

$^{13}\text{CO}_2$  AND  $^{14}\text{CO}_2$  MEASUREMENTS ON SOIL ATMOSPHERE

SAMPLED IN THE SUB-SURFACE UNSATURATED ZONE

IN THE WESTERN GREAT PLAINS OF THE US

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ABSTRACT. Soil gas samples were obtained from the unsaturated zone at eight sites in the Great Plains. Three of these sites were sampled extensively for gas composition and carbon isotopes. Sampling equipment consisted of a nest of gas probes vertically spaced by roughly 3m at most sites, generally approaching the water table. Water wells, 10cm in diameter, were screened in the topmost layer groundwater. Inverted cattle tanks were used to collect  $\text{CO}_2$  samples from the soil surface. The major gas components were analyzed with emphasis on  $\text{CO}_2$ ,  $\delta^{13}\text{C}$ , and  $^{14}\text{C}$  measurements. The same components were studied in groundwater samples. Higher than atmospheric  $\text{CO}_2$  concentrations were found in all soil samples. Root respiration and oxidation of organic matter were sources for the additional  $\text{CO}_2$ . When lignite was present in the unsaturated zone, gaseous oxygen reacted almost completely, and  $\text{CO}_2$  levels rose to 19%. Near the surface, annual cycles in total  $\text{CO}_2$ ,  $\delta^{13}\text{C}$ , and  $^{14}\text{C}$  were observed.  $^{14}\text{C}$  activities were close to present post-bomb levels at the surface and generally declined with depth. At some sites, oxidation of lignite caused decline of  $^{14}\text{C}$  levels to 1 or 2% of their surface value at 8m depth. Without lignite, the  $^{14}\text{C}$  activity remained above 50% at all depths. Concentrations of total carbon and its isotopes in ground water remained very stable throughout the study. This implies that geochemical processes in the aquifer vary on time scales longer than the seasonal effects observed in the near-surface unsaturated zone.

INTRODUCTION

The chemistry of  $\text{CO}_2$  in soil above the groundwater table has been the subject of several publications. These can be grouped according to the following criteria: 1) depth and number of sampling points in a vertical profile, 2) number

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of collections made to detect seasonal variation, 3) measurement of stable isotopes  $^{13}\text{C}/^{12}\text{C}$ , 4)  $^{14}\text{C}$  determination, 5) oxygen concentrations, and 6) the nature of soil gas transport through soil layers.

Seasonal  $\text{CO}_2$  variation was studied by Atkinson (1977), Enoch and Dasberg (1971), Miotke (1974), Rightmire (1978), and Reardon, Allison, and Fritz (1979). Galimov (1966), Kunkler (1969), Reardon, Allison, and Fritz (1979), Reardon, Mozeto, and Fritz (1980) and Kunkler (1969) are of particular interest here because they record measurements made with deep probes (5m and 290m, respectively) and theorize on diffusion as a transport model for soil gases.

This study is based on measurements that include all of the above criteria. Also, two selected examples show how stratigraphic differences in the depth profile lead to distinctly different behavior of all soil gas components. Field measurements were made in the Great Plains, at 2 sites in the Texas Panhandle and at 6 sites in southwestern North Dakota. Data are presented here for 3 of the North Dakota sites; 2 of these, near a lignite mine at Gascoyne, North Dakota, were extensively studied. Additional data appear in Thorstenson et al (1983). This paper includes site descriptions, sampling methods and analytical techniques, and inferences drawn from the data. The companion paper (Thorstenson et al, 1983) attempts to model the vapor-phase transport of  $^{12}\text{CO}_2$ ,  $^{13}\text{CO}_2$ , and  $^{14}\text{CO}_2$ .

#### COLLECTION TECHNIQUES

Soil gas pumped from the gas probes and dissolved gas extracted from groundwater samples were analyzed by gas chromatography at the U S Geological Survey laboratory in Reston. The analyzed gas species were  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and Ar.  $\text{CO}_2$  contained in soil gases and bicarbonate- and  $\text{CO}_2$  dissolved in the groundwater samples were extracted and analyzed for  $^{14}\text{C}$  activity at SMU  $^{14}\text{C}$  laboratory.  $^{13}\text{C}/^{12}\text{C}$  stable isotope ratios were measured for all samples.

