US GEOLOGICAL SURVEY, WATER RESOURCES DIVISION, RADIOCARBON MEASUREMENTS I

F J PEARSON, JR and MARTHA BODDEN

US Geological Survey, Isotope Hydrology Laboratory National Center, Reston, Virginia 22092

The Water Resources Division of the US Geological Survey has operated a low-level tritium laboratory since the late 1950's. In 1970, ¹⁴C-measuring facilities were added to that laboratory to provide analyses of ground water and other carbonates, primarily for research and field projects of the Division.

¹⁴C analyses are made by liquid scintillation counting of benzene synthesized from sample carbonate by the reactions:

$$CO_3 = \xrightarrow{H^+} CO_2 \xrightarrow{Li} Li_2C_2 \xrightarrow{H_2O} C_2H_2 \xrightarrow{catalyst} C_6H_6$$

The C_2H_2 is produced by the method of Guntz (1896, 1898), more recently described by Barker (1953) and Hubbs and Bien (1967). To make Li_2C_2 , we use about twice the stoichiometric amount of Li and add CO_2 at pressures of < 15cm Hg to keep the temperature of the reaction relatively low (dull red heat). After CO_2 is added, the mixture is held at the same temperature while open to a vacuum for ca 1 hr. With samples of normal size, ca 3ml C_6H_6 , C_2H_2 yields are consistently above 90%. The C_2H_2 is purified and dried by passing it over NaOH pellets and glass beads coated with 85% $H_3\text{PO}_4$. It is then catalytically polymerized to C_6H_6 . The catalyst used is a commercial petroleum cracking catalyst, requiring only drying before use. The polymerization yields generally exceed 85% and the C_6H_6 is free of impurities that might cause quenching (Fraser *et al*, 1974). The method has been described in detail by Noakes, Kim, and Stipp (1966) and, more recently, by Fontes (1971).

The C₆H₆ is counted on a Picker Nuclear Liquemat 220* liquid scintillation counter with photomultiplier tubes selected for optimum ¹⁴C sensitivity. The absence of quenching is vertified for each sample by the external standard channels ratio method. Samples through WRD-156 were counted in low-potassium glass vials, which held 4ml, 3ml sample benzene and 1ml toluene + scintillator. This arrangement had a background of ca 4.0cpm and a net modern count, 0.95 x NBS oxalic acid, 3ml C₆H₆, of ca 21cpm. Samples following WRD-156 were counted in a 4ml capacity Teflon vial, identical to design "A" of Calf and Polach (1974). This vial, with 3ml sample benzene and 1ml toluene + scintillator, had a background count of ca 4.0cpm and a net modern count of 24cpm.

^{*} Products are named for identification only and do not imply endorsement by US Geological Survey.

Results are based on a modern of 0.95 x NBS oxalic acid, and 14 C half-life of 5568 years. Errors are based on counting statistics and are $\pm 1_{\sigma}$, except for those samples whose counts approach either modern or background for which 2_{σ} limits are reported. Ground-water analyses are described at the beginning of that section.

Unless otherwise identified, collectors and submitters are USGS, WRD, personnel from the office specified.

ACKNOWLEDGMENTS

We are grateful to Meyer Rubin and Sam Valastro for providing check samples and other assistance in establishing this laboratory, and to T A Wyerman for his invaluable assistance in optimizing the counting procedure. ¹³C analyses were made by C T Rightmire.

SAMPLE DESCRIPTIONS

I. CHECK SAMPLES

| Sample no. | Age (yr) | Other lab no. | Age (yr) | Reference |
|--------------------------------------|--|-------------------------------------|---|--|
| WRD-27 WRD-28 WRD-29 WRD-63 | 2330 ± 100 8950 ± 150 $31,000 \pm 2350$ 3960 ± 100 | W-2051 W-568 W-2043 Tx-966 | 2200 ± 250 9000 ± 400 $28,000 \pm 1000$ 4050 ± 80 | M Rubin, 1971, pers commun R, 1960, v 2, p 165 R, 1970, v 12, p 319 R, 1972, v 14, p 467 |

See also WRD-1, Washington series, and WRD-197-200, -203, -205, Southern Great Basin, Nevada and California series.

II. GROUND-WATER SAMPLES

Ground-water carbonate for $^{14}\mathrm{C}$ analysis is collected in the field by direct precipitation of $\mathrm{SrCO_3}$ from 100L of sample. The procedure is similar to that used by the IAEA (B Payne, 1970, written commun). In the laboratory, the wet precipitate is poured into a flask and $\mathrm{CO_2}$ evolved with acid. Samples containing a large amount of sulfide precipitated with the carbonate are oxidized with $\mathrm{H_2O_2}$ to prevent $\mathrm{H_2S}$ formation when acid is added.

Separate samples for determination of δ¹³C of dissolved carbonate are obtained by adding an NH₄OH•SrCl₂ solution to 1L of sample in the field (Gleason, Friedman, & Hanshaw, 1969). δ¹³C values, reported below relative to PDB, are for these samples.

