13}\text{C}$ value and CO_2 concentration of the atmosphere immediately following a flood event. The depth to which the atmosphere penetrates the streambed as a flow recedes is limited by water-filled pore space and water blocking pore passages.

The $\delta^{13}\text{C}$ value of the bicarbonate in a flow affects the $\delta^{13}\text{C}$ value of the streambed atmosphere and probably has its greatest effect soon after a flow. The $\delta^{13}\text{C}$ value of the bicarbonate in a flow is determined by the chemical

reactions the water was subjected to as it flowed overland and in gullies to collect in a channel.

Channel flow is also a source of moisture to aid chemical and biological activity. The chemical activity of interest is fractionation caused by carbonate chemistry. The biological activities of interest are organic decay by microorganisms and plant-root respiration. Temporarily perched water occurred below the streambed surface during winter and early spring at sites 2 and 3, but not at site 1.

4. EXPERIMENTAL RESULTS

Ten samples of streambed atmosphere per site were collected between July 27, 1982 and June 15, 1983. Streambed atmosphere was drawn from an approximate depth of one meter at each site. Each sample was analyzed for CO₂ concentration and $\delta^{13}\text{C}$ value. The samples taken on 2/8/83 at site 2 and site 3 were accidentally lost after the CO₂ concentrations had been determined. CO₂ concentration versus time, $\delta^{13}\text{C}$ versus time, precipitation during the week preceding sampling and average monthly temperature are shown as graphs in Figure 11. The data are given in Tables 6, 7, 8 and 9 respectively.

The CO₂ concentration of site 1 ranged from 0.94 percent CO₂ by volume (% CO₂ volume) on 8/24/82 to 0.29% CO₂ volume on 2/8/83 and $\delta^{13}\text{C}$ values ranged from -20.75‰ on 8/24/82 to -17.53‰ on 7/27/82. The average $\delta^{13}\text{C}$ value for the data is -19.38‰.

The CO₂ concentration of site 2 ranged from 0.21% CO₂ volume on 7/27/82 to 0.022% CO₂ volume on 1/6/83 and $\delta^{13}\text{C}$ values ranged from -19.02‰ on 8/24/82 to +2.60‰ on 1/6/83. The +2.60‰ datum is a result of analytical error and probably should be close to -9.5‰. The -9.5‰ value was chosen because the $\delta^{13}\text{C}$ values of December and March