During the sampling procedure for  $^{14}\text{C}$  in the field, the  $\text{CO}_2$  in soil gases was absorbed in a 5-molar solution of carbon-free KOH. In the laboratory, this solution was acidified whereby the  $\text{CO}_2$  was released, then isolated and converted into benzene for  $^{14}\text{C}$  analysis by scintillation counting. Fractionation was avoided during these chemical conversions by ensuring high reaction yields, ie, between 99 and 100%. During collection, similar yields were achieved with a suitable collector flask design (fig 1). The flow of sample gas was dispersed through a fritted glass plate. The fine stream of bubbles rose through 8cm of 5-molar KOH solution. Collected  $\text{CO}_2$  was released in the same vessel; no transfer of the

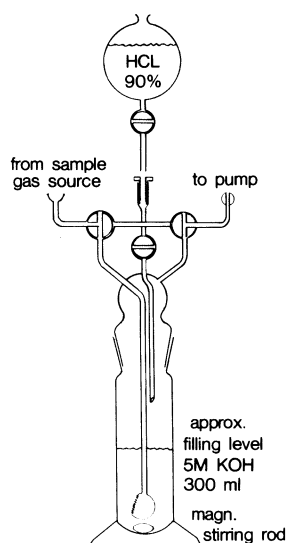


Fig 1. Soil gas collector

solution was necessary. The required amount of acid was introduced through a separate inlet; a built-in small stirring rod assured steady progress of this reaction. Laboratory tests demonstrated a collection efficiency of 99.8% and no detectable fractionation. The NBS oxalic acid standard was used. The collectors contained 300ml of 5-molar KOH solution which can theoretically absorb 15.8L of  $\text{CO}_2$  if only the efficient "hydroxide-to-carbonate" reaction is considered. We planned to collect between 7 and 8L of  $\text{CO}_2$  from each soil gas probe. We made rapid assessment of the  $\text{CO}_2$  concentration in the soil gases by measuring the weight gain of a small ascarite<sup>1</sup>-filled glass tube through which the dried gas was pumped at a flow-gauge-monitored rate of 0.5L per minute.

Figure 2 schematically depicts field equipment. The valves on top of the collector flask allow the bypass flow of the gas during initial cleanout of the well and during the ascarite test. Not shown on this drawing are heating tapes around the hoses and collectors to make the field work possible during the hard winter months in North Dakota.

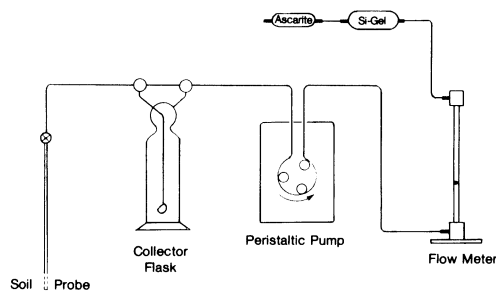


Fig 2. Field installation for soil gas collection

<sup>1</sup> Brand name for NaOH-coated asbestos; used for identification purposes only

Water was pumped from the water table wells with a Middelburg pump, consisting of a metal tube equipped with check valves at the top and bottom and a pulsating silicone rubber bladder inside the tube. The pumped water was fed into a 25L plastic carboy. KOH (in pellet form),  $\text{SrCl}_2$ , and  $\text{FeSO}_4$  were added to the filled carboy. The dissolved  $\text{CO}_2$  and  $\text{HCO}_3^-$  in the water reacts to  $\text{SrCO}_3$ , which flocculates readily in the presence of  $\text{FeSO}_4$  and settles rapidly in the neck of the inverted carboy. A faucet attached to the cap allowed draining of the sediment into 0.5L bottles. In the laboratory, the sediment was transferred into a hydrolysis system where it was acidified under vacuum. The released  $\text{CO}_2$  was processed as above. We also sampled the surface layer of the soil gas at both sites. An inverted cattle tank 2m in diameter was sealed tightly to the ground. Above-ground vegetation was removed from the site, but no attempt was made to remove the roots. Inside the tank, six shallow glass trays filled 1cm deep with 5-molar KOH solution served as  $\text{CO}_2$  collectors. Since no pumping was done, no atmospheric air was drawn through the soil into the tank, and  $\text{CO}_2$  reached the collector trays only through diffusion from the root zone.