Tritium analyses are made on most samples collected for ¹⁴C. Results are used to determine whether any admixture of recent water from faulty well construction, sampling technique, or natural water flow paths is likely to have effected the ¹⁴C content of the water.

For ¹⁴C samples, field measurements of alkalinity and pH are made, and laboratory analyses of 10 or more common dissolved constituents are made. From these data, distribution of dissolved species and degree

of saturation of water related to several minerals are calculated using the computer program WATEQ (Truesdell and Jones, 1973). Values of total dissolved carbonate content,

$$(C_{total} = H_2CO_3 + HCO_3 + CO_3 + CaHCO_3 + MgHCO_3 + etc)$$
, reported below are from this program.

It is well known that the measured ¹⁴C content of a ground-water carbonate depends on more than just the age of the water. Various schemes have been proposed to adjust measured ¹⁴C values to calculate ages, eg, papers from IAEA (1967, 1970, 1974). Our experience has been that no one scheme is universally satisfactory. Instead, we examine each series, using geochemical, stable isotope, conventional hydrologic, and any other available data to discern extent of processes, other than radio-active decay, which affect measured ¹⁴C content. In some series, no ages are given because no unambiguous geochemical interpretation of the system could be made or because the wells sampled produced mixtures of waters from within the hydrologic system. Where ages are reported, comments describe ¹⁴C adjustment procedure and geochemical information used.

A. United States

South-Central Washington series

Samples were part of study of characteristics of regional ground-water flow in an 11,600sq km area including the Pasco Basin and surrounding areas, S-central Washington. All wells draw water from basalt of Columbia River Group or from interbed zones in basalt sequence. The well numbers give Township/Range-Section-sequential letter and number. Samples coll and subm by A M LaSala, Jr and G C Doty, Richland, Washington. Comment: ¹⁴C data are accordant with regional flow pattern suggested by hydrologic information (LaSala, Doty & Pearson, 1973). General range of values similar to those reported from Pullman-Moscow Basin, Washington (Crosby & Chatters, 1965). Errors reported to submitter incorrectly and pub (LaSala, Doty & Pearson, 1973).

Fresno and Kings Co, San Joaquin Valley, California series

Extensive use of ground water for irrigation in the San Joaquin Valley has led to many studies of the ground-water hydrology of the region. A tritium study (Haskell, Leventhal, & Bianchi, 1966), based on 1963 sampling of wells along 2 traverses on W side, suggested flow rates much greater than those estimated by conventional hydrologic methods (Poland, 1973). Consequently, in 1966-1968, and 1970, the USGS sampled and tested tritium content of well waters along the same 2 traverses to resolve the contradiction. The 1970 sampling was expanded to include wells 8 to 13km SE, analyzed for both T and ¹⁴C (results listed below). Well numbers give Township/Range-Section-sequential letter and and number. Coll Aug 1970 by Raoul LeBlanc; subm by J F Poland, Sacramento, California.

TABLE 1
South-Central Washington series

| | | | I and cauto | 147.11 11 | Total dissolved | | | |
|------------|----------------------|-----------|-------------|-------------------|-------------------------|-----------|--|--|
| Sample no. | Well no. | Date coll | alt (m) | well depth (m) | $ m carbonate \ (mM/L)$ | %₁³C % | $	ext{Tritium} \ 	ext{TU} \pm 	ext{I}_{m{\sigma}}$ | 14 C $\%$ modern \pm 1_{σ} |
| WRD-100 | 5/28-5D1 | 10/18/71 | | | | - H | | 10.4 . 0.9 |
| WRD-102 | 5/28-6R2 | 9/94/71 | | | | 1.01 | \ | 10.4 ± 0.3 |
| WRD. 55 | 6/98.11101 | 10/91/70 | 110 | 0 | | -10.2 | 4.2 ± 0.5 | 5.7 ± 0.4 |
| WDD E7 | 6 /09 17 11 | 10/21/10 | 311 | 272 | 3.44 | -16.0 | <1.7 | 3.4 ± 0.4 |
| 101 CL G/W | 0/23-13]1 | 10/22/10 | 320 | 193 | 3.39 | -15.8 | <1.2 | 3.8 ± 0.4 |
| W ND-101 | 0/29-8M1 | 10/19/71 | | | | | 3.9 ± 0.4 | 82.9 ± 0.7 |
| WKD-103 | 7/32-36Q1 | 9/20/71 | | | | -14.8 | 11+05 | 84+04 |
| W.R.D- 60 | 8/24-201 | 9/28/70 | 196 | 266 | 4 98 | 19.1 | 200 + 007 | F. O - O J |
| WRD- 58 | 8/99-99A1 | 11/17/70 | 989 | 2 6 | 2.50 | 1.0.1 | 13.0 - 7.1 | 20.0 ± 0.00 |
| WDD 40 | 0 / 91 94111 | 0//11/11 | 707 | 244 | 3.15 | | 8.1 ± 0.5 | 10.5 ± 1.3 |
| 04 - CAW | 0/31-34H1 | 9/9//0 | 139 | 117 | 2.34 | -7.4 | <0.8 | 1.8 ± 0.6 |
| WKD- 53 | 9/23-23G1 | 10/7/70 | 243 | 350 | 4.10 | -13.9 | 53.8 ± 2.9 | $67.8 \pm 0.5*$ |
| WKD- 52 | 9/26-27K1 | 10/12/70 | 449 | 204 | 2.61 | -11.5 | \ 7. | 146 + 04 |
| WKD- 41 | 9/30-18H1 | 8/28/70 | 125 | 315 | 4.99 | 7.7 | | 1:0 0:1 |
| WRD- 54 | 10/22-25F1 | 10/6/70 | 262 | 480 | 07.6 | 7.7 | 71.0 | 0.0/ |
| WRD. KG | 11/0/11/11 | 04/61/11 | 1 1 | 707 | 6/17 | 0.01 | \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\ | 18.9 ± 0.6 |
| 00 -CIVI 1 | I NI + I - I + I I I | 01/01/11 | 2/2 | 124 | 1.92 | -12.4 | 0.8 ± 0.3 | 38.7 ± 0.7 |

