Available online at www.sciencedirect.com

ScienceDirect

Procedia Environmental Sciences 25 (2015) 28 – 35

Procedia Environmental Sciences

7th Groundwater Symposium of the
International Association for Hydro-Environment Engineering and Research (IAHR)

Usage of carbon isotopes in characterizing groundwater age, flow direction, flow velocity and recharge area

H. Bhandary[a]*, M. Al-Senafy[a] and F. Marzouk[a]

[a]*Water Research Center, Kuwait Institute for Scientific Research, P.O. Box 24885, Safat, Kuwait*

Abstract

Carbon-13 and Carbon-14 isotopes were utilized in this study to determine the age, flow direction, flow velocity and recharge area of groundwater in the two main aquifers of Kuwait. For this purpose 20 groundwater samples were collected from the Kuwait group aquifer and lower Dammam formation aquifer. The collected groundwater samples were analyzed for ^{14}C activity and ^{13}C activity. ^{14}C activity was measured using accelerator mass spectrometry (AMS) and expressed as percentage modern carbon (pmc) while ^{13}C was measured using an isotope ratio mass spectrometer (IRMS) and expressed as permil (‰) in the form of CO_2 gas. The interpretation of the analysis results of carbon isotopes data indicated that the general groundwater flow direction is towards north east and the estimated groundwater velocities are 11 to 30 m/a for Kuwait group aquifer and 12 to 21 m/a for Dammam formation aquifer. Based on the estimated groundwater velocities, the approximate location of the recharge areas of these aquifers was identified. The groundwater ages calculated for Kuwait group aquifer varied from 800 a B.P for modern ground water in the northern part to 22500 a B.P for very old groundwater in the northeastern part, while the age of Dammam formation groundwater is 26000 to 36000 a B.P.

Peer-review under responsibility of the Scientific Committee of the IAHR Groundwater Symposium 2014

Keywords: Carbon-13; carbon-14; aquifer; recharge

1. Introduction

With limited natural water resources, the sustainable and integrated management of all sources of water is high priority for Kuwait. Carbon isotopic characterization of the aquifer system of Kuwait will

* Corresponding author. Tel.: +965-24989839; fax: +965-24989819.
E-mail address: hkaup@kisr.edu.kw

Peer-review under responsibility of the Scientific Committee of the IAHR Groundwater Symposium 2014
doi:10.1016/j.proenv.2015.04.005

give better idea of the source, age and movement pattern of water within the system, leading to the formulation of an optimum development and exploitation pattern for this resource. The environmental isotopes, i.e., hydrogen (H), carbon (C), nitrogen (N), oxygen (O) and sulfide (S) are naturally occurring isotopes of elements found in abundance in the environment. These are the principal elements of hydrological, geological and biological systems. They are used to trace not only groundwater provenance but also recharge processes, subsurface processes, geochemical reactions and reaction rates [1]. The stable isotopes oxygen-18 (^{18}O) and deuterium (^{2}H) were used in different hydrological studies to investigate the origin of water in the aquifer system in the study area. The radioactive isotopes, such as carbon-14 (^{14}C) and tritium (^{3}H), are used to estimate the age and circulation of groundwater. The carbon isotopes were utilized in this study to characterize the groundwater system in Kuwait, and to determine its origin, flow, recharge area and age in two main aquifers.

2. Groundwater sampling

To evaluate the origin, flow and age of groundwater in the two main aquifers of Kuwait, the Kuwait group and Dammam Formation, 20 groundwater samples were collected. The identified sampling locations were distributed all over Kuwait and details like coordinates, water level, well depth, elevation, etc., were collected. Fourteen groundwater samples were collected from Kuwait group aquifer, where as five samples from Dammam formation aquifer and one sample collected from dual completion aquifer. The groundwater sampling locations are presented in Fig. 1.