#### DESCRIPTION

Most of the data presented in this paper were collected from sites in southwestern North Dakota and near the Gascoyne lignite mine in Bowman County. Two of these sites (unmined) were extensively studied and provide the basis for the models proposed by Thorstenson et al, (1983). The intensity of sampling at the other North Dakota sites has been variable.

The Gascoyne area of North Dakota has been under study by the Water Resources Division of the U S Geological Survey since the early 1970's. The early investigations are reported in Fisher and Thorstenson (1983).

Samples for  $^{14}\text{C}$  analysis were collected at some sites as early as 1977. The water table wells at Sites 1, 4, and 6 were drilled in the summer of 1980. The general stratigraphic relationship between the lignite, water table, ground surface, and sampling nests for the two intensive-study sites (4 and 6) are shown in figure 3. These sites are discussed in some detail below; shorter descriptions of the other sites follow.

**NORTH DAKOTA SITE 4 (T131N, R099 W, sec 33DCD)** This site is located on a local topographic high (ca 15m) accompanied by a local high in the water table, at 17.4m below ground surface. Recharge at this site must therefore be vertical. From the surface to a depth of ca 8m, the rocks consist of siltstone and claystone. A thin stringer of lignite may be present at ca 5m. Bulk x-ray diffraction (XRD) of core samples showed

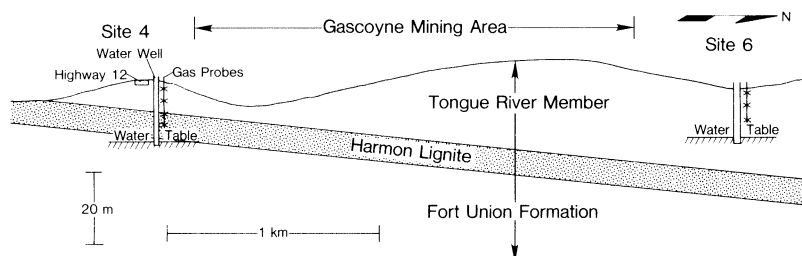


Fig 3. Cross section through Gascoyne mining area

abundant quartz, kaolinite, chlorite, illite, and smectite in the sites and clays. Dolomite ranges from 15 to 20%; calcite is absent. Abundant gypsum (15%) is present in the upper part of the lignite; sulfides are absent. Harmon lignite is present from 8 to 16m, underlain to the water table (17m) by mudstone and siltstone. The bottom two gas probes were screened in the lignite, which is sufficiently close to ground surface to be strongly oxidized. Except for the gypsum near its top, the only XRD-identifiable minerals in the lignite are small amounts of quartz, feldspar, and clays. The lignite is eroded away south of Site 4. The top two gas probes were screened above the Harmon lignite, and the two lower probes were screened in it.

NORTH DAKOTA SITE 6 (T131N, R099W, sec 21CCB) Site 6 is located between two wheat fields just north of the mine, in a very slight topographic low that will temporarily pond water after heavy rains. The water table is at ca 14.3m, ca 5m above the top of the Harmon lignite. Bulk x-ray diffraction on cores showed abundant quartz, kaolinite, chlorite, illite, and smectite. Both pyrite and gypsum are present at and below the water table. Calcite and dolomite (10%-20% each) are present throughout the unsaturated zone and just into the water table, but disappear below it. Groundwater was sampled at two wells that reach depths of 15.9m and 17.4m. Thus, water was sampled at depths of 1.2m and 2.7m, respectively, below the water table.

NORTH DAKOTA SITE 1 (T131N, R099W, sec 36 BCC) At Site 1, an unmined area east of the mine, a 1m stringer of lignite is present just above the water table at ca 13m. Also, a perched water table (the gas probes pumped water) was present at depths of 3m to 9m until at least 1977. Prior to this, the deep

samples at Site 1 resembled samples from similar depths at Site 4 in both  $\text{CO}_2$  and  $^{14}\text{CO}_2$  content. The perched water lens disappeared sometime between 1977 and 1980. From 1980 to the present, the data from all depths show extreme variability; it was initially believed that the grouting had cracked or that some other sampling problem existed. However, more recent analysis of the data shows that the partial pressure of  $^{14}\text{CO}_2$  is generally (not always) nearly constant, suggesting a lack of atmospheric influence. No plausible model for processes at this site is available.

