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CARBON ISOTOPE INVESTIGATION
AT KUFRA, LIBYAN ARAB REPUBLIC

by

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# CARBON ISOTOPE INVESTIGATION AT KUFRA
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As part of the regional groundwater studies being carried out in Cyrenaica by the Institute of Geological Sciences for the Libyan government, radiocarbon dating is being used to investigate the relative rates of movement and stratification of groundwaters in the Surt basin. A necessary objective of this programme is to define the degree of interconnection between groundwaters in the Surt basin and Kufra basin to the south and carbon isotope studies were made initially on two groundwaters at the Kufra farm, as well as on carbonaceous material occurring in the sandstone formations at Kufra. This report is concerned with results of the Kufra samples, although sampling is also being undertaken at locations elsewhere i Cyrenaica and the results will be described in a later report.

Sampling

Sampling was carried out during March 1972 by the author. Carbon was concentrated using an ion exchange technique modified from Crosby and Chatters (19 this method was chosen in preference to a precipitation method, in view of the low total solids in the Kufra groundwater and the low carbonate concentrations which would otherwise have required several hundred litres of water to be collected to extract the necessary weights of carbon. The apparatus used required an uninterrupted flow of around 200 ml/minute for around 24 hours through two columns the first to remove $SO_4$, Cl and $NO_3$ and the second to adsorb the $HCO_3$. The technique could, however, only be used on wells continuously discharging at a fair constant rate and this restricted the choice of sites at the time of the visit. The two wells selected for sampling were WW 9 and WW 11, both adjacent to each oth on the experimental farm site and details are given in Table 1. The sampling apparatus set up at WW9 is shown in Figure 1. Three samples of wood from a horiz in the sands were submitted at the same time for isotope analysis. These samples were from cuttings collected during the drilling of three production wells and det are given in Table 2. Although on conventional geological grounds it appeared unlikely that the age dating from $^{14}C$ would be strictly relevant, the material was processed because of its possible value in obtaining stable isotope corrections of the groundwater ages. The possibility of contamination with modern carbon during the collection process of both groundwater and wood samples was considered to be negligible. Samples were processed for the Institute at the Scottish Research Reactor Centre, East Kilbride.

## Results

The various results on samples taken are listed in Table 3 and include carbon isotope, tritium and age determinations. The activity of $^{14}C$ in groundwater is not usually directly proportional to the age of the water, since carbon from a variety of sources may be contributing to the total activity. The main source of radiocarbon is that derived from $CO_2$ in the atmosphere and soil zone of the recharge area and this reservoir will be in approximate equilibrium with the existing vegetation. As percolation and flow commence the carbon is cut off from its source and the $^{14}C$ will start to decay (the half life of $^{14}C$ is 5560 years). The carbon dioxide will react with carbonate minerals in the aquifer according to the equation:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3$$
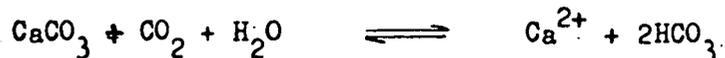
and since the carbonate does not contain radiocarbon, the $^{14}C$ will be diluted in the ratio 1:1. Isotopic or ion exchange reactions may occur with the aquifer which may further dilute the initial radiocarbon, and dilution by decaying fossil plant debris, $CO_2$ from natural gas deposits or magmatic sources may also occur in some environments.

A correction factor (P) may be applied to the measured activity values (Ingerson and Pearson 1963) based on knowledge of the $\delta^{13}C$ ratio of the sample ($\delta^{13}C_{sm}$), on the ration in limestone ($\delta^{13}C_{ls}$) and in plant material of the recharge area ($\delta^{13}C_{pl}$):

$$P = \frac{\delta^{13}C_{sm} - \delta^{13}C_{ls}}{\delta^{13}C_{pl} - \delta^{13}C_{ls}}$$

Limestones usually have $\delta^{13}C = 0 \pm 3$ and plants in temperate latitudes have $\delta^{13}C = -25 \pm 3$. In arid areas however, it is found that plants are more enriched in the heavier carbon isotope and $\delta^{13}C$ values of $-17 \pm 2$ appear to be common. This is borne out in the present case by analysis of a palm tree stump near Augila which had a $\delta^{13}C$ value of $-16.7$, and the $\delta^{13}C_{pl}$ value used for the correction in this study was $-17$.

There is also the possibility that some dilution has occurred from plant debris in the formation similar to that analysed. The value of P used was 0.594 and this would suggest that no significant contribution from this source had occurred. A greater certainty in the correction factor should be obtained however when additional plant and limestone materials from the region have been analysed.

