Radio Dating of Water Sample Collected From Katsina State Using Nuclearhydrological Isotopes Techniques

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Abstract

Water molecules were often found to be radioactive within the period of thermonuclear test (i .e. 1950s to 1970s) this increased tritium concentration in the atmosphere.Thus tritium concentration in groundwater reflect atmospheric tritium levels when the water was last in contact with the atmosphere, therefore, any measurable tritium concentrations in groundwater system provides clear evidence of recharge occurring into the system during the last four decades.Since 1970s, the atmospheric tritium concentration has decreased. Thus, the presence of excess tritium in groundwater indicates recharge on a time scale of approximately 60 years. Ten (10) samples were collected at variable location along with geographical coordinate of the sampling points in Funtua metropolis. The samples were collected from surface and groundwater which undergo three stages of tritium analysis viz: Screening, Tritium enrichment (Electrolysis) and Scintillation counting. The results showed that recharge to groundwater of Funtua metropolis is a mix of modern and sub-modern water which is younger than (55) fifty five years by the mid-2000s.

Keywords: Tritium, Isotopes, Tritium unit (TU), thermonuclear explosion, Atmosphere, Radioactive elements

1.0   Introduction

Groundwater is very crucial to the development of agricultural and industrial activities in Katsina state in particular and world at large. Funtua local government is considered to be the industrial and agricultural base of the state. It was estimated that more than half of various farm product produced in the state are from this area [1].

Unfortunately, in recent years industrial and agricultural activities has been frequently thwarted by the intermittent seasonal nature of the groundwater which lead to the closure of many industries and poor irrigation farming in the area. Therefore this research work intends to measure the replenishment of groundwater in the area from the tritium bomb era (1950s).

Water, being a matter, consists of various isotopes of which most frequently occurring are those of hydrogen (H) and oxygen (O), while a smaller fraction consist of their rare isotopes of deuterium(D) , tritium (T) and Oxygen eighteen(^{18}O)[2,3,4]. All of these isotopes are stable except tritium (T) which is radio isotope with half-life of 12.32yrs. Tritium is produced naturally in the Earth's atmosphere, though its main use in hydrology stems from its production in large quantities by atmospheric testing of thermonuclear bombs. During this period, artificial tritium of 236x1018Bq was released into the earth [5], which amounts to about 181 times higher than that of natural tritium in the earth. Since 1952, tritium contents of precipitation and groundwater increased and reached a peak in 1963. Tritium activities in continental precipitation prior to the advent of nuclear weapons testing in 1952 were in the range of 1 to 20 TU's [1]: tritium concentration in surface water on land is found to be 2-8TU (0.2 - 0.9Bq/L) whereas 1TU (0.1Bq/L) in the surface ocean. In late 1963, a moratorium on atmospheric testing was declared, and tritium activities in precipitation have decreased since then to pre-1953 levels. Tritium is thus used as an indicator of pre-1953 or post-1953 recharge of groundwater. The case of absence of tritium, however, could be indicative of either recharge not being significant during the above-cited period, or the travel times involved in the systems being longer than the time required for the decay of the isotope during its transport [6]. The tritium content of water is expressed in tritium units (TU). One tritium unit is defined as one atom of ^{3}H per 1018atoms of hydrogen, which is equivalent to a specific activity of 0.118 Bq/L or 3.19 pCi/L of water.

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2.0 Material and Method
2.1. Hydrology the Study Area

Funtua metropolis, the largest local government in Katsina state of Nigeria, is located at latitudes 11^o31'N and longitudes 7^o18'. Also, it covers an area of about 448km^2 [1].Groundwater potential is higher in the limited areas of sedimentary rock, and it occurs in perched aquifers as well as in confined and semi confined aquifers. The groundwater potential is seasonal in the basement complex area and the success ratio of borehole is lower because of the limited depth of regolith, its clay content, and the localized occurrences of factures and joints. However, the basement area has higher surface runoff potential. There are two dams in this area: Gwaigwaye and Mairuwa dams. Gwaigwaye dam is about 900m in length and about 150m width with an area of about 135000m^2[1]. Informations about Mairuwa dam are not available. Figure 1 shows the map of the dams in Katsina State.