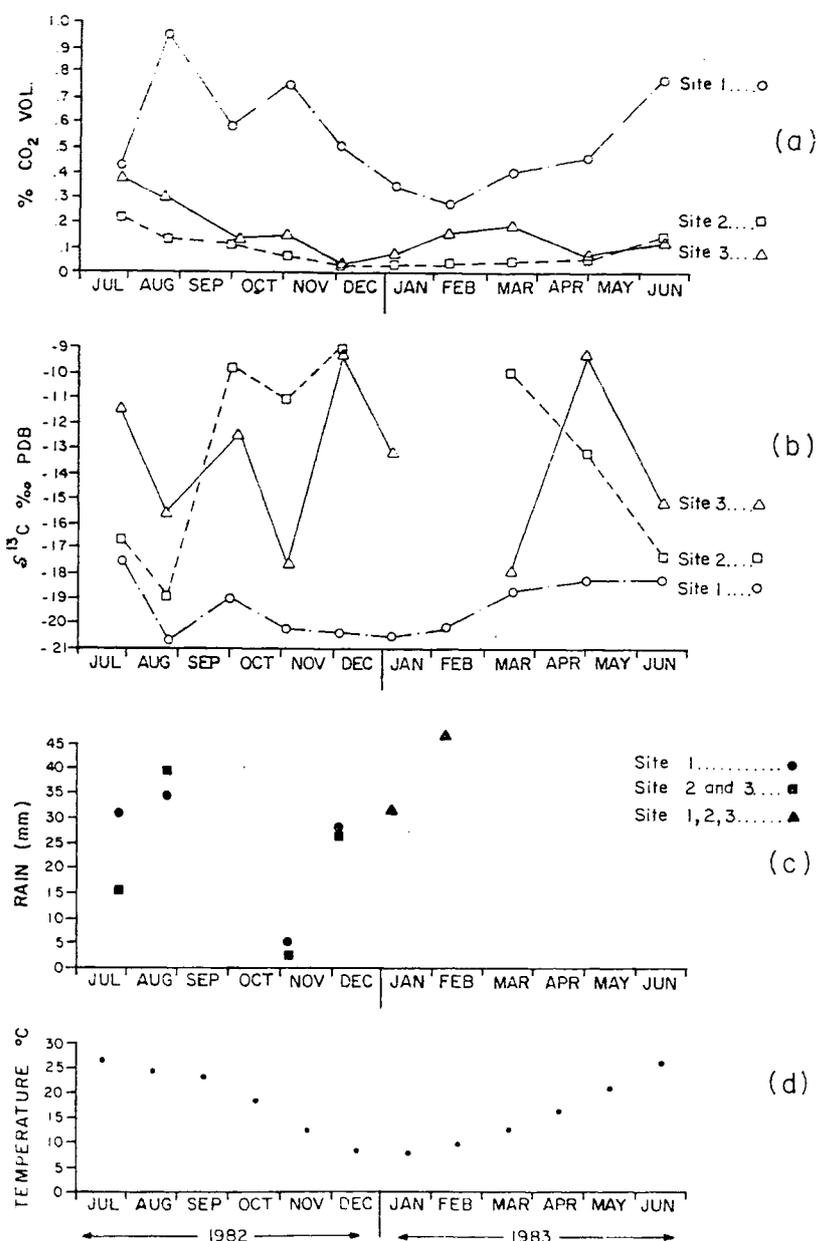


Figure 11. Experimental Results, Precipitation Data and Monthly Temperature for Walnut Gulch Watershed.

- (a) percent CO₂ volume versus time for each sampling site
- (b) δ¹³C ‰ w.r.t. PDB versus time for each sampling site
- (c) cumulative precipitation a week preceding sampling
- (d) average monthly temperature at Tombstone, Arizona

Table 6. Percent CO₂ by Volume for Streambed Atmosphere at each Site and Air at Tombstone.

| Percent CO ₂ by Volume | | | | |
|-----------------------------------|---------------|---------------|---------------|----------------------|
| <u>DATE</u> | <u>SITE 1</u> | <u>SITE 2</u> | <u>SITE 3</u> | <u>TOMBSTONE AIR</u> |
| 1 7/27/82 | 0.42 | 0.21 | 0.39 | |
| 2 8/24/82 | .94 | .13 | .31 | 0.034 |
| 3 9/30/82 | .59 | .11 | | |
| 4 10/5/82 | | | .12 | |
| 5 11/2/82 | .74 | .077 | .16 | |
| 6 12/2/82 | .51 | .029* | .030* | |
| 7 1/6/83 | .35 | .022 | .066 | .036 |
| 8 2/8/83 | .29 | .030 | .16 | .033 |
| 9 3/17/83 | .40 | .036 | .18 | .033 |
| 10 4/30/83 | .46 | .054 | .063** | |
| 11 6/15/83 | .76 | .13 | .11** | |

*Sampled at an approximate depth of 35 cm due to temporarily perched water at an approximate depth of 40 cm.

**Sampled at an approximate depth of 30 cm due to temporarily perched water at an approximate depth of 35 cm.

Table 7. $\delta^{13}\text{C}$ Values for streambed atmosphere at each site and air at Tombstone, Arizona.

| DATE | *SITE 1 | | *SITE 2 | | *SITE 3 | | TOMBSTONE AIR |
|------------|--|---|--|---|--|---|---------------|
| | $\delta^{13}\text{C}$ w.r.t. PDB BEFORE PURIFI. | $\delta^{13}\text{C}$ w.r.t. PDB AFTER PURIFI. | $\delta^{13}\text{C}$ w.r.t. PDB BEFORE PURIFI. | $\delta^{13}\text{C}$ w.r.t. PDB AFTER PURIFI. | $\delta^{13}\text{C}$ w.r.t. PDB BEFORE PURIFI. | $\delta^{13}\text{C}$ w.r.t. PDB AFTER PURIFI. | |
| 1 7/27/82 | -17.53 | -16.57 | -11.31 | -11.31 | -8.32 | -8.32 | |
| 2 8/24/82 | -20.75 | -19.02 | -15.66 | -15.66 | | | |
| 3 9/30/82 | -18.95 | - 9.89 | | | | | |
| 4 10/5/82 | | | -12.36 | -12.36 | | | |
| 5 11/2/82 | -20.24 | -11.10 | -17.67 | -17.67 | | | |
| 6 12/2/82 | -20.34 | - 9.07 | - 9.08 | - 9.08 | | | |
| 7 1/6/83 | -20.47 | + 2.60 | -13.22 | -13.22 | -7.91 | -7.91 | |
| 8 2/8/83 | ** -19.78 | LOST | LOST | LOST | | | |
| 9 3/17/83 | -19.32 | -18.78 | ** -9.83 | -18.44 | -18.00 | -18.00 | -8.07 |
| 10 4/30/83 | -18.52 | -18.28 | ** -13.03 | - 9.37 | - 9.16 | - 9.16 | |
| 11 6/15/83 | -18.58 | -18.28 | ** -16.82 | -17.37 | ** -14.94 | -15.16 | |

*Values are average of two samples

**A reason for value being heavier than after purification (besides analytical error) is that $^{12}\text{C}^{16}\text{O}_2$ might have a proton attached which would cause the mass spectrometer to read a mass of 45. Protons would be available if water vapor froze out with CO_2 (Long, 1983). (Note: Samples taken 2/8/83 and thereafter were analysed both before and after purification to check fractionation, if any, caused by purification procedure. No significant fractionation was detected.)