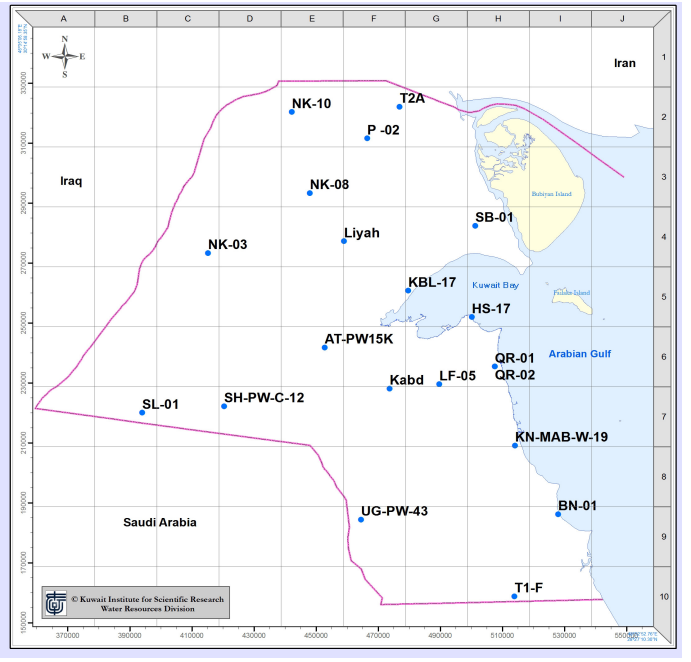

Fig. 1. Groundwater sampling locations.

After identifying the groundwater sampling wells, the groundwater sampling was commenced. The static groundwater level was measured and then an electric submersible pump was used for purging the

screened interval to enable the collection of representative groundwater samples. The groundwater samples for the ^{14}C analysis, on the other hand, had to satisfy the International Atomic Energy Agency (IAEA) laboratory requirements of 2.5 g of carbon, as suggested by the IAEA expert. Thus, for water containing 250 mg/l bicarbonate, a water sample of 60 l should be sufficient. If the total carbon content is lower than 250 mg/l, proportionally larger volumes of water are needed. The procedure for precipitating the carbonates from the groundwater is very simple, but requires paying attention to details, particularly in minimizing air exposure. The mixed precipitate of barium sulphate and barium carbonate is formed by adding barium chloride to the water after adjusting the pH to convert all bicarbonates. Normally, such a precipitate is fine grained and requires several hours to settle completely. An iron salt and flocculating agent are added to promote the formation of coarse agglomerates and to shorten the settling time.

3. Laboratory analysis

The ^{14}C activity and ^{13}C were analyzed for the collected 20 groundwater samples in an IAEA-sponsored isotope laboratory in the Netherlands. The ^{14}C activity was measured using accelerator mass spectrometry (AMS) and expressed as percentage modern carbon (pmc) [2], and ^{13}C was measured using an isotope ratio mass spectrometer (IRMS) and expressed as permil (‰) in the form of CO_2 gas [1]. The standard used is Pee Dee Belemnite (PDB) and the precision of measurement is ±0.5‰. The ^{14}C activity was corrected using $\delta^{13}C$, and the apparent age of the groundwater samples wasere calculated using the Pearson's model [3] and Empirical model assuming that the initial ^{14}C radioactivity (A_0) as 90.76 pmc, which is the activity of modern groundwater (P02), and as 100 pmc. The measured 14C activity, $\delta^{13}C$, corrected ^{14}C activity and calculated ages of groundwater are presented in Table 1.

Table 1. Carbon-14 and carbon-13 results of groundwater samples.

Sample ID	^{14}C activity (pmc)	$\delta^{13}C$ (‰)	^{14}C activity Corrected (pmc)	^{14}C age (Empirical Model ka BP) A_0 as 90.76pmc	^{14}C age (Pearson ka BP)
Kuwait Group Aquifer					
T2A	22.95	-10.19	22.26836	11617.6	12419.16
NK-10	29.61	-13.35	28.91488	9457.977	10259.54
P -02	93.15	-12.25	90.76074	0.000271	801.5667
SB-01	6.79	-7.71	6.555439	21728.79	22530.35
NK-08	11.95	-8.79	11.56234	17036.81	17838.38
NK-03	12.09	-9.33	11.71056	16931.5	17733.06
KBL-17	23.43	-7.65	22.61787	11488.83	12290.39
HS-17	15.19	-9.34	14.71356	15044	15845.56
AT-PW15K	8.22	-9.04	7.957356	20126.36	20927.92
LF-05	69.27	-11.11	67.33773	2468.168	3269.734
T1-F	55.49	-18.55	54.76305	4177.287	4978.854
QR-02	49.77	-11.28	48.39831	5198.853	6000.42
Liyah	12.24	-8.42	11.8341	16844.73	17646.29
KN-MAB-W-19	61.07	-10.44	59.2861	3521.113	4322.68
Dammam Formation Aquifer					
Kabd	1.31	-9.58	1.269526	35302.61	36104.18
SH-PW-C-12	1.69	-6.54	1.627778	33247.32	34048.89
SL-01	2.69	-7.75	2.597283	29383.91	30185.48
BN-01	4.31	-7.35	4.158093	25492.88	26294.45
Dual Completion Aquifer					
UG-PW-43	16.02	-7.26	15.45257	14638.8	15440.36