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|--|------------|-----------|---|------------|-------------------|-----------------|------------------|----------------------|
| | | | | | Total dissolved | | | |
| | | | Land surface | Well depth | carbonate | δ^{13} C | Tritium | $^{14}\mathrm{C}~\%$ |
| Sample no. | Well no. | Date coll | alt (m) | | $(\mathrm{mM/L})$ | % | $TU \pm 1\sigma$ | modern $\pm 1\sigma$ |
| 1470.7 | - 1 | 11/10/70 | 869 | 305 | 2.85 | | <1.9 | 1.7 ± 0.7 |
| WKD- 31 | 11/20-34KI | 19/17/01 | 913 | 187 | 3.60 | -10.9 | 100 ± 5 | |
| WKD- 01 | | 14/14/10 | 017 | 101 | 9.16 | 19.0 | 17 + 0.3 | |
| WRD- 42 | | 9/21//0 | 0/0 | Spring | 2.10 | 117:5 | 00/ | |
| WRD- 43 | | 9/11/70 | 323 | 366 | 2.80 | 1.01- | 0.0 | |
| WRD. 44 | | 9/15/70 | 131 | 230 | 2.93 | -15.7 | 2.8 ± 0.4 | |
| WRD. 45 | | 8/27/70 | 282 | 237 | 3.06 | -13.1 | <0.0> | |
| of Carry | | 8/97/70 | 955 | 338 | 3.07 | -11.8 | <0.7 | |
| WND- TO | | 0/1/0/0 | 9 6 6 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 | 888 | 5.99 | -12.2 | <0.7 | |
| WKD- 40a | | 01/0/6 | 1 6 | 164 160 | 9 50 | 14.8 | 60 + 66 | |
| WRD- I | | 2/1/69 | C/.I | 104-169 | 5.03 | C.T.I. | 11.1 | |
| WRD. 9 | | 5/10/69 | 175 | 111-151 | 3.17 | -14.2 | | |
| WPD, 59 | | 11/10/70 | 290 | 341 | 3.00 | -16.8 | <1.1 | |
| W C. J. V. | | 10/8/71 | <u>.</u> | | | -13.8 | <2.3 | 8.0 ± 0.5 |
| COI-CIAN | | 0/0/70 | 950 | 8. 7. | 5.66 | -11.6 | <0.8 | |
| WKD- 48 | | 9/44/70 | 433 | 000 | i | 10.2 | 80> | |
| WRD-104 | | 10/6/71 | | | 6 | 5.1. | | |
| WRD- 50 | | 10/27/70 | 334 | 276 | 3.02 | -11.3 | <1.8 | |
| WP 171 | | 7/11/79 | | (shallow) | | | \ \ -1.1 | • |
| WKD-1/1 | | 7/11/1 | | (| | | ~ - ~ | |
| WRD-172 | | 9/13/72 | | (deeb) | | | C:1/ | |
| | | | | | | | | |

*Originally and incorrectly reported to AML as 63.2 \pm 0.5% modern. **Also analyzed as Tx-894; % modern = 13.4 \pm 0.4 (S Valastro, 1970, written commun).

| Sample no. | Well no. | Tritium $TU \pm 1\sigma$ | δ¹³C ‰ | 14 C $\%$ modern $\pm 1_{\sigma}$ |
|--|--|--|----------------------------------|--|
| WRD-87 WRD-88 WRD-97 WRD-98 WRD-99 | 17S/20E-31F1 18S/17E-13N2 18S/19E-31G2 18S/17E-31Q1 19S/18E-10N1 | 1.0 ± 0.4 < 0.8 < 0.7 $ < 0.7$ | -22.9 - 4.8 -28.2 - 8.2 | 14.8 ± 0.9 3.2 ± 0.4 1.0 ± 0.2 1.2 ± 0.4 2.6 ± 0.1 |

Comment (FJP): wells normally produce water from several horizons and adjusted ages of resulting mixture cannot be made. Generally low T and ¹⁴C contents suggest rapid flow rate estimated from previous T work is incorrect (Poland, 1973).