#### DISCUSSION OF THE RESULTS

Our measurements are discussed and interpreted in Thorstenson et al (1983). Measurement of the  $\text{CO}_2$  concentration in each soil gas well provides the fundamental data. The gas analyses are presented in Thorstenson et al (1983, Table 2);  $\text{CO}_2$  data are plotted in figures 4 and 5. Figure 4 shows results for Site 6. All data points are plotted in a

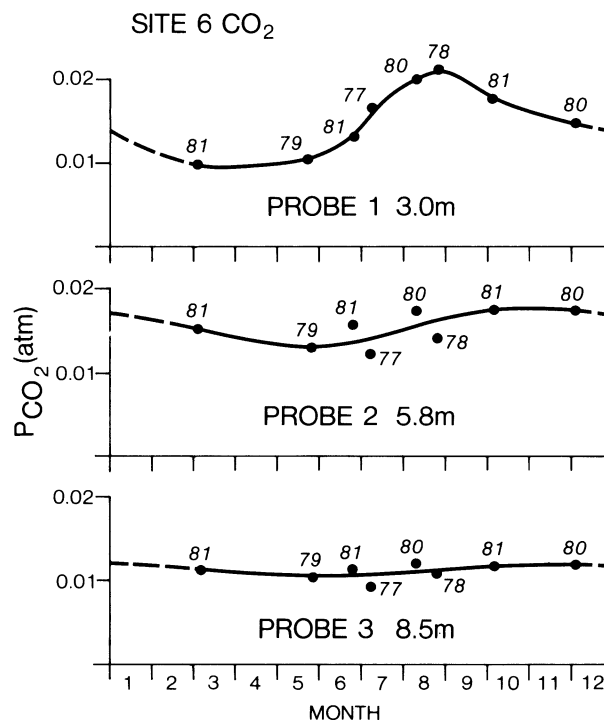


Fig 4. Gascoyne, North Dakota Site 6,  $\text{CO}_2$  concentrations

one-year cycle according to the month and day on which they were obtained, independent of the year of measurement. The observed  $\text{CO}_2$  concentrations at all depths vary between 1 and 2% of the total gas volume. The pronounced seasonal variation (100%) observed at the first probe (3m deep) correlates with the annual fluctuation of plant growth but is delayed by approximately two months (the peak of vegetation growth is in June, and the observed peak at Probe 1 is in August). A further delay of two months is observed at Probe 2 at 5.8m depth. Variation dropped to 30%. At 8.5m depth, 10%

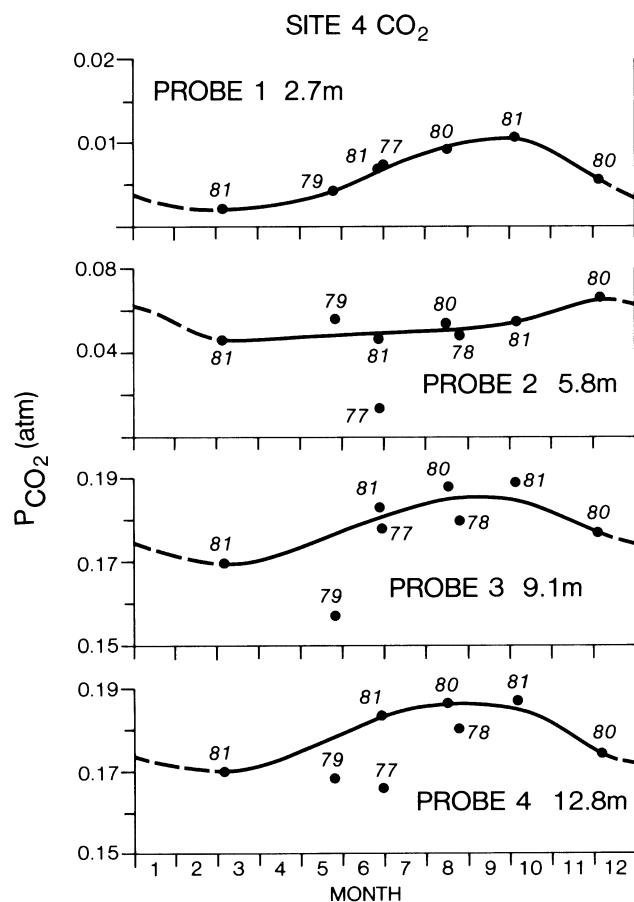


Fig 5. Gascoyne, North Dakota Site 4,  $\text{CO}_2$  concentrations: note changes of scale

variation is observed, but the peak is not well defined.