The corrected age was calculated from the equation:

$$\text{Age} = 8033 \ln \frac{A_o}{A_o}$$

where $A_o$ is the working modern count rate and $A_o = A_m/P$, where $A_m$ = the measured activity and P is the correction factor.   Only one of the samples produced an age greater than the limit of the method, although further counting is in progress on all samples to extend the range of the method to around 60 000 years.


## Significance of results

All three samples of wood from intervals in the production wells have produce[d] ages in excess of the range obtainable using $^{14}C$ methods, as had been expected. Geobotanical work is in progress on these samples in an attempt to provide an indication of stratigraphic age.

Groundwaters from the two Kufra wells have yielded different ages which was not expected in view of the proximity of the wells although their open intervals differ (see Table 1).   WW 9 with the younger age is deeper and therefore has a greater open interval than WW 11, but this is the only significant difference in t[he] two wells, assuming the solid casing is not leaking .   It was not know at what depths the pumps were installed, but if the depths were different, this may have a bearing on the interpretation.   Two explanations appear possible however :

1.  Stratification.  It is likely that some age stratification would occur within the Nubian aquifer, and although improbable from site evidence, waters of different ages may have been pumped from the two wells.

2.  Recycling of irrigation water.  Both wells are in the oldest part of the experimental farm and it may be that recycled water has contaminated the samples.   WW 9 is nearer the centre of the trial farm which might provide an explanation of selective contamination, but since the wells are only about 1 km apart this hardly appears significant.   Tritium results indicate that no recent (post 1953) component of water occurs in the samples, but solution of modern $CO_2$ would occur in the soil zone by any percolating excess irrigation waters.

From the above evidence it is not possible to choose between the two alternat[ives] and further knowledge of the movement of the excess irrigation water for instance by chemical sampling would be necessary to decide whether the samples are likely t[o] have been contaminated by modern carbon.   The age range of the two samples, assuming no contamination, compares with those found at Dakhla, Kharga and Bahariy[a] oasis in the western desert of Egypt where the youngest water had an age of 19 000 years;   at Bahariya, shallow water with an age of 26 000 years was found overlying water of > 30 000 years age (Vogel and Ehhalt 1963).   Further sampling in the Kufra basin and a study of possible recycling is desirable to assess the significa[nce] of the ages so far determined.

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Table 1. Site details of groundwater sampling localities, Kufra farm

| Well | Well Depth | Open interval m | Date of collection | Pumping rate l/s | Volume of water sampled in l. | Max. theoretical yield of carbon gm |
|---|---|---|---|---|---|---|
| WW 9 | 320 | 122–320 | 18–20.3.72 | 75 | c.740 | c.7.40 |
| WW 11 | 232 | 122–232 | 20–22.3.72 | 75 | c.805 | c.8.05 |

Table 2. List of sites from which wood samples were collected

| Well | Depth of Sample m | Date of collection | Sample description and comments |
|---|---|---|---|
| C 81(a) | 265–167 | 29.1.72 | Wood fragments mixed with coarse-grained, pure quartz sand |
| C 81(b) | 186–210 | 28.1.72 | Wood fragments with pure quartz sand matrix. Fragments up to 3.5 cm long |
| C 53 | 192–198 | 29.1.72 | Wood fragments |

Table 3. Carbon isotope age and tritium results for Kufra samples.

| Sample | Lab.[1] Ref. | Sample[2] activity | % Modern[3] | $\delta^{13}C$[4] | Correction factor P[5] | Apparent[6] Age BP | Corrected[7] Age | Tritium[8] (T.U.) |
|---|---|---|---|---|---|---|---|---|
| WW 9 | SRR-75 | 0.383 | 4.971 | -10.1‰ | 0.594 | 24096±150 | 19932±1500 | -0.9 |
| WW 11 | SRR-76 | - | - | -10.7‰ | - | 44,150 | 44,150 | 0.9 |
| C 81(a) | SRR-78 | - | - | -23.8‰ | - | 42,400 | 42,400 | - |
| C 81(b) | SRR-79 | - | - | -22.4‰ | - | 46,400 | 46,400 | - |
| C 53 | SRR-80 | - | - | -21.7‰ | - | 46.400 | 46.400 | - |

1 - Reference number of Radiocarbon Lab. Scottish Research Reactor Centre.

2 - $^{14}C$ counts per minute/gm. (cpm/gm).

3. - Calculated from $R_s/R_m$ x 100 where $R_s$ is the sample activity, and $R_m$ is the working modern count rate which is $7.705\pm0.015$ $^{14}C$ cpm/gm.