Southern Great Basin, Nevada and California series

Samples are from 4 groups of moderately hot (25° to 39°C) springs discharging, at valley level, from a regional carbonate rock aquifer system from an area > 11,600km. Samples were coll May and June 1973 to evaluate utility of environmental isotopes for definition of a hydrogeologically complex ground-water flow system. The hydrogeology and hydrochemistry of the region were described by Winograd (1971); δ^{13} C and 14 C analyses are in progress. Tritium content of all sources was <1 TU. Coll and subm by I J Winograd, Reston, Virginia.

Comment (IJW): agreement in ¹⁴C content between spring pairs in Pahranagat Valley, Death Valley, and Muddy R areas was expected due to mean identity of water chemistry. The wide divergence (1.8 to 11.6% modern) of the 3 springs at Ash Meadows was a surprise, in view of similar water chemistry and ¹³C content. Differences may reflect mixing of water from 2 sources or extreme hydrodynamic dispersion in a heterogeneous fractured aquifer.

Two orifices exist at Fairbanks Spring. WRD-197 was of SW orifice, as was DE-670293 (R, 1973, v 15, p 470); DE-670294 was of NE orifice. Grove *et al* (1969) do not describe which orifice they sampled.

Arkansas Hot Springs series

Following are from hot and cold wells and springs in vicinity of Hot Springs, Arkansas, which are part of the hydrologic system including the Arkansas Hot Springs. Sampling was part of geochemical and hydrologic study for management of Hot Springs National Park. Pearson, Bedinger, and Jones (1972) described preliminary results (WRD-146-156), and a final report on the work, including all basic data, is made by Bedinger *et al* (1973). Coll and subm Feb 1972 (WRD-146-156) and Sept 1972 (WRD-164-170) by M S Bedinger, Little Rock, Arkansas, and F J P. *Comment*: carbonate geochemistry of this system is as straightforward as any we have encountered. Adjustment of measured ¹⁴C values by

Southern Great Basin, Nevada and California, series Table 2

| | | COULTICITY | Journal Oreat Dustry, Merida and Carrest | | , , , , , , , , , , , , , , , , , , , | | | |
|-------------------------|------------|-------------------|--|----------------------|---------------------------------------|----------------------|---------------------|----------------------------------|
| | | | | Total | | | Other 14C samples | samples |
| | | | | carbonate 813C | 3^{13} C | 14C % | Sample | % modern |
| Area | Sample no. | . Name | Location | $(\mathrm{mM/L})$ %0 | 00% | $modern \pm 1\sigma$ | no. | $+ l\sigma$ |
| Pahranagat | WRD-196 | Hiko Spring | SE1/4,sec14,T4S,R60E | 4.92 | -7.0 | 6.5 ± 0.3 | | |
| Valley, Nevada | WRD-203 | Ash Spring | NW1/4, sec6, T6S, R61E | | -6.7 | | 118 | $6.3 \pm 1.2*$ |
| Spring Mts, | WRD-200 | 200 Indian Spring | NW1/4, sec16, T16S, R56E | 4.27 | -7.8 | 8.8 ± 0.4 | W-1841 DE-670347 | $11.0**$ $18.6 \pm 1.7 \ddagger$ |
| Nevada Ash Meadows, | WRD-197 | WRD-197 Fairbanks | $\mathrm{NE}{}_{/\!4},\!9,\mathrm{T}17\mathrm{S},\!\mathrm{R}50\mathrm{E}$ | 5.44 | -4.8 | 1.8 ± 0.2 I | W-1858 DE-670293 | $6.9**$ $5.1 \pm 0.8 \ddagger$ |
| Nevada | | opring | | | | П | DE-670294 | $2.4 \pm 0.8 $ |
| | WRD-198 | Crystal Pool | NE1/4, sec3, $T18S$, $R50E$ | 5.34 | -5.5 | | DE-670298 | $10.8\pm1.3\dagger$ |
| | WRD-199 | | NE1/4, sec19, T18S, R51E | 5.60 | -5.4 | 3.9 ± 0.3 I | DE-670303 | $3.0 \pm 1.3 \ddagger$ |
| Death Valley, | WRD-201 | | NE1/4, sec36, T28N, R1E | 6.20 | -5.5 | 4.8 ± 0.3 | | |
| California | WRD-204 | Texas Spring | $NE_{1/4}$, sec 23, T27N, R1E | 5.75 | -5.0 | | , | • |
| Muddy R | | | NE1/4, sec16, T14S, R65E | 5.00 | 6.7 | 8.7 ± 0.3 | 119 | 8.8 + 1.3* |
| (near Moapa), Nevada | | Sirrig | | | | | | |
| | WRD-202 | | $\mathrm{NE}_{1/4}$,sec21,T14S,R65E | 4.82 | 8.9— | 9.0 ± 0.4 | | |
| | | Warm Spring | | | | | | |

*Mifflin (1968). Sample no. is Spring no. in Appendix Table 5. Lab source of ¹⁴C analyses not given. **Grove et al 1969, Table 1; errors not reported. † R, 1973, v 15, p 470.