The analysis results of ^{14}C and the subsequent calculation of age [4] indicated that the collected groundwater ages are different at different parts of Kuwait and age increased with the well depth. The groundwater collected from Raudatain (P02) was found to be modern water with highest ^{14}C activity and the Kabd groundwater to be the oldest with the lowest ^{14}C activity. The groundwater sample at landfills (LF05) showed the mixing of modern water with old groundwater. The groundwater of Dammam aquifer was found to be old groundwater with age of more than 20,000 y. Analysis results could not be achieved for the sample QR-01 due to the contamination of the sample with hydrogen sulphide.

4. Results and discussion

4.1. Groundwater age and flow direction

The environmental ^{14}C measurement of these groundwater samples indicated that they are rain waters recharged ~22,500 a B.P (at SB-01) to 800 a B.P. (at P-02), as shown in Fig 2. The Kuwait Group Aquifer located in the northeastern part are saline and very old (~22,500 a B.P), indicating that the general groundwater flow direction of the Kuwait Group Aquifer is towards the northeast (i.e., toward the Arabian Gulf). The iso-^{14}C ages of groundwater is shown are Fig. 3, which shows that in the central part the groundwater flow is quiet complex, whereas in the northern and northeastern part, the general groundwater flow direction is towards the Arabian Gulf.

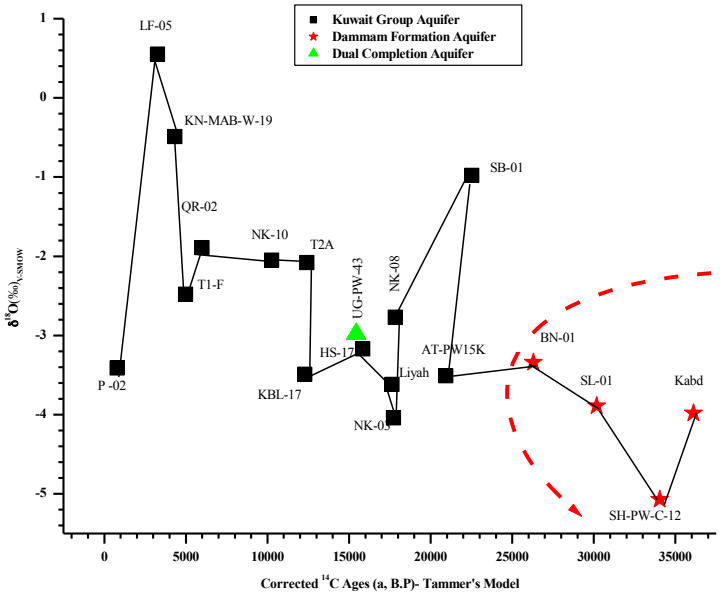

Fig. 2. $\delta^{18}O$ vs corrected ^{14}C ages.

The groundwater at P-02, located at the northeastern part, is a mixture of modern and old waters as it has measureable ^{3}H content and ^{14}C values of 93.15 pMC. Also, it falls close to Local Meteoric Water Line (LMWL), which suggests that it receives some component of direct modern day precipitation recharge. The groundwater sample near the landfill site (LF-05) falls along the regression line for the Kuwait Group Aquifer. However, as seen from the hydrochemistry results, there is no evidence of the leachate contamination in the adjoining groundwater and, hence, no natural precipitation recharge

occurring to the groundwater through the leachate site. Since ^{14}C method is not sensitive for ages above 20,000 a, the groundwater samples having an estimated ^{14}C age of more than 20,000 could be still older, which can be confirmed through other dating methods like ^{36}Cl. The corrected ^{14}C age distribution suggests that the general groundwater flow direction in Dammam Formation is towards the northeast. The various age correction models (Empirical, Pearson's, Tammer's [5]) gave comparable ^{14}C ages, as shown in Fig 4. In the northwest part and along the bay, the Kuwait and Dammam aquifers are isotopically similar and hence, possibly, they are interconnected (mixed groundwater are ~11,000 to 22,000 a B.P). However, whether the groundwater flow at these locations is up-gradient or down-gradient needs to be verified from the piezometric observations.