Entirely different observations were made at Site 4 (fig 5). Here the observed concentrations increase strongly with depth and reach 19% at 9.1m. This depth corresponds roughly to the top surface of the lignite which, through oxidation, acts as a strong source for  $\text{CO}_2$ . The seasonal variation is evident in the most shallow probe but is almost imperceptible at 5.8m. The deeper probes again show a distinct seasonal variation. Oxygen, although present at these depths in concentrations  $\leq 0.3\%$ , shows a definite minimum corresponding to the  $\text{CO}_2$  maximum (see Thorstenson et al, 1983, tables 1 and 2). This suggests a possible control of  $\text{CO}_2$  concentrations by  $\text{O}_2$  availability, although the nature of processes that show seasonal effects at this depth is unclear.

Oxidation of lignite or of more recent organic matter has been observed at all test sites in the Gascoyne area. This process shows great variability and is limited in extreme cases by the oxygen supply. Oxygen concentration at these sites varies inversely with  $\text{CO}_2$  concentration (fig 6). The linear regression of 84  $\text{O}_2$ - $\text{CO}_2$  data pairs gave 20.912% oxygen at 0%  $\text{CO}_2$  which compares well with 20.946% for atmospheric air.

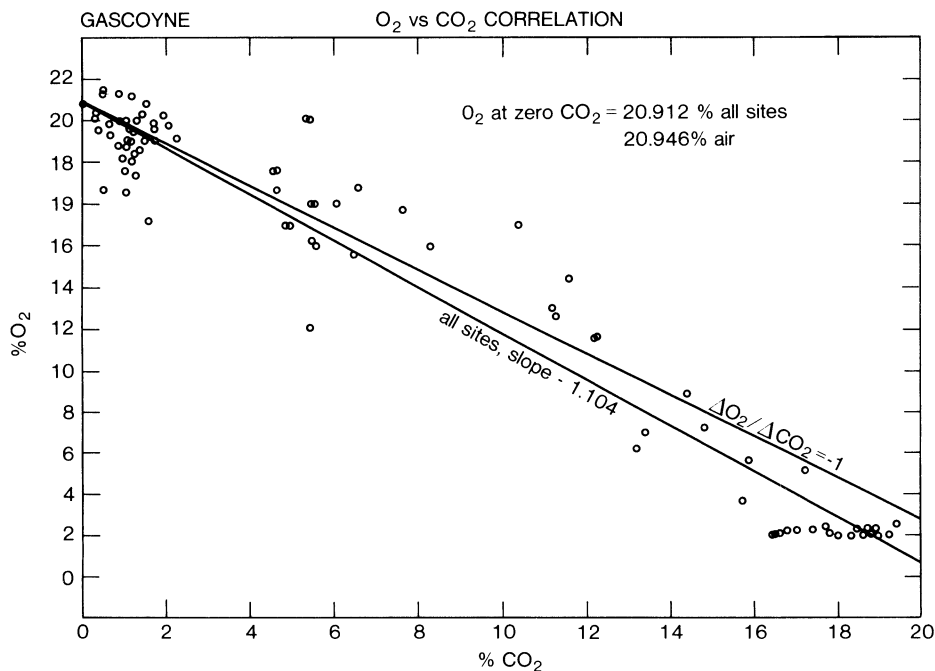


Fig 6. Gascoyne, North Dakota all sites

The correlation factor of the data is .974, and the slope of the regression line is -1.104 which indicates an oxygen deficiency assuming a 1:1 mole ratio of oxygen consumed to  $\text{CO}_2$  produced. This deficiency could result from more complex reactions between the lignite and oxygen, or from oxidation of inorganic soil components such as pyrite.