4 - $\delta^{13}C = (^{13}R$ sample$/^{13}R$ standard -1) x 1000 where $^{13}R$ is the $^{13}C/^{12}C$ ratio of the material and R standard is the ratio in the PDB standard

5 - P is the correction factor based on $\delta^{13}C$ isotope measurements to account for the dilution effect by dead carbonate carbon. See text.

6 - Age calculated by radiocarbon laboratory assuming 100% plant derived carbon in sample

7 - Corrected age is that calculated as described in text and is the true age for the sample

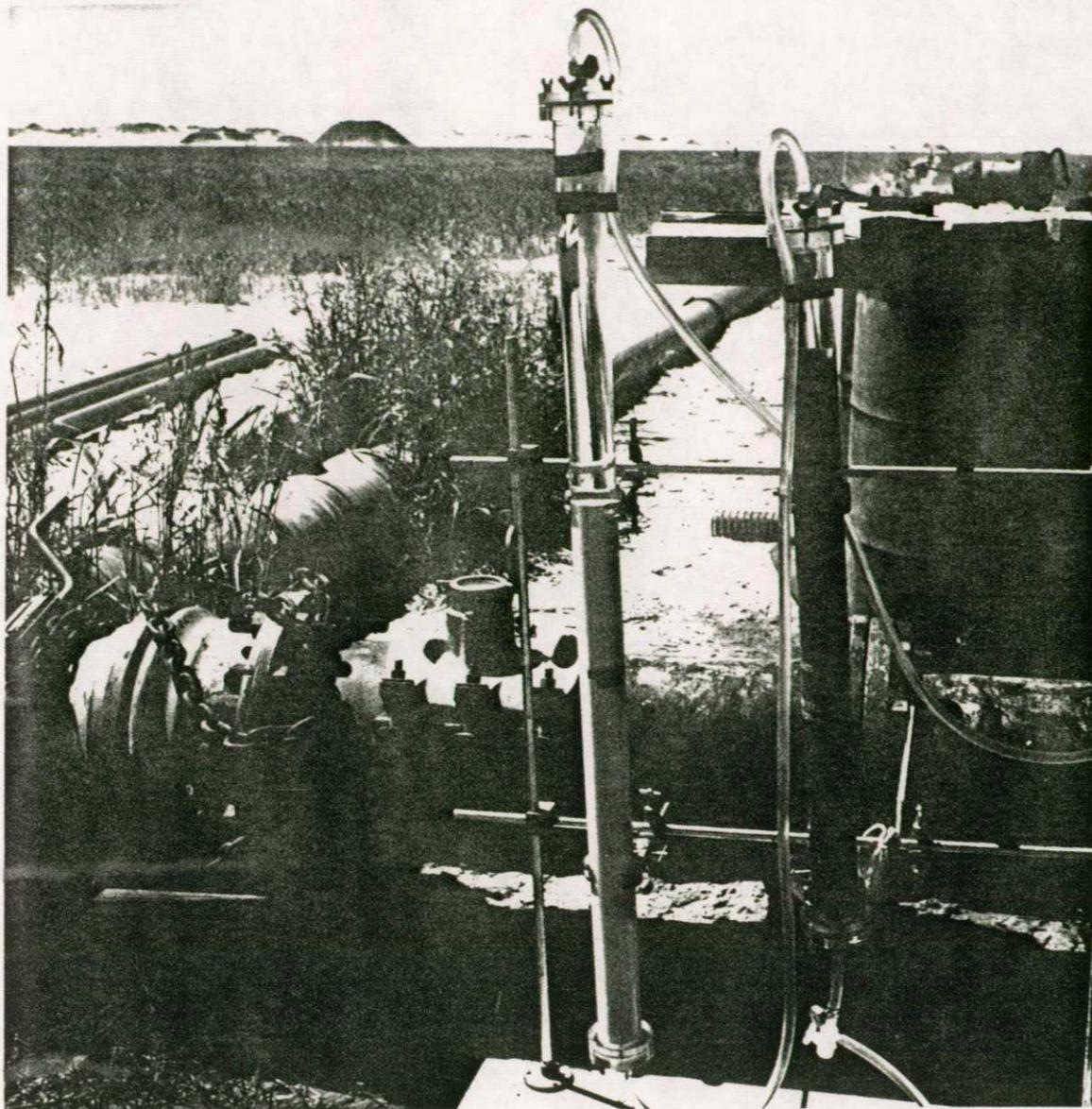8 - 1 tritium unit = 1 tritium atom per $10^{18}$ hydrogen atom.

Figure 1.    Processing groundwater at WW-9, Kufra trial farm,
for extraction of carbon, using ion exchange apparatus.    Strong
anions are removed on the left hand column and the effluent then
passes to the right hand column on which the bicarbonate is
adsorbed.