TABLE 3
Arkansas Hot Springs series

| | | in Kansas II | rikansas 110t opinigs senes | ciles | | | | |
|-------------------------|------------------------|--|-----------------------------|-------------------------|------------|-----------------------------|---------------------------------|--------------|
| | | | | Calcium | | | | |
| | Local* well (W-) or | | Total dissolved | + magnesium + | | | | Adinsted |
| Sample no. | spring (S-) no. | Location | carbonate (mM/L) | $ m strontium \ (mM/L)$ | 813C %0 | Tritium $TU \pm 1_{\sigma}$ | $^{14}C\%$ modern $\pm 1\sigma$ | age Vr BP |
| | 1 | Cold Wells and Springs | | | | | | |
| WKD-168 | W-19 | NW14, SW14, NE14, Sec23, T2S, R19W | | 0.01 | -22.5 | 41.8 ± 2.0 | 101.7 ± 1.6 | 0 |
| WKD-166 | W-20 | SE1/4,NW1/4,NW1/4,Sec26,T2S,R19W | | 0.01 | -23.7 | 85.3 ± 1.6 | 98.9 ± 1.5 | 0 |
| WRD-170 | W-16 | NE1/4,NE1/4,SW1/4,Sec14,T2S,R19W | | 0.21 | -23.6 | 27.7 ± 1.6 | 111.8 ± 1.3 | 0 |
| WRD-165 | S-11 | NW1/4,SW1/4,NE1/4,Sec32,T2S,R18W | | 1.06 | -13.8 | 1.5 ± 0.8 | 39.5 ± 0.8 | 3730 |
| WRD-164 | W-21 | NW1/4,SW1/4,SW1/4,Sec27,T2S,R19W | | 1.26 | -14.4 | 1.3 ± 0.4 | 35.5 ± 0.5 | 4130 |
| WRD-167 | S-7 | NE1/4,NW1/4,SE1/4,Sec31,T2S,R18W | | 1.15 | -15.8 | 0.7 ± 0.6 | 37.3 ± 0.4 | 4840 |
| WRD-150 | W-26 | $NE_{1/4},NW_{1/4},SE_{1/4},Sec32,T2S,R19W$ | | 1.34 | -14.3 | 2.8 ± 0.5 | 31.2 ± 0.5 | 0209 |
| WRD-156 | W-25 | $\mathrm{NE}l_4,\mathrm{NW}l_4\mathrm{SE}l_4,\mathrm{Sec}32,\mathrm{T}25,\mathrm{R}19\mathrm{W}$ | 3.94 | 1.72 | -13.8 | 1.2 ± 0.8 | 23.7 ± 0.3 | 7180 |
| WRD-155 | S-5 | $SE_{1/4},NW_{1/4},SE_{1/4},Sec22,T2S,R19W$ | 4.06 | 1.79 | -14.9 | 3.1 ± 0.6 | 22.2 ± 0.3 | 7620 |
| WRD-169 | W-12 | SE1/4, NE1/4, NW1/4, Sec13, T2S, R19W | | 1.45 | -15.5 | 0.9 ± 0.5 | 21.2 ± 0.4 | 8940 |
| WRD-149 | | SE1/4,NW1/4,NE1/4,Sec32,T2S,R19W Hot Springs | 4.15 | 1.80 | -13.3 | 1.5 ± 0.4 | 19.4 ± 0.3 | 8850 |
| WRD-152 | |) | 2.70 | 1.29 | -14.1 | $\frac{30}{50} + 0.5$ | 369+05 | |
| WRD-153 | | | 2.74 | 1.29 | -14.2 | 0.7 ± 0.8 | 35.1 + 0.6 | |
| WRD-146 | | All within: | 3.18 | 1.32 | -14.8 | 3.1 ± 0.6 | 35.6 ± 0.7 | |
| WRD-151 | | $^{ angle}$ NW1/4,SE1/4,Sec33,T2S,R19W | 2.97 | 1.31 | -14.3 | 0.7 ± 0.4 | 38.7 ± 0.7 | |
| WRD-154 | Collecting | | 2.97 | 1.32 | -14.4 | 1.0 ± 0.7 | 30.4 ± 0.6 | |
| | reservoir | | | | | | | |
| WRD-148 | No. 49 | | 3.07 | 1.30 | -16.1 | 0.9 ± 0.4 | 86.8 ± 0.9 | |
| | Average Hot Springs | ot Springs | | | -14.6 | | 35.6 | 4430 |
| * Bedinger et al. 1973. | al. 1973. | | | | | | | |

* Bedinger et al, 1973.