The  $^{14}\text{C}$  data are presented in table 1 and figures 7 and 8. In addition to the data from soil gas probes are also given the measurements of atmospheric air, surface soil gas, and water samples. In tabular form, the data show small variations in the range of a few per cent of modern  $^{14}\text{C}$  activity, which can not be seen in figures.

Seasonal variations occur at the soil surface level. A lower percentage of  $^{14}\text{C}$  during the winter might be due to oxidation of older organic matter in the absence of significant root respiration. Thus, surface  $^{14}\text{C}$  level cannot reach the post-bomb  $^{14}\text{C}$  level in the atmosphere, which decreased in 1980/81 to 136% modern. Our free atmospheric air measurements were made with air intake 1.8m above the soil surface, at the edge of a wheat field. Our measurements of 126 and 129% modern are slightly below the value of the well-mixed atmosphere in 1981.

The absolute concentration of the subsurface  $^{14}\text{C}$  data reflects the stratigraphic difference between the two sites. Remarkable at both sites is the constant level of  $^{14}\text{C}$  activity through the seasonal cycles which strongly affected the total  $\text{CO}_2$  concentration in the shallow probes. At Site 6 (fig 7),

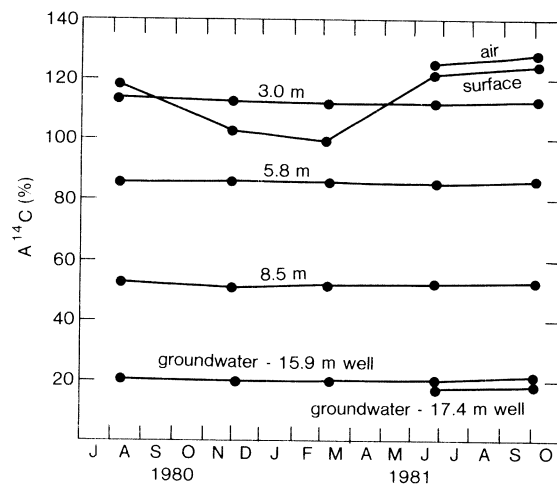


Fig 7. Gascoyne, North Dakota Site 6,  $^{14}\text{C}$  concentrations

TABLE 1. GASCOYNE, NORTH DAKOTA:  $^{14}\text{C}$  ACTIVITIES IN % MODERN  
*Modern is 95% activity of old NBS standard. Data are not corrected for  $\delta^{13}\text{C}$ .*

| Site/Well    | May 1979 | Aug 80 | Dec 80 | March 81     | June 81             | Oct 81 |
|--------------|----------|--------|--------|--------------|---------------------|--------|
| <b>No. 6</b> |          |        |        |              |                     |        |
| Air          |          |        |        |              | 125.99              | 129.05 |
| Surface      |          | 118.08 | 103.62 | 99.07        | 122.67              | 124.83 |
| 3.0m         | 114.13   | 113.26 | 112.79 | 112.18       | 112.52              | 112.33 |
| 5.8m         | 90.90    | 86.24  | 86.29  | 86.02        | 85.47               | 86.84  |
| 8.5m         | 51.16    | 53.07  | 51.28  | 52.45        | 52.30               | 52.96  |
| Water 15.9m  |          |        |        |              | 17.95, 16.64        | 18.84  |
| Water 17.4m  |          | 21.24  | 20.33  | 20.10        | 19.21, 21.31, 19.45 | 20.41  |
| <b>No. 4</b> |          |        |        |              |                     |        |
| Surface      |          |        |        | 115.17       | 123.64              | 116.77 |
| 2.7m         | 103.00   | 95.13  | 83.72  | 81.52        | 87.38               | 91.70  |
| 5.8m         | 10.00    | 10.92  | 8.79   | 8.82         | 9.29                | 10.71  |
| 9.1m         | 1.75     | 1.43   | 2.35   | 2.72         | 2.22                | 1.81   |
| 12.8m        | 2.09     | 2.08   | 2.32   | 2.82         |                     | 2.40   |
| Water 19.4m  |          | 6.73   | 6.51   | 6.26         | 5.89                | 5.01   |
| <b>No. 1</b> |          |        |        |              |                     |        |
| Surface      |          |        |        |              | 121.50              | 117.95 |
| 3.0m         |          |        |        | 3.21         | 2.99                | 5.46   |
| 5.2m         |          | 1.85   | 1.81   | 2.06         | 1.57                | 6.03   |
| 10.9m        |          | 20.35  | 9.04   | 3.65         | 3.12                | 1.45   |
| 13.7m        |          |        |        | 38.06, 37.89 |                     |        |
| Water 16.5m  |          |        |        |              |                     |        |