Table 8. Precipitation and stream flows a week preceding sampling dates.
 (From Southwest Rangeland Watershed Research Center, Tucson, Arizona)

Note: See Figure 2 for locations of rain gauges numbered 16, 17, 22, 23, 28.

| DATE | Precipitation for sites 2 and 3 (mm) | | | Precipitation for site 1 (mm) | | |
|--|--------------------------------------|------|------|-------------------------------|---------------------|---------------------|
| | Rain gauges used #16 | #17 | #22 | #23 | Rain gauge used #28 | |
| 7/20/82 | 10.7 | 16.5 | 14.5 | 15.8 | | 21.6 |
| 7/21/82 | 0 | 0 | 0.8 | 0 | | 2.5 |
| 7/22/82 | 0 | 0 | 0 | 0 | | 0 |
| 7/23/82 | 0 | 0 | 0.8 | 0 | | 0 |
| 7/24/82 | 0 | 0 | 1.0 | 1.3 | | 4.6 |
| 7/25/82 | 0 | 0.8 | 0 | 0 | | 0.8 |
| 7/26/82 | 0 | 0 | 1.0 | 1.0 | | 1.8 |
| Stream flow occurred on 7/20/82 for all three sites. | | | | | | |
| 8/17/82 | 0 | 0 | 0 | 0 | | 0 |
| 8/18/82 | 0.8 | 1.3 | 1.8 | 1.3 | | 0.5 |
| 8/19/82 | 0.5 | 2.0 | 1.5 | 2.5 | | 1.3 |
| 8/20/82 | 22.1 | 25.4 | 8.9 | 8.9 | | 8.9 |
| 8/21/82 | 2.5 | 4.1 | 1.8 | 1.8 | | 0 |
| 8/22/82 | 0 | 0 | 0 | 0 | | 0 |
| 8/23/82 | 11.7 | 17.8 | 15.2 | 23.6 | | 23.1 |
| Stream flow occurred on 8/20, 8/23 for all three sites. No precipitation since 9/11/82 for all three sites.) This applies for No stream flows since 9/11/82 for all three sites.) sampling dates) 9/30/82 and 11/2/82. | | | | | | |
| 11/25/82 | Rain gauge used #13 | | | | | Rain gauge used #80 |
| 11/26/82 | 1.8 | | | | | 2.5 |
| 11/27/82 | 1.3 | | | | | 2.5 |
| 11/28/82 | 0 | | | | | 0 |
| 11/28/82 | 0 | | | | | 0 |

Table 8--Continued

(From Southwest Rangeland Watershed Research Center and Tombstone Weather Station, Tombstone, Arizona)

Note: See Figure 2 for location of rain gauges numbered 13, 80.

| DATE | Precipitation for sites 2 and 3 (mm) | Precipitation for site 1 (mm) |
|--|--------------------------------------|-------------------------------|
| | Rain gauge used #13 | Rain gauge used #80 |
| 11/29/82 | 0 | 0 |
| 11/30/82 | 8.9 | 10.2 |
| 12/01/82 | 17.8 | 17.8 |
| Precipitation at all three sites assumed to be the same as measured at Tombstone for winter and spring because rain storms cover large areas during winter and spring. | | |
| Precipitation for all three sites | | |
| 12/26/82 through 12/29/82 | had no precipitation | |
| 12/30/82 | 2.0 | |
| 12/31/82 | 15.2 | |
| 1/01/83 | 15.2 | |
| 2/01/83, 2/02/83, 2/05/83, 2/07/83 | had no precipitation | |
| 2/03/83 | 15.2 | |
| 2/04/83 | 26.7 | |
| 2/06/83 | 5.1 | |
| 3/10/83 through 3/16/83 | had no precipitation | |
| 4/23/83 through 4/29/83 | had no precipitation | |
| 6/08/83 through 6/14/83 | had no precipitation | |

Table 9. Average monthly air temperature at Tombstone, Arizona*.
(From Gelderman, 1970).

| | <u>Degrees Celsius</u> |
|-----------|------------------------|
| January | 8.39 |
| February | 9.89 |
| March | 12.4 |
| April | 16.5 |
| May | 20.7 |
| June | 25.6 |
| July | 26.1 |
| August | 24.9 |
| September | 23.3 |
| October | 18.6 |
| November | 12.6 |
| December | 8.50 |

* 56 years of record

were between -9‰ and -10‰ and the CO₂ concentrations for December, January and March were similar. The sample of 12/2/82 was taken from an approximate depth of 35 cm due to temporarily perched water. A total of 2.67 cm of precipitation occurred on 11/30/82 and 12/1/82. The average $\delta^{13}\text{C}$ value for the data (excluding the +2.60‰ datum) is -13.27‰.

The CO₂ concentration of site 3 ranged from 0.39% CO₂ volume on 7/27/82 to 0.030% CO₂ volume on 12/2/82 and $\delta^{13}\text{C}$ values ranged from -18.00‰ on 3/17/83 to -9.08‰ on 12/2/82. The sample of 12/2/82 was taken from an approximate depth of 35 cm due to temporarily perched water at an approximate depth of 40 cm. A total of 2.67 cm of precipitation occurred on 11/30/82 and 12/1/82. The samples taken 4/30/83 and 6/15/83 were from an approximate depth of 30 cm due to perched water at the approximate depths of 37 cm and 34 cm, respectively. The average $\delta^{13}\text{C}$ value for the data is -13.51‰.