almost any conventional method using δ^{13} C or water chemistry (Ingerson and Pearson, 1964; Pearson and Hanshaw, 1970; Tamers, 1967; Wendt *et al*, 1967) gives essentially the same results. In preliminary report (Pearson, Bedinger, and Jones, 1972), all ages adjusted using:

$$^{_{14}}C_{adj}\,=\,^{_{14}}C_{meas}\,\,x\,\,\frac{-23}{\delta^{_{13}}C_{meas}}\,\,.$$

Here and in the final report (Bedinger et al, 1973), cold wells and springs were adjusted using:

$$^{14}\mathrm{C_{adj}} \, = \, ^{14}\mathrm{C_{meas}} \, \div \, 1 \, - \left(\!rac{\mathrm{C_{alkaline\;earth}}}{\mathrm{C_{total}}}\!
ight) \, .$$

Variable CO_2 outgassing among Hot Springs gives unreliable C_{total} values, so adjustment was made only for average of hot springs using:

$$^{14}C_{adj} = {}^{14}C_{meas} \ x \ \frac{-24}{\delta^{13}C_{sample}} \ .$$

Adjusted ages and other geochemical data provide tests of assumptions made in digital models of water and heat flow in the Hot Springs system. Results show that the age of Hot Springs water is due largely to residence time in cold-water portion of the flow system rather than to an extended period in the zone of heating.

Edwards Aquifer, Texas, series

Following are from wells in the Edwards and assoc limestones aquifer in the San Antonio area, Texas (Garza, 1966; Petitt and George, 1956). The part of the Edwards studied is on the down-thrown, coastal side of the Balcones fault zone, near which, the Edwards supplies huge amounts of oxidizing Ca-HCO₃ water for irrigation and municipal supply, including that of the City of San Antonio. It discharges in springs used for recreation NE of San Antonio. Down dip (toward coast) there is a zone of rapid transition to water of a Ca-SO₄ to Na-Cl type, reducing enough to contain H₂S. These results are 1st of a series coll as part of comprehensive study of hydrology of the Edwards. Well numbers are those used by Texas Water Development Board (Rettman, 1969). Samples WRD-71-86 coll July, 1970 and WRD-110-129 coll July, 1971 by F J P, M B, and Paul Rettman. Subm by F J P. Comment: initial results agree with previous hydrologic concept of rapid water movement through oxidized part and relatively much slower movement in reducing part of aquifer. Detailed interpretation must await further geochemical work.

Southeast Florida series

Following results are from study of the use of deep saline aquifers for injection of liquid wastes and constitute a vertical section of hydrogeologic framework in SE Florida, near Miami. Study is to determine sources and relative ages of native fluids, degree of vertical hydraulic

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interconnection or separation, and whether saline water is residual from past sea-water intrusions or from recent influx of "moden" sea-water from adjacent Straits of Florida as part of an active ground-water circulation system.

Preston sample coll April 1972 by F W Meyer; Kendale samples coll July 1971 through March 1972 during drilling by D J McKenzie. Subm by M I Kaufman.

| Sample no. | Name | Lat, Long, aquifer, & depth | 14 C $\%$ modern $\pm 1\sigma$ |
|------------|---------------|------------------------------|--|
| WRD-159 | Preston Well | 25° 49′ 46″ N, 80° 17′ 15″ W | 97.5 ± 0.5 |
| | Field, S1476 | Biscayne Aquifer | |
| | | Depth 32.6m | |
| | Kendale Lakes | 25° 41′ 24″ N, 80° 24′ 53″ W | |
| | Test Well | Floridan Aquifer | |
| WRD-162 | | Depth 393.2m | 5.6 ± 0.7 |
| WRD-157 | | Depth 586.4m | 4.3 ± 0.8 |

Comment (MIK): results indicate effective vertical hydraulic separation between Biscayne aquifer (modern) and upper Floridan aquifer (≈5% modern). Although not definitive, age of upper Floridan waters and the extremely small amounts of ¹⁴C from greater depths suggest a residual rather than a recent origin. Additional ¹⁴C data is planned from future wells.

Northwest Florida series

WRD-160. Pensacola South Monitor Well <2.0% modern

From lower Floridan aquifer, depth 483m, (30° 34′ 17″ N, 87° 14′ 17″ W). Part of study of use of deep saline aquifers for injection of liquid wastes. Represents native aquifer water from injection horizon 2.4km S of industrial waste injection system in NW Florida, near Pensacola. Fresh water occurs within this aquifer ca 32.2km upgradient. Dated to determine relative age of aquifer water. Coll Nov 1971 by L Slack and M I Kaufman. Subm by Kaufman. Comment (MIK): results suggestive of lethargic flow system and relatively old waters near injection site. Additional ¹⁴C data is planned for overlying and upgradient waters to evaluate hydraulic separation and rates of ground-water movement.