In June 1981, 2 or 3 subsequent water samples were pumped on Sites 1 and 6.

the 3m probe shows a  $^{14}\text{C}$  activity of 112% modern with a maximal seasonal variation of 2%; the deeper probes steadily decline in  $^{14}\text{C}$  activity from 5 to 8% per meter depth. The shallow water table was sampled at two different levels. A lower activity was observed closer to the surface; 1.5m lower in the groundwater reservoir, the activity was greater by 2% at 20% of modern. All seasonal changes are minimal and vary by  $< 2\%$ . The water was pumped at a rate of  $< 20\text{L}$  per hour. Even this slow rate caused a water level drawdown of 1m. Water levels recovered within 24 hours, apparently without changing the isotopic composition either systematically or significantly. Subsequent samplings from both wells at Site 6 and from a well at Site 1 were made in June 1982 (table 1). The  $1\sigma$  sample error of these tests is  $\pm .65\%$ . The  $^{14}\text{C}$  data are within  $1\sigma$  for all sample groups except for the second of the three where the  $2\sigma$  error ranges overlap. Thus, the results are valid for a substantial volume of water surrounding each well. An alternative assumption of rapid achievement of a local equilibrium is less probable since all data on carbon isotopes show values different from the corresponding soil gas data. This is consistent with the assumption of a zero-flux lower boundary for the unsaturated zone used in diffusion models (Thorstenson et al, 1983).

At Site 4 (fig 8), the 2.7m probe shows a relatively slight seasonal  $^{14}\text{C}$  trend reflecting the surface variation. The  $^{14}\text{C}$  activity averages 91% of modern, and the variation lies within  $\pm 12\%$ . All deeper probes and the water at the

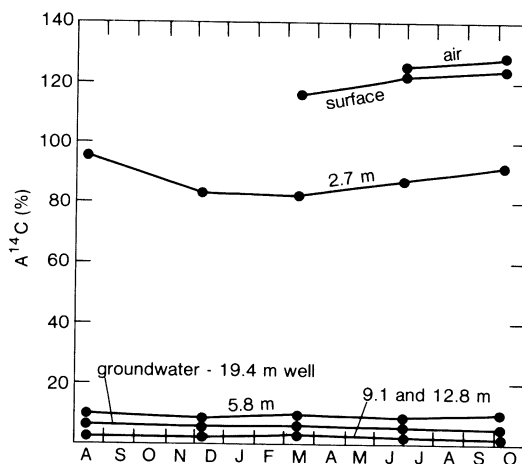


Fig 8. Gascoyne, North Dakota Site 4,  $^{14}\text{C}$  concentrations

phreatic surface show  $^{14}\text{C}$  activities of  $< 10\%$  and no seasonal variation. This is consistent with the position of these probes close to or within the lignite beds.

The accuracy of the tabulated  $^{14}\text{C}$  data is a function of counting time and sample size. Except for the small free-air samples, we worked with 3cc benzene samples for liquid scintillation counting. Counting time varied between 1400 min for samples in the 85 to 125% modern range to 3000 min for samples in the 1 to 2% modern range. The resulting  $1\sigma$  errors average  $\pm .6\%$  for modern samples and  $\pm .25\%$  for low-level samples. The free-air samples have  $1\sigma$  errors of 1.9% for the June 1981 and 1.4% for the October 1981 measurements.