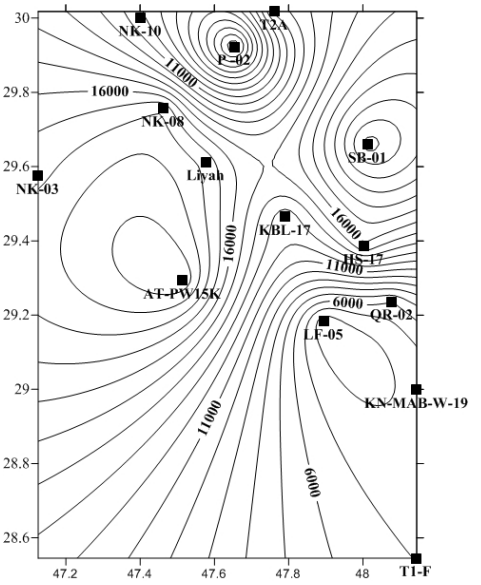

Fig. 3. Iso-^{14}C ages of groundwater for Kuwait Group Aquifer.

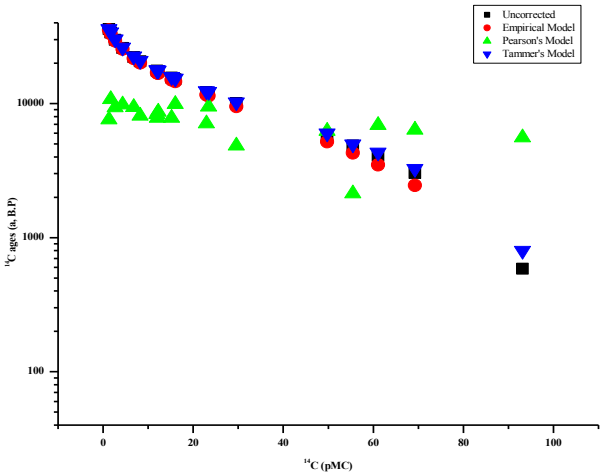

Fig. 4. ^{14}C ages vs ^{14}C (pMC) for different age correction models.

4.2. Groundwater velocity and location of recharge area

From the estimated groundwater (corrected ^{14}C) ages, an estimate on the groundwater velocity was made by dividing the distance between the two locations along the flow path by the product of porosity and difference in their groundwater ages. The estimated groundwater velocities (filtration velocities) are given in Table 2. The velocities range from 11 to 30 m/a in the Kuwait Group of Aquifers and 12 to 21 m/a in the Dammam Formation.

Table 2. Estimated groundwater velocities based on ^{14}C ages (aAssuming a porosity of 0.6)

Flow path	Distance (km)	Difference in ^{14}C ages (a)	Filtration velocity (m/a)*
	Kuwait Group of Aquifer		
NK-10 - Liyah	~47	7387	11
NK-03 - SB-01	~86	4797	30
	Dammam Formation		
SL-01- SH-PW-C-12	~28	3863	12
SL-01 - Kabd	~49	5919	14
SH-PW-C-12- Kabd	~26	2056	21

The ^{14}C ages, as shown in Fig. 5, of the groundwater samples of the Kuwait Group Aquifer did not show good correlation with the depth of the sample. This possibly indicates that the Kuwait Group Aquifer is not well stratified and is hence a single aquifer. However, as seen from Figs. 5 and 6 ($\delta^{18}O$ vs depth), in some parts, the aquifer is stratified and is shown as dotted rectangle, wherein there is a good correlation.

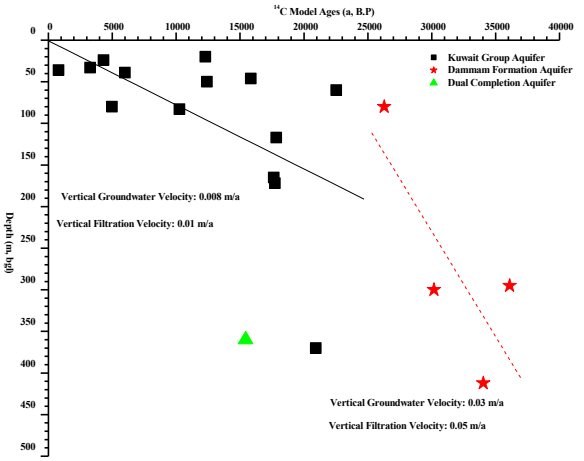

Fig. 5. Vertical distribution of ^{14}C ages.