Table 4
Edwards Aquifer, Texas, series

| | | Total | | | |
|------------|--------------|-----------|--------------|------------------|----------------------|
| | | dissolved | | | |
| | | carbonate | | Tritium | ¹⁴C % |
| Sample no. | Well no. | (mM/L) | ‰ | $TU \pm 1\sigma$ | $modern \pm 1\sigma$ |
| WRD-111 | 8-1900* | 3.76 | - 4.9 | 30.5 ± 2.2 | 116.0 ± 1.1 |
| WRD-110 | 8-1950* | 3.48 | -9.3 | 28.3 ± 1.6 | 118.0 ± 1.1 |
| WRD-119 | YP-69-50-101 | 4.90 | -11.5 | 21.0 ± 1.5 | 72.5 ± 0.6 |
| WRD-115 | YP-69-45-401 | 4.66 | -8.5 | 11.7 ± 0.8 | 65.6 ± 0.7 |
| WRD-114 | TD-69-47-302 | 4.62 | -8.4 | 2.4 ± 0.3 | 62.4 ± 0.6 |
| WRD-117 | TD-68-42-806 | 4.05 | -5.7 | < 0.8 | 24.5 ± 0.6 |
| WRD-118 | AY-68-35-904 | 4.49 | -8.5 | 1.9 ± 0.7 | 59.9 ± 1.0 |
| WRD-112 | AY-68-36-102 | 5.36 | -8.9 | 13.9 ± 0.8 | 73.6 ± 0.6 |
| WRD-116 | DX-68-23-301 | 5.30 | -9.2 | 6.7 ± 0.4 | 65.1 ± 0.6 |
| WRD- 72 | AY-68-29-109 | 6.98 | -10.8 | 5.4 ± 0.4 | 73.8 ± 0.7 |
| WRD- 75 | AY-68-37-104 | 4.83 | -8.6 | $4.4 \pm 0.3**$ | 83.6 ± 1.1 |
| WRD- 85 | TD-69-40-901 | 4.95 | - 9.6 | 11.5 ± 1.2 | 52.2 ± 0.7 |
| WRD- 86 | AY-68-37-701 | 4.50 | -8.1 | < 0.7 | 55.6 ± 0.7 |
| WRD- 77 | TD-68-41-801 | 4.60 | -6.2 | <0.8** | 5.8 ± 0.4 |
| WRD-122 | AY-68-43-809 | 4.44 | -5.3 | | 34.2 ± 0.6 |
| WRD-125 | AY-68-43-703 | 4.42 | _ | | 22.8 ± 0.6 |
| WRD-124 | AY-68-44-210 | 4.46 | -5.4 | <1.0 | 32.0 ± 0.4 |
| WRD-121 | AY-68-38-101 | 4.10 | -4.3 | | 21.0 ± 0.6 |
| WRD-123 | KX-68-30-601 | 5.14 | — 3.3 | <1.8 | <1.4 |
| WRD- 84 | AY-68-45-802 | 5.44 | -3.2 | | <1.0 |
| WRD-129 | AY-68-45-802 | 4.81 | -6.9 | | <1.1 |
| WRD-128 | AY-68-45-101 | 5.20 | -3.1 | | <2.2 |
| WRD-127 | AY-68-38-301 | 6.55 | -4.0 | | <1.2 |
| WRD- 78 | AL-68-50-201 | 4.44 | -2.9 | | 2.7 ± 0.4 |
| WRD- 80 | AY-68-43-702 | 4.87 | -4.7 | | 22.3 ± 0.6 |
| WRD- 82 | AY-68-37-702 | 7.18 | 0.0 | < 0.6 | 3.9 ± 0.6 |
| WRD- 71 | AY-68-45-301 | 5.13 | - 4.6 | | <2.4 |

^{*} Stream samples.

B. Pakistan

Punjab series

Samples are part of study to determine if salty ground water in irrigated doabs of upper Indus Plains, Punjab, Pakistan, is residual from conditions existing prior to irrigation or is currently being formed by evaporation of irrigation water. For details of study, see Seaber et al (1974).

Coll Feb and March 1971 by Ata and Gafar, WASID Lab, Govt Pakistan, and W Back, R Cherry, and P Seaber. Subm by C T Rightmire, Reston, Virginia.

^{**} Coll in spring, 1968.

| Sample no. | Name | Lat (N) | Long (E) | δ ¹³ C %c | Alkalinity (mM/L) r | 14 C $\%$ modern $\pm 1_{\sigma}$ |
|------------|-------------------|-----------------|----------|--------------------------------|------------------------|---|
| WRD- 91 | Kurala | 31°41′ | 72°58′ | - 5.8 | 4.21 | 78.6 ± 1.2 |
| WRD- 92 | Thatta Khushi | 31°11′ | 72°14′ | -19.7 | 5.44 | 68.1 ± 1.0 |
| WRD- 93 | Shorkot Road | 30°47' | 72°15′ | - | 2.69 | 58.7 ± 1.1 |
| | hand pump | | | | | |
| WRD- 94 | Kamalia | $30^{\circ}47'$ | 72°35′ | -8.9 | 5.19 | 72.8 ± 0.9 |
| WRD-106 | Gojra | 31°10′ | 72°41′ | -10.5 | 5.05 | 70.5 ± 0.6 |
| WRD-107 | Lyallpur | 31°24′ | 73°06′ | -6.6 | 11.61 | 82.5 ± 0.7 |
| WRD-108 | Test well, ZW-357 | 31°38′ | 73°55′ | | 6.17 | 69.2 ± 0.7 |
| WRD-109 | Toba Tek Singh | 30°59′ | 72°29′ | - 6.0 | 4.38 | 97.3 ± 0.8 |

Comment (CTR): due to lack of vertical control and possible mixing within wells, results of these ¹⁴C determinations cannot be interpreted within regional hydrologic framework.