The sites had lowest CO₂ concentrations during winter and highest CO₂ concentrations during the rainy part of summer, in general. The $\delta^{13}\text{C}$ of a site was usually more negative (lighter) as CO₂ concentration increased. Site 1 consistently had CO₂ concentrations greater than site 3. The same relationship holds for site 3 compared to site 2. The $\delta^{13}\text{C}$ values of site 1 were consistently lighter than the $\delta^{13}\text{C}$ values of the other sites. Sites

2 and 3 often changed their relationship concerning which of the two sites had the lighter $\delta^{13}\text{C}$ value.

5. DISCUSSION OF RESULTS

Discussion of Site 1 Results

The results of work at site 1 show CO₂ concentration versus time varied significantly (Figure 11). The variation was correlated with plant and microorganism activity. The rise from 7/27/82 to 8/24/82 was a result of a significant increase of soil moisture due to summer rain. This allowed plants and microorganisms to increase their metabolism. The values of 7/27/82 and 8/24/82 might have been significantly greater if stream flow had not recently preceded the sampling. The rise of CO₂ concentration from 9/30/82 to 11/2/82 could be attributed to CO₂ escaping from streambed water as the streambed moisture evaporated. The sharp rise from 4/30/83 to 6/14/83 seemed to be a result of increasing temperature and ample moisture from an abnormally wet spring which allowed increased plant and microorganism activity.

Results show the $\delta^{13}\text{C}$ values of the streambed CO₂ were consistently heavier than any of the $\delta^{13}\text{C}$ values of the dominant vegetation (Table 5, Table 7). The consistently heavier $\delta^{13}\text{C}$ values might have been due to gas exchange between atmosphere and streambed, but it was more likely due to mixing of root-respired CO₂ with CO₂ in isotopic equilibrium with HCO₃⁻ derived from carbonate

solution. Calcareous soils exist throughout the uplands from site 1 (Gelderman, 1970). Samples of the streambed from depths of 15 cm to 30 cm and 76 cm to 91 cm were examined and showed approximately 0.04 grams of CaCO_3 per gram of streambed. Also, the CO_2 concentration of 8/24/82 was 323% greater than that of 2/8/83, yet the difference between the $\delta^{13}\text{C}$ values was only 0.61‰. The presence of CaCO_3 and consideration of the varying CO_2 concentrations and $\delta^{13}\text{C}$ values suggest that little mixing, if any occurred between atmospheric CO_2 and streambed CO_2 .

Another interesting point of the $\delta^{13}\text{C}$ results of site 1 was the $\delta^{13}\text{C}$ value of the streambed CO_2 showed much less variation in comparison to site 2 or site 3. As mentioned above, mixing of root-respired CO_2 with CO_2 in isotopic equilibrium with HCO_3^- could cause the streambed CO_2 of site 1 to obtain a $\delta^{13}\text{C}$ value much heavier (more positive) than the data of Table 7 indicate. However, site 1 was continually being recharged by large amounts of root-respired CO_2 as shown by the CO_2 concentration data of site 1 (Table 6). The constant and large amount of recharge by root-respired CO_2 continually "pushed" the streambed CO_2 to obtain a $\delta^{13}\text{C}$ value around -25‰. A "middle ground" of $\delta^{13}\text{C}$ values was reached between the ever-present effect of CO_2 in isotopic equilibrium with HCO_3^- and continual recharge of root-respired CO_2 .

The $\delta^{13}\text{C}$ value of the streambed CO_2 became lighter from 7/27/82 to 8/24/82 because plants and microorganisms contributed more CO_2 to the streambed as soil moisture increased. The streambed CO_2 became lighter from 9/30/82 to 1/6/83 in part, because the onset of winter lowered the temperature of the streambed moisture which shifted the isotopic equilibrium between HCO_3^- and gaseous CO_2 to more negative values. That is, the $\delta^{13}\text{C}$ equilibrium value of CO_2 is approximately 2.5‰ more negative at 2°C than at 25°C (Mook, Bommerson, Staverman, 1974; Deuser and Degens, 1967). The $\delta^{13}\text{C}$ value of the streambed CO_2 became heavier from 9/30/82 to 11/2/82 partly because the amount of CO_2 in isotopic equilibrium with HCO_3^- decreased as the streambed dried. The decreasing amount of CO_2 in isotopic equilibrium with HCO_3^- allowed the CO_2 from plant roots to increase its relative contribution to the $\delta^{13}\text{C}$ value of the streambed CO_2 . The streambed CO_2 became heavier from 1/6/83 to 6/14/83 because the $\delta^{13}\text{C}$ value of CO_2 in isotopic equilibrium with HCO_3^- became more positive with increasing temperature.

Discussion of Site 2 Results

The results of the analyses of samples from site 2 show CO_2 concentration followed a smooth decrease from summer to winter and a smooth increase from winter to summer (Figure 11). The decrease from 7/27/82 to 9/30/82 was probably due mostly to surface flows absorbing CO_2 .