2.2 Reviews

Tritium concentrations in groundwater system of the Basement Complex Terrain of Kano metropolis (Nigeria) were used to determine mean-residence time of groundwater in the Aquifer. The groundwater was exploited for both domestic and industrial use. Using Isotope Techniques in groundwater, samples were collected from 28 selected motorized boreholes in the year 2010, the results generally, indicated that recharge togroundwater of Kano metropolis is 'Modern' (water younger than 50 years) [7].
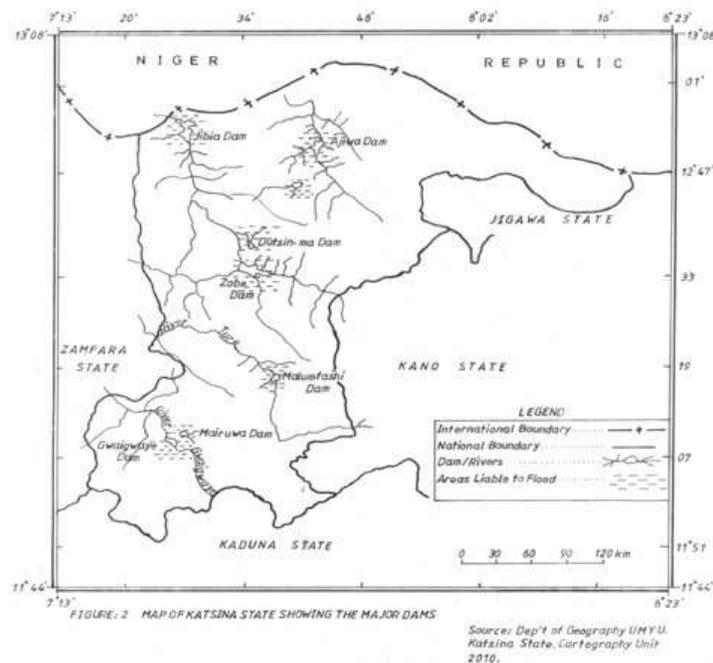
Fig.1. Major dams in Katsina state.

3.0 Tritium Concentration

Tritium concentration in surface water and groundwater increased after the beginning of thermonuclear test and becomes larger than that of precipitation after the end of aerial thermonuclear tests. In groundwater, tritium concentration can be varied from place to place even in a small area. The formation rate of tritium depends on cosmic rays produced by neutron flux. The neutron flux is four times greater in the polar region than in the equatorial region [8]. Therefore, tritium concentration is higher in higher latitudes even after the artificial tritium has disappeared. Groundwater dating based on tritium uses the fact that the initial concentration A_0 (expressed in TU) in recharging groundwater decreases with time according to the decay equation

A (t) = $A_o e^{-\lambda t}$ (1)

where A (t) is the tritium concentration measured in a sample after decay over time t and λ is the decay constant.

3.1 Sample Collection and Methodology

The samples were collected on monthly basis inthis researcher work. Latitude, longitude, altitude and instiu temperature of the sampling points were dully recorded. The water samples were collected in a high-density polyethylene bottle and stored in dark room at room temperature. The geology and hydrological data of the area were not recorded and also the chemical analysis of the sample water was not done.

### 3.1.1   Surface-water Sampling

The sample of unfiltered, unacidified Surface water was collected from two selected dams,. This is done after the water was well stirred so as to get a true isotopic representative of the surface water aquifer in the sample water and immediately a high-density bottle was deep into the water filled up and closed from inside the water in order to avoid fractionation.

3.1.2   Groundwater Sampling

The sample of unfiltered, unacidified groundwater is collected from random selected hand-pump motorized boreholes that are in continuous abstraction and whose depth, location and hydraulic information is known. The samples were collected after pumping for about 5 minute, if water was not already being pumped prior to arrival at the pump site. This is to purge the boreholes of stagnant water around the pump parts, so that the water sample is isotopic representative of the aquifer.