The locations in the dotted rectangle in Fig. 6 represent the locations other than the northwest and along the bay. This suggests that along the groundwater flow path, flow within the Kuwait Group Aquifer is distinct till it reaches the northwest part, wherein the mixing occurs, and then the flow is distinct for some distance and finally mixes again along the bay. The correlation is fairly good in the case of the Dammam Formation indicating it is well stratified (multi-aquifer). An estimate on groundwater velocity was made based on the vertical distribution of groundwater ^{14}C ages (0.04 m/a and 0.15 m/a for the Kuwait Group of Aquifers and the Dammam Formation, respectively). The depth-wise distribution of

$\delta^{13}C$ did not show a clear picture of the stratification of both the aquifers owing to the complex geochemical processes (dissolution, bacterial reduction, etc.) occurring along the flow.

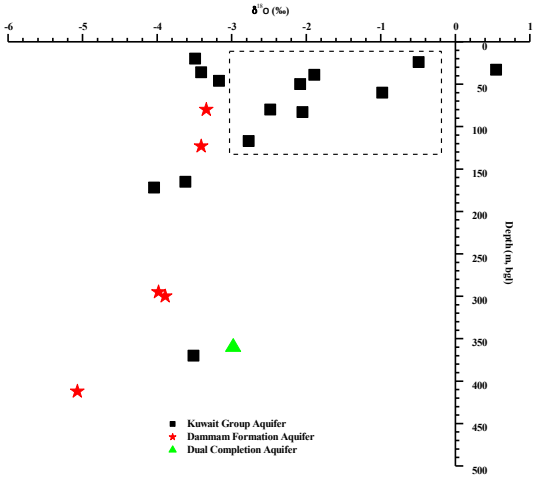

Fig. 6. Vertical distribution of $\delta^{18}O$ of groundwater.

Based on the aforementioned estimated groundwater velocities, the approximate location of the recharge areas of the Kuwait Group Aquifers and Dammam Formation was calculated to be at ~200 km from NK-03 (transit time= 17,733 a) and at ~360 km from SL-01 (transit time= 30,185 a), respectively, towards west.

5. Conclusions

The Kuwait Group Aquifer located in the northeastern part is very old (~22,500 a B.P), and the general groundwater flow direction of the Kuwait Group Aquifer is towards northeast (i.e., towards the Arabian Gulf).

The brackish groundwaters of the Dammam Formation are recharged about 26,000 to 36,000 year B.P.

At the northwest part and along the bay, the Kuwait and Dammam aquifers are interconnected (mixed groundwater are ~11,000 to 22,500 year B.P).

In the northern part, freshwater zones exist tapping the Kuwait Group Aquifer, and they receive direct modern day precipitation recharge.

Horizontal groundwater velocity estimated based on environmental ^{14}C ages are 11 to 30 m/a and 12 to 21 m/a for the Kuwait Group Aquifer and Dammam Formation, respectively.

The ^{14}C ages of the groundwater samples of the Kuwait Group Aquifer did not show good correlation with the depth of the sample. This possibly indicates that the Kuwait Group Aquifer is not well stratified. The correlation is fairly good in the case of the Dammam Formation indicating they are stratified.

Based on the estimated groundwater velocities, the approximate location of the recharge areas of the Kuwait Group Aquifers and the Dammam Formation was calculated to be at 200 km from NK-03 (Transit time= 17,733 year) and at 360~ km from SL-01 (transit time = 30,185 year), respectively, towards west.

Acknowledgements

The authors would like to express their gratitude to International Atomic Energy Agency (IAEA) for their in-kind contribution for the project. The constant support and encouragement of the Kuwait Institute for Scientific Research (KISR) management is gratefully acknowledged.

References

[1] Clark I, Fritz P. Environmental isotopes in hydrogeology. New York: CRC Press LLC, 2000.
[2] Povinec PP, Aramaki T, Burr GS, Jull AJT, Kwong LLW, Togawa O. *Radiocarbon* 2004. **46** (2):583.
[3] Pearson FJ Jr. Use of C-13/C-12 ratios to correct radiocarbon ages of material diluted by limestone. In the Proceeding of the 6th International Conference on Radiocarbon and Tritium Dating, Pullman, Washington DC, June 1965, pp 357–366.
[4] Pearson FJ, Hanshaw BB. Sources of dissolved carbonate species in groundwater and their effects on carbon-14 dating. In *Isotope Hydrology* Vienna: IAEA; 1970, p. 271–286.
[5] Tamers MA. Validity of radiocarbon dates on groundwater. *Geophysical Survey* 1975. **2**: 217–239.