The continued decrease from 9/30/82 to 1/6/83 was probably a result of decreasing plant and microorganism activity. The continuous increase from 1/6/83 to 6/14/83 was due to increased plant and microorganism activity as air temperature increased. CO_2 concentration could have been expected to decrease from 4/30/83 to 6/14/83 because plant activity would have decreased as soil moisture significantly decreased, but Tombstone had an unusually wet winter and spring. Also, significant precipitation occurred during April (4.1 mm). The data of 12/2/82 through 3/17/83 are of particular interest because they show CO_2 concentrations very near or less than the average CO_2 concentration of air (0.034% Vol. CO_2). Streambed CO_2 being used by the dissolution of carbonate minerals due to the influx of moisture containing H_2CO_3 (equations 1 and 2) could cause the P_{CO_2} of the streambed atmosphere to be less than the P_{CO_2} of atmosphere under these conditions:

1. The streambed atmosphere is a limited reservoir of CO_2 .
2. The P_{CO_2} of the streambed atmosphere was approximately equal to the P_{CO_2} of the atmosphere prior to a significant influx of moisture to the streambed.
3. Recharge of CO_2 to the streambed is a relatively slow process.

4. The pH of rain and runoff infiltrating the streambed was lower than the pH of the moisture already existing in the streambed.

Table 8 shows that more than 2.54 cm of rain fell directly onto the streambeds at Walnut Gulch during the week prior to the sampling dates of 12/2/82, 1/6/83 and 2/8/83. The rain would obtain a pH of 5.7 if exposed only to atmospheric CO₂ (Krauskopf, 1979) and could obtain a lower pH after reacting with air pollutants. The pH of the streambed moisture is probably 7.5 to 8.0 at equilibrium (Krauskopf, 1979). Thus, a large amount of rain with a pH less than the pH of the streambed moisture fell directly onto the streambeds of Walnut Gulch during the week preceding those sampling dates when the P_{CO₂} of the streambed was less than the P_{CO₂} of the atmosphere.

The consistently low values of CO₂ concentration at site 2 require explanation. Parada's data (1981) for the CO₂ concentration of soil gas in recharge areas (with one exception) and my data for CO₂ concentration at site 1 (with one exception) were consistently at least an order of magnitude greater than the CO₂ concentration of air. Four reasons are listed to explain why site 2 had consistently low CO₂ concentration values.

1. The conglomerate layer below the streambed surface keeps streambed gases near the streambed surface which increases the

likelihood that streambed CO_2 will escape to the atmosphere.

2. The streambed material is highly permeable, which allows streambed CO_2 to easily escape to the atmosphere.
3. The distance of four meters from the nearest bank (south bank) gives root-respired CO_2 diffusing toward the sampling pipe, a good chance of escaping to the atmosphere before reaching the pipe.
4. The height of the nearest bank (approximately three meters) allows root-respired CO_2 to escape from the bank soil.

The $\delta^{13}\text{C}$ of streambed CO_2 at site 2 showed great variation over time and was consistently heavier (more positive) than the $\delta^{13}\text{C}$ of streambed CO_2 at site 1 (Figure 11). The consistently heavier values were probably a result of site 2 not receiving as much root-respired CO_2 as site 1, which increased the relative importance of CO_2 in isotopic equilibrium with HCO_3^- in determining the $\delta^{13}\text{C}$ value of streambed CO_2 at site 2. The large variation of $\delta^{13}\text{C}$ values over time was likely due to a great variation of input by root-respired CO_2 to site 2. A great variation of input by root-respired CO_2 , in turn, caused the relative importance of CO_2 in isotopic equilibrium with HCO_3^- to vary greatly. The relative importance of root-respired CO_2 at

site 2 was greatest during the rainy part of summer, appears to have decreased as winter approached and increased as summer approached (Figure 11). Not surprisingly, the $\delta^{13}\text{C}$ value of streambed CO_2 was most negative on the sampling date 8/24/82, which corresponded to the time of year when plant and microorganism activity were probably greatest. The $\delta^{13}\text{C}$ values and CO_2 concentrations of samples taken 12/2/82 and 3/17/83 suggest that atmospheric CO_2 was a dominant contributor to the streambed CO_2 of site 2. The variation of the $\delta^{13}\text{C}$ of streambed CO_2 toward a lighter value from 9/30/82 to 11/2/82 was caused by decreasing streambed moisture, which reduced the amount of CO_2 in isotopic equilibrium with HCO_3^- .

Discussion of Site 3 Results

Site 3 results show CO_2 concentrations were significantly lower than the values of site 1 and lower also than the results reported by Parada (1981) for soil gas in recharge areas. Four reasons are listed to explain why site 3 had low CO_2 concentration values.

1. The sewage effluent stream impedes root-respired CO_2 from the nearest (south) bank from recharging site 3. The water table caused by the effluent stream acts as a barrier.
2. Root-respired CO_2 from the farther (north) bank must travel approximately 15 meters to

recharge site 3. This distance of travel probably allows a considerable amount of CO_2 to escape from the streambed.

3. The streambed conglomerate keeps gases near the streambed surface, which allows CO_2 to easily escape the streambed.
4. The moisture of the effluent is a constant sink to absorb CO_2 .