3.1.3   The Radioactive Isotopes of Hydrogen, ^{3}H

The radioactive isotope of hydrogen, ^{3}H, naturally originates from a nuclear reaction between atmospheric nitrogen and thermal neutrons in the upper atmosphere [9]:

$$^{14}N + n \rightarrow 3H + {}^{12}C \quad (2)$$
$$^{2}H + n \rightarrow {}^{3}H + \boldsymbol{gammaray} \quad (3)$$
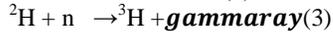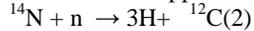
The ^{3}H thus formed naturally and bomb tritium enters the hydrologic cycle after oxidation to $^1H^3HO$, it reaches the surface of the earth as part of rain water, in which it is essentially a conservative tracer. Production rate of natural tritium in the atmosphere is estimated to be 2500 atoms/m2/s (troposphere: 840, stratosphere: 1660)[10]. Tritium finally decays according to the equation:

$$^{3}H \rightarrow {}^{3}He + \boldsymbol{\beta}- \tag{4}$$

with $E_{\beta max} = 18 KeV$ and half-life of 12.32 years.
The experimental analysis of Tritium is carried out in three stages viz:

- Screening,
- Electrolysis
- Scintillation counting.

3.1.4   Screening

Water samples for tritium analysis were distilled in order to remove particles and purify it of all forms of impurity. Thus an initial screening of the tritium concentration was carried out. This step can be left out, if water with known environmental tritium concentration, i.e. well >100 TU, is sampled. 10ml of the sample were mixed with 11ml Ultima Gold liquid scintillator in a counting vial. The samples were then placed in the Low-Level liquid scintillation analyzer,Packard Tri-Carb 2770TR/SL., and counted for three cycles of four hours. Samples found with tritium concentration of less than 100TU were subsequently enriched by electrolysis.

3.1.5   Electrolysis

Electrolytic enrichment of tritium more than 10 times is recommended prior to the measurement by a liquid scintillation counter. A volume of some 500 mil of the screen sampled water was mixed with four gram of sodium peroxide and introduced into the electrolytic cell. A direct current of some 5-10 ampere at 12V was passed through the cell, which was cooled because of process heat generation. After several days (at least five days), the electrolyte volume was reduced to some 20 mil. This volume reduction of 25 times produces a corresponding tritium enrichment factor of about 20. Samples of standard known tritium concentration (spike) were run in one cell of each batch to check on the enrichment attained. The screen sampled water was electrolyzed to hydrogen and oxygen. Tritium, the heaviest isotope of hydrogen, strongly enriches in water phase rather than in hydrogen gas, therefore, tritium separation factor between water and hydrogen is highly significant[4].

3.1.6   Counting

To measure tritium, it is recommended to use a low-background type liquid scintillation counter, which is equipped with an anti-coincident counter, and lead shield that largely reduces background of cosmic ray and other form of radiation. For liquid scintillation counting, the enriched water sample is directly distilled (vacuum distillation) from the now highly concentrated electrolyte. A ten mil volume of the vacuum distilled water sample is mixed with eleven mil (11ml) Ultima Gold cocktail in a counting vial. The sample is then placed in the Packard Tri-Carb 2770TR/SL Low-Level liquid scintillation analyzer and counted for 2-3 cycles of 4 hours [11]. Detection limits are 0.2TU for enriched samples.

4.0   Theoretical Consideration

The great dilution by H_2O results in very low concentrations which can be measured only by means of tritium's radioactivity, usually after an isotopic enrichment treatment. Thus tritium activity needs to be calculated throughout the period of the project as explained below.

4.1 Calculation of Tritium Content In Water
4.1.1 Calculation of Counting Efficiency (C.E.)
The activity of the standard solution at the midpoint of counting time (dpm/ml) is determined as follows:

The standard solution has a certain activity at the date of its preparation but this activity changes with time due to the radioactive decay phenomena [12]. Therefore, the time between the date of preparation of the standard solution and midpoint of counting date is computed.

The decay factor used was $e^{-\lambda t}$

where $\quad \lambda = In\left[\dfrac{2}{T_{1/2}}\right]$ (5)

$T_{1/2} =$ half- life of tritium = 12.32 year, t = midpoint of counting.