C. Kenya

North Eastern Province series

A body of fresh ground water underlies drainageways of Ewaso Ngiro R and Lagh Dera for ca 200km SE and E of Habaswein and is a major natural resource of arid North Eastern Prov. Samples coll to elucidate recharge mechanisms and perhaps flow rate to help plan use of this fresh water. Samples coll May, 1973 by F J P and W V Swarzenski, and Simon Wanuki, Water Dept, Govt Kenya. *Comment*: higher measured ¹⁴C values are assoc with fresher water body, but correlation is not strict between ¹⁴C and salinity. Samples fall into several groups; members of each show a striking correspondence between measured ¹⁴C contents and $(C_{tot})^{-1}$ values. Our hypothesis to account for this correspondence is that each of the ¹⁴C-C_{tot} groups represents a single recharge event. The different ¹⁴C contents within each group are due to additions of varying amounts of ¹⁴C free carbonate—by aquifer carbonate solution or mixing with older water—to water from a single recharge event.

Because of lack of general knowledge about arid-region carbonate chemistry and samples to show chemical and isotopic variations with depth in the aquifer, we do not assign absolute ages to these waters. It is probable, though, that recharge events recurred at intervals of a few milennia. Details of study are given by Pearson and Swarzenski (1974).

Table 5
North Eastern Province series

| Sample no. | Well no. C– | Lat | Long | Chloride (mg/L) | Total dissolved carbonate (mM/L) | δ ¹³ C ‰ | ¹⁴ C % modern ± 1σ |
|------------|----------------|--------|---------|--------------------|---|------------------------|----------------------------------|
| WRD-184 | 3788 | 0°26′N | 40°01′E | 40 | 7.1 | -12.6 | 38.4 ± 0.5 |
| WRD-183 | 3715 | 0°30′N | 39°51′E | 64 | 7.2 | -13.8 | 39.4 ± 0.5 |
| WRD-182 | 3727 | 0°38′N | 39°42′E | 50 | 8.2 | -11.6 | 37.9 ± 0.5 |
| WRD-194 | 2685 | 0°21′N | 40°52′E | 142 | 6.0 | -12.7 | 48.4 ± 0.5 |
| WRD-177 | 3655 | 1°02′N | 39°27′E | 100 | 9.8 | -10.6 | 58.2 ± 0.6 |
| WRD-193 | 3831 | 0°02′S | 40°27′E | 82 | 9.5 | -11.5 | 12.8 ± 0.3 |
| WRD-178 | 3218 | 1°02′N | 39°29′E | 67 | 10.9 | -11.1 | 57.6 ± 0.5 |
| WRD-195 | 3821 | 0°14′N | 40°21′E | 256 | 7.4 | -13.4 | 42.1 ± 0.5 |
| WRD-181 | 3792 | 0°46′N | 39°37′E | 140 | 10.2 | -10.5 | 64.1 ± 1.4 |
| WRD-187 | 3685 | 0°51′N | 39°34′E | 109 | 10.0 | | 87.7 ± 0.7 |
| WRD-180 | 3753 | 0°52′N | 39°27′E | 130 | 12.8 | -9.8 | 52.4 ± 0.5 |
| WRD-188 | 3751 | 0°28′N | 39°44′E | 278 | 9.9 | -11.4 | 18.6 ± 0.3 |
| WRD-189 | 3752 | 0°39′N | 39°35′E | 182 | 13.0 | -9.6 | 21.0 ± 0.3 |
| WRD-192 | 3726 | 0°37′N | 40°01′E | 150 | 18.2 | -11.9 | 35.0 ± 0.4 |
| WRD-185 | 3893 | 1°28′N | 39°16′E | 576 | 8.5 | -9.5 | 2.8 ± 0.1 |
| WRD-191 | 3769 | 0°55′N | 39°53′E | 816 | 11.1 | -10.5 | 13.3 ± 0.4 |
| WRD-190 | 3804 | 0°42′N | 39°28′E | 2700 | 31.0 | -10.6 | 7.3 ± 0.3 |
| WRD-179 | 3822 | 1°02′N | 39°06′E | 2240 | 55.2 | -8.0 | 6.7 ± 0.2 |
| WRD-186 | 3830 | 1°12′N | 39°15′E | 2720 | 38.7 | -8.9 | 28.9 ± 0.4 |
| WRD-176 | 3770 | 0°01′S | 40°00′E | 3650 | 22.4 | - 9.4 | 4.4 ± 0.3 |

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