Statement number 4 is counterbalanced by site 3 plants respiring more CO_2 per year than plants subjected to water stress. Site 3 plants on the south bank have continuous moisture supplied to them by the effluent stream.

The CO_2 concentration data generally follow plant activity with a decrease of CO_2 concentration from summer to winter and an increase of CO_2 concentration from winter to spring. The datum of 8/24/82 could have been significantly greater if preceding channel flows had not occurred. The sample of 12/2/82 was taken from a depth of 30 cm due to standing water at 34 cm. The low value of 12/2/82 (0.030% CO_2) could have been caused by the same mechanism that explained the low CO_2 concentrations of samples taken 12/2/82 through 3/17/83 for site 2. The significant rise of CO_2 concentration from 12/2/82 to 1/6/83 was unexpected because January was a cold month, which reduced biological activity, and ample moisture was available to absorb CO_2 . The increase may have been due to a significant increase of

organic material in the effluent as evidenced by the large increase of B.O.D. from 11/29/82 to 12/3/82 (Table 3). Samples of 4/30/83 and 6/14/83 were taken from the depth of 30 cm because of standing water at an approximate depth of 37 and 34 cm, respectively. The standing water was due to a shift of the sewage effluent stream and/or increased discharge of sewage effluent. Not surprisingly, the samples of 4/30/83 and 6/14/83 had low CO₂ concentrations due to a greater contribution of atmospheric air.

The results of measurements of samples from site 3 show $\delta^{13}\text{C}$ values were consistently heavier at site 3 than site 1, and the $\delta^{13}\text{C}$ of the streambed CO₂ varied greatly (Figure 11). The variation indicates the relative contribution of carbonate equilibrium (which is moisture and temperature dependent) to the $\delta^{13}\text{C}$ value of the streambed CO₂ varied with respect to the contributions of CO₂ respired from roots and decay of organic matter. The $\delta^{13}\text{C}$ values of site 3 were consistently heavier than site 1 due to site 3 not recharging with root-respired CO₂ as well as site 1. Therefore, carbonate equilibrium made a greater relative contribution to the $\delta^{13}\text{C}$ of the streambed CO₂ at site 3 than at site 1. The same reasoning that applied to the rise and fall of the $\delta^{13}\text{C}$ at site 2 from 7/27/82 to 12/2/82 applies to site 3 for the same time period. Site 3 had lighter values than site 2 for the dates of 9/30/82 and 11/2/82, respectively. This could have

resulted from the continuous moisture supply at site 3 keeping plants more active during the drought period of fall. With plants more active, root-respired CO_2 makes a bigger contribution to $\delta^{13}\text{C}$ of the streambed atmosphere. The $\delta^{13}\text{C}$ of 12/2/82 at site 3 closely matches that of site 2 because of the shallow depth of sampling for each site and streambed moisture allowed the effect of carbonate equilibrium to be relatively more important. The $\delta^{13}\text{C}$ became lighter from 12/2/82 to 1/6/82 probably as a result of the organic matter in the effluent having a light $\delta^{13}\text{C}$ value. There was excess organic matter in the effluent (Table 3) that was noted in the CO_2 concentration discussion. The variation of $\delta^{13}\text{C}$ from 3/17/83 to 6/14/83 correlates with what would be expected considering the respective CO_2 concentrations.

Discussion of Calculated $\delta^{13}\text{C}_{\text{o.s.}}$ Values

The $\delta^{13}\text{C}$ values of streambed atmosphere are a result of the mixing of atmospheric CO_2 with sources of CO_2 derived from plant-root respiration, decay of organic matter and inorganic carbonates. All sources other than atmospheric CO_2 are here termed "other sources." A mass balance may be described as follows:

$$\delta^{13}\text{C}_{\text{o.s.}} = \frac{\delta^{13}\text{C}_{\text{sample}} \cdot C_{\text{sample}} - \delta^{13}\text{C}_{\text{air}} \cdot C_{\text{air}}}{(C_{\text{sample}} - C_{\text{air}})} \quad (4)$$

where C denotes % CO_2 volume; $\delta^{13}\text{C}_{\text{o.s.}}$ denotes the $\delta^{13}\text{C}$

value of the mixing of CO_2 from other sources; $\delta^{13}\text{C}$ sample denotes the $\delta^{13}\text{C}$ value of a sample; and $\delta^{13}\text{C}$ air and C air are the arithmetic averages of the air samples (-8.10‰, 0.034‰). A change of $\delta^{13}\text{C}_{\text{O.S.}}$ is due to the contribution(s) of a new source or sources and/or a change in the relative contribution from carbonate equilibria and organic materials. The graph of $\delta^{13}\text{C}_{\text{O.S.}}$ versus time for each site is shown in Figure 12. Data values are given in Table 10.

The $\delta^{13}\text{C}_{\text{O.S.}}$ showed little variation with time for site 1. Little variation indicates no new source made a significant contribution to $\delta^{13}\text{C}_{\text{O.S.}}$ and the percent of contribution by each part of other sources remained relatively constant with respect to each other.