The net counts per minute for samples-blanks and standard solution after electrolytic enrichment step is determined as follows:

$$(net\ cpm)_{sample\ or\ standard} = (average\ cpm)_{sample\ or\ standard} - (average\ cpm)_{background}$$

The net cpm per ml (net cpm/ml) for samples-blanks and standard solution after the enrichment step is determined by using the following formula:

$$net\ cpm/ml = \frac{(net\ cpm)_{sample\ or\ standard}}{volume\ of\ sample\ counted\ (normally\ 3\ ml)}$$ (6)

The counting efficiency (C. E.) is calculated as follows:

$$C.E. = \frac{(net\ cpm)_{standard}}{Activity\ of\ standard\ solution} \times 100$$ (7)

The net cpm/ ml for all samples-blanks and standard solution taking part in the enrichment step is determined as follows:

$$net\ cpm/ml = \frac{Activity\ of\ standard\ solution}{ml} \times 100$$ (8)

4.1.2 Calculation of Electrolysis Efficiency (E.E)
The electrolysis efficiency of each standard solution (E.E. standard) taking part in the enrichment step is calculated using the following equation:

$$E.E. = \frac{dpm/ml}{dpm_o/ml} \times \frac{V}{V_o}$$ (9)

where

$$dpm_o/ml = \frac{(dpm/ml)_{standard\ solution} \times volume\ of\ standard\ used}{V_o}$$ (10)

$V_o =$ initial volume before enrichment = 250 ml

$V =$ final volume after enrichment

The volume of the standard used is 1 ml, which is added to 249 ml of tritium-free water (dead water). This dead water is obtained from the Western Desert Oasis known to have no tritium.

The enrichment factor, B, for each standard solution cell, which took part in the enrichment step, is calculated as follows:

$$B = -[\frac{\log \frac{V}{V_o}}{\log E.E._{\cdot standard}}]$$ (11)

The average enrichment factor (B*) for three standard solutions is determined. The Electrolysis Enrichment Efficiency of each water sample of unknown tritium content is calculated as follows:

$$\log E.E._{\cdot Sample} = \frac{-1}{B^*} \log \frac{V_o}{V}$$ (12)

(dpm/ml) for each sample and unknown tritium content is calculated as follows:

$$(dpm_o/ml)_{Sample} = \frac{(dpm/ml)_{standard}}{E.E._{\cdot Sample}} \times \frac{V}{V_o}$$ (13)

The concentration of tritium expressed as T.U. for each water sample is determined as follows:

$$T.U. = \frac{(dpm_o/ml)}{0.0072}$$ (14)

The tritium activity of natural water samples is usually expressed in terms of tritium unit;

1   T.U. = 1 tritium atom/ 10^{18} hydrogen atom, or   1 T.U. = 7.2 dpm/l = 0.0072 dpm/m

5.0 Result and Discussion
The results of tritium analysis of water samples collected under this work was obtained using liquid scintillation analyzer. Table 5.1 shows the measured tritium of water samples collected from Funtua metropolis. The detection limits were 0.2 TU for enriched samples.

Table 5.1 The analytical result of the water samples collected from the study area along sided with the geographical coordinate and date of sample collection.

Sampled Date	Sample Identification	Tritium concentration in (TU)	Latitude (m)	Longitude (m)	Altitude (m)
25/05/2010	MDWS19	3.2 ± 0.3	N1135.175'	E00714.220'	2106
03/01/2011	MDWS20	3.4 ± 0.3	N1135.218'	E00714.248'	2100
25/05/2010	GDWS21	2.5 ± 0.3	N1134.555'	E00712.326'	2075
03/01/2011	GDWS22	2.4 ± 0.3	N1134.584'	E00712.493'	2058
03/01/2011	DWWS23	2.3 ± 0.3	N1131.581'	E00715.063'	2150
13/01/2011	JWWS24	2.6 ± 0.3	N1130.006'	E00719.063'	2351
05/01/2011	BWWS25	2.9 ± 0.3	N1131.908'	E00719.185'	2305
09/01/2011	FWWS26	3.7 ± 0.3	N1131.629'	E00718.688'	2320
09/01/2011	KWWS27	2.5 ± 0.3	N1131.463'	E00718.160'	2337
25/01/2011	TWWS28	1.0 ± 0.3	N1131.233'	E00719.055'	2315