$^{13}\text{C}$  data are shown in table 2. We have not attempted a detailed explanation of the data, which have been included to provide a complete data set. A point worth mentioning is that detectable methane (limit  $\sim .01\%$ ) was observed only once (Site 4, probes in the lignite - May 1979). Surface samples show a strong seasonal variation in  $\delta^{13}\text{C}$  which is similar to that observed by Rightmire and Hanshaw (1973). More negative values in spring and summer reflect the influx of biogenic  $\text{CO}_2$  during the growth season; a negative peak of  $-24.6\%$  is compatible with the Calvin cycle vegetation in the area (vander Merwe, 1982). As shown with the  $^{14}\text{C}$  data, oxidizing lignite causes a distinctly different distribution of carbon isotopes with increasing depth. At Site 6, where there is no lignite in the unsaturated zone, the  $\delta^{13}\text{C}$  values increase with depth and lie close to  $-17\%$  at 8.5m below surface. The June measurement for the 3m probe was lost and we are not certain whether the annual cycle is reflected at this depth. The two deeper probes and the groundwater samples show variations within  $2\%$ . These variations cannot be related with certainty to an annual cycle. The free-air measurements are lower than the typical  $-7.5\%$  value for the well mixed atmosphere. As indicated earlier, we suspect that the samples may have been collected too close to ground surface.

Data from Site 4 strongly reflect the presence of lignite. The two deepest gas probes (9.1m and 12.8m) give results in the  $-24\%$  range, which is close to an estimated value of  $-26\%$  for lignite. The series of successive water measurements performed in June 1981 yield very constant  $\delta^{13}\text{C}$  values for each well. This supports the conclusions derived from the  $^{14}\text{C}$  data. The data presented here are expressed in standard form as ratios of  $^{14}\text{C}/^{12}\text{C}$  (expressed as pmc) or  $^{13}\text{C}/^{12}\text{C}$  (expressed as  $\delta^{13}\text{C}$ ). Thorstenson et al (1983) demonstrate the importance of considering  $^{12}\text{CO}_2$ ,  $^{13}\text{CO}_2$ , and  $^{14}\text{CO}_2$  as separate entities, which behave according to their own partial pressures, reacting and diffusing independently of each other.

TABLE 2. GASCOYNE, NORTH DAKOTA:  $\delta^{13}\text{C}$  IN ‰ RELATIVE TO PDB STANDARD

| Site/Well    | May 1979 | Aug 80 | Dec 80 | March 81 | June 81          | Oct 81 |
|--------------|----------|--------|--------|----------|------------------|--------|
| <b>No. 6</b> |          |        |        |          |                  |        |
| Air          |          |        |        |          |                  |        |
| Surface      |          | -23.5  | -18.3  | -18.1    | -8.1             | -7.8   |
| 3.0m         | -24.2    | -22.6  | -22.6  | -22.5    | -24.6            | -24.0  |
| 5.8m         | -21.8    | -20.1  | -20.0  | -20.8    | -21.7            | -22.5  |
| 8.5m         | -18.5    |        | -18.2  | -17.1    | -17.8            | -20.9  |
| Water 15.9m  |          |        |        |          | -6.7, -6.8       | -17.9  |
| Water 17.4m  |          | -5.3   | -6.7   | -6.2     | -6.4, -6.4, -6.4 | -7.3   |
|              |          |        |        |          |                  | -6.4   |
| <b>No. 4</b> |          |        |        |          |                  |        |
| Surface      |          |        |        | -19.7    | -23.9            | -22.6  |
| 2.7m         | -27.9    | -20.3  | -20.8  | -21.5    | -20.8            | -21.3  |
| 5.8m         | -27.9    |        | -22.2  | -23.3    | -23.9            | -22.8  |
| 9.1m         | -29.4    | -24.0  | -24.0  | -24.0    | -23.7            | -23.2  |
| 12.8m        |          | -24.1  | -24.0  | -23.8    | -23.1            | -23.9  |
| Water 19.4m  |          | -17.1  | -16.7  | -16.8    | -16.6            |        |
| <b>No. 1</b> |          |        |        |          |                  |        |
| Surface      |          |        |        |          | -23.4            | -19.4  |
| 3.0m         |          |        |        | -18.1    |                  | -17.9  |
| 5.2m         |          |        |        |          |                  | -17.5  |
| 10.9m        |          | -17.0  | -18.9  | -17.5    | -17.6            | -17.5  |
| 13.7m        |          | -16.6  | -15.4  | -17.4    | -16.0            |        |
| Water 16.5m  |          |        |        |          | -11.0, -11.7     | -11.3  |

In June 1981, 2 or 3 subsequent water samples were pumped on Sites 1 and 6.

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