The $\delta^{13}\text{C}_{\text{O.S.}}$ showed great variation with time for site 2. The variation indicates that CO_2 derived from carbonate equilibrium and CO_2 respired by plant roots and microorganisms contributed different percentages to the total $\delta^{13}\text{C}_{\text{O.S.}}$ during the sampling period. The $\delta^{13}\text{C}_{\text{O.S.}}$ of 12/2/82 through 3/17/83 are not considered reliable. These data show CO_2 concentrations very near the average CO_2 concentrations of the air samples. These low CO_2 concentrations cause equation 4 to produce unreliable values because the denominator of equation 4 is nearly equal to zero. Excluding the $\delta^{13}\text{C}_{\text{O.S.}}$ of 12/2/82 through 3/37/83, the $\delta^{13}\text{C}_{\text{O.S.}}$ data still indicate carbonate equilibrium

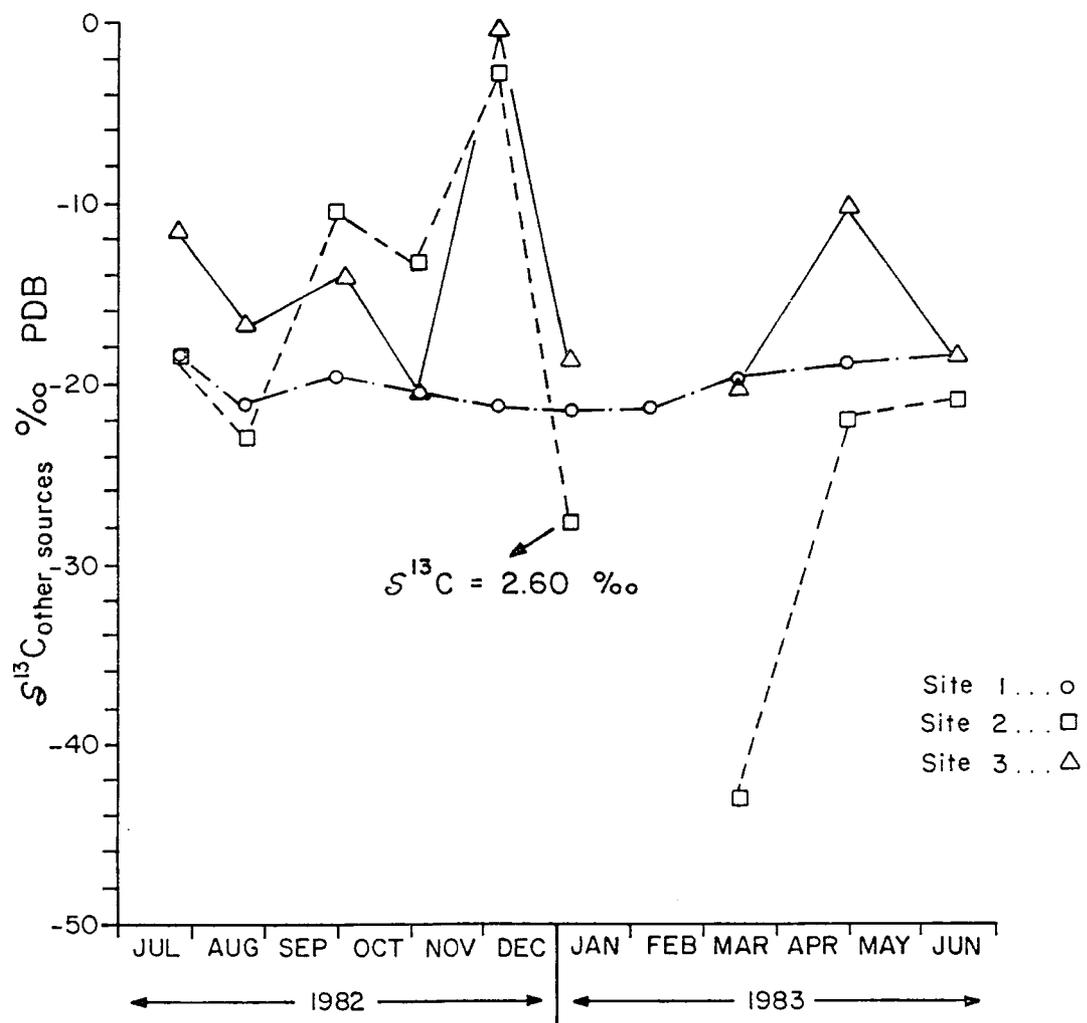


Figure 12. $\delta^{13}C_{\text{o.s.}}$ Values Versus Time.