Tritium is a relatively short-lived isotope, having a half-life of 12.32 years [13, 14]. Thus, the hydrological evaluation of tritium measurements in natural water not more than a few decades old is now based principally on the determination of bomb-induced tritium in order to distinguish more recent from older waters [15]. Low tritium concentrations, around 0.8TU to 4TU indicates mix of sub modern and modern water, but any concentration less than 0.8TU shows that the water stems principally from the pre-bomb period (before 1952). Relatively high concentrations, greater than 10 TU, indicate that the water partly or wholly from post-bomb precipitation [15, 16]. The groundwater tritium concentration in Funtua metropolis, range from $1.0 \pm 0.2 TU$ to 3.7 ± 0.4 TU with a mean value of 2.4 ± 0.3 TU. These relatively low concentrations indicate that the groundwater is a mix of sub modern and modern water and it also implies that the groundwater in the study area was younger than fifty five (55) years by the mid 2000s.

6.0   Conclusion

Tritium provides information about groundwater's age (Mean residence time), which refers to the last time the water, was in contact with the atmosphere.The southern part of the state groundwater tritium concentration range from $1.0 \pm 0.2 TU$ to 3.7 ± 0.4 TU with a mean value of 2.4 ± 0.3 TU. These relatively low concentrations indicate that the groundwater is a mix of sub modern and modern water and it also implies that the groundwater in the study area was younger than fifty five (55) years by the mid-2000s [15, 16].

7.0   Acknowledgement

Reference

[1]   Tukur M.L. 2009. *Funtua metropolis : A history of Maska District and Funtua metropolis.*University of Wisconsin-Madison, 1998. *Radiation safety for radiation workers handbook.*

[2]   Yurtsever, Y. and Araguas, L. A. (1993). Environmental isotope applications in hydrology: An overview of the IAEA's activities, experiences, and prospects. Proc. of the Yokohama Symp. July 1993. IAHS Publ. No. 215

[3]   Gudmundsson,K (2000).Isotopic tracing of moisture in buildings.Nordic Journal of Building Physics, Vol.2pp22

[4]   International Hydrological Progrmme (2001). 11th International Course on Hydrogen and Oxygen Isotopes in Hydrology. ISBN: 4-9980619-3-3, Nagoya University COOP.

[5]   United Nations Scientific Committee on the Effects of Atomic Radiation (1982). 1982 report on "Ionizing radiation: sources and biological effects", United Nations, New York.

[6]   Nair, RA.,Pendharkar, A.S. Navada,S.V.and Rao,S.M.(1979)Groundwater studies in Matrashtra. Development of isotope techques and field experience. Proc.Symp.Isotope Hydrology, 19-23 June 1978, Neuherberg, IAEA, Vienna 803-826

[7]   Sani M.G. et al (2012). Mean-Residence Time of Groundwater in the Basement ComplexTerrain of Kano Metropolis (Nigeria) Estimated from Tritium Radioisotope, *Journal of Applied Physics (IOSR-JAP)ISSN: 2278-4861. Volume 2, Issue 5 (Nov. - Dec. 2012), PP 36-41*

[8]   Fontes, J.C.(1980). Environmental isotopes in groundwater hydrology. Handbook of environmental isotope geochemistry, 75-140,Elsevier, Amsterdam.

[9]   Libby, W. F. (1946). Atmospheric helium-3 and radiocarbon from cosmic radiation. Phys. Rev. 69: 671-672.

[10]   United Nations Scientific Committee on the Effects of Atomic Radiation (1982). 1982 report on "Ionizing radiation: Sources andbiological effects", United Nations, New York.

[11]   Pakard instrument company(1995). Tri-Cab Liquid scintillation Analyzerrs: models 2100TR/2300

[12]   Franz,s. (1995). Liquid Scintillation Spectrometry in environmental measurements. The science of the Total Environment 173/174;29-40

[13]   Clark, I.D. and Fritz, P. (1997). Environmental isotopes in hydrology. Lewis Publishers, New York, 328p.

[14]   International Atomic Energy Agency (1981). Statistical treatment of environmental isotope data in Precipitation. Technical Report Series No. 206. STI/DOC/10/206.

[15]   William E. Motzer (1994). Age Dating GroundwaterUnpublished paper.http://www.environmentalisotopes.com

[16]   Campana, M. E. and Mahin, D. A. (1985). Model-derived estimate of groundwater mean ages, recharge rates, effective porosities and storage in a limestone aquifer, *Journal of Hydrology. 76*: 217-264