Table 10. $\delta^{13}\text{C}_{\text{other sources}}$ Values for each Site.

| <u>Date of Sample</u> | $\delta^{13}\text{C}$ <u>Site 1</u> ‰ w.r.t. PDB | $\delta^{13}\text{C}$ <u>Site 2</u> ‰ w.r.t. PDB | $\delta^{13}\text{C}$ <u>Site 3</u> ‰ w.r.t. PDB |
|---------------------------|--|--|--|
| 1 7/27/82 | -18.36 | -18.25 | -11.62 |
| 2 8/24/82 | -21.23 | -22.92 | -16.58 |
| 3 9/30/82 | -19.62 | -10.68 | |
| 4 10/05/82 | | | -14.01 |
| 5 11/02/82 | -20.83 | -13.53 | -20.25 |
| 6 12/02/82 | -21.21 | - 2.81 | - 0.49 |
| 7 1/06/83 | -21.82 | -27.90 | -18.62 |
| 8 2/08/83 | -21.74 | Lost | Lost |
| 9 3/17/83 | -19.77 | -43.25 | -20.32 |
| 10 4/30/83 | -19.10 | -22.18 | -10.44 |
| 11 6/14/83 | -18.77 | -20.87 | -18.38 |

varied its contribution to total $\delta^{13}\text{C}_{\text{O.S.}}$ relative to the contribution of plant and microorganism activity.

The $\delta^{13}\text{C}_{\text{O.S.}}$ showed great variation with time for site 3. The great variation indicates the same conclusions for site 3 as was discussed for site 2. The $\delta^{13}\text{C}_{\text{O.S.}}$ value of 12/2/82 is not considered reliable because the CO_2 concentration of 12/2/82 was very near in value to the average CO_2 concentration of the air samples. The nearly equal values cause the demoninator of equation 4 to be nearly equal to zero.

CONCLUSIONS

1. Large variations of CO_2 concentration and $\delta^{13}\text{C}$ values of streambed CO_2 were observed from month to month over a year's time. However, there seemed to be an annual cycle that reflected changing moisture conditions, temperature conditions and relative contributions to streambed CO_2 by plant and microorganism activity, atmospheric CO_2 and CO_2 in isotopic equilibrium with HCO_3^- .

2. The large variations of the $\delta^{13}\text{C}$ values of streambed CO_2 from month to month at sites 2 and 3 were attributed to a large variation of the relative effect of CO_2 in isotopic equilibrium with carbonate derived HCO_3^- . Root-respired CO_2 recharged those sites slowly, which allowed the relative effect of CO_2 in isotopic equilibrium with HCO_3^- to greatly increase after a runoff event or significant precipitation. A runoff event or significant precipitation absorbed streambed CO_2 and thus reduced the amount of CO_2 in the streambed that had a $\delta^{13}\text{C}$ value around -25% .

3. The least variation of the $\delta^{13}\text{C}$ value of streambed CO_2 occurred at site 1. Site 1 recharged easily with root-respired CO_2 and therefore, site 1 had a consistent and large contribution of root-respired CO_2 . Also,

the consistent and large contribution of root-respired CO_2 kept the $\delta^{13}\text{C}$ of the streambed CO_2 near -20‰ .

4. There seemed to be an annual cycle for the $\delta^{13}\text{C}$ value of streambed CO_2 at site 1. It appears that root-respired CO_2 acted as a constant source of CO_2 with a $\delta^{13}\text{C}$ value around -25‰ and as a result, the $\delta^{13}\text{C}$ value of the streambed CO_2 fluctuated with the temperature-dependent $\delta^{13}\text{C}$ value of CO_2 in isotopic equilibrium with HCO_3^- (Figure 11).

5. The variation of CO_2 concentration of streambed atmosphere was due to absorption of CO_2 by streambed moisture, fluctuations of CO_2 production by plant and microorganism activity due to environmental conditions and physical factors that limited the amount of CO_2 recharge by root respiration.

6. Root-respired CO_2 had a $\delta^{13}\text{C}$ value around -25‰ w.r.t. PDB because the dominant vegetation of each site had the Calvin (C_3) carboxylation pathway.

7. Root-respired CO_2 was a major factor determining the $\delta^{13}\text{C}$ value and CO_2 concentration of the streambed atmosphere. However, local physical conditions (shape and size of streambed cross section, hydraulic conductivity of streambed materials, etc.) influenced the amount of root-respired CO_2 that reached the sampling point.

8. Atmospheric CO₂ contributed significantly to the streambed atmosphere following flood events; the relative importance of atmospheric CO₂ diminished as a function of the ease with which root-respired CO₂ recharged a site.

SUGGESTIONS FOR FURTHER WORK
IN SEMI-ARID CLIMATE

1. Research is needed concerning the seasonal variation of $\delta^{13}\text{C}$ and CO_2 concentration in a streambed that has plants (at the sampling site) with different carboxylation reactions than the organic matter washed down from uplands, that is, C_4 and CAM plants at the site of sampling and C_3 plants in the uplands. This would give an indication of the contribution that the decay of organic matter makes relative to the $\delta^{13}\text{C}$ value of the streambed atmosphere derived from root-respired CO_2 .

2. Streambed atmosphere should be sampled essentially as described in this report, except that each site should be sampled from two or more depths. This would make it possible to evaluate the effects of vertical gradients, if any.

3. A thermistor or other temperature measuring device should be installed near the bottom end of each sampling tube. Temperature data would remove some of the guess work from calculations involving temperature dependent reactions (i.e., fractionation of isotopes between HCO_3^- and gaseous CO_2).

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