**Application of Chlorine-36 Technique in Determining the Age of Modern Groundwater in Al-Zulfi Province**

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**Abstract.** The present study aims to estimate the residence-time of groundwater based on bomb-produced $^{36}\text{Cl}$. Water samples were collected from some selected wells located around Al-Zulfi province, Riyadh central region, Saudi Arabia. $^{36}\text{Cl}/\text{Cl}$ ratios in the water samples are determined by Inductively Coupled Plasma Mass Spectrometry (ICPMS) and Liquid Scintillation Counting (LSC). $^{36}\text{Cl}/\text{Cl}$ ratios in the groundwater were estimated to be $1.0\sim2.0\times10^{-10}$. The shallow unconfined aquifer of the area is mainly replenished by the water infiltration from the seasonal rains. Estimates of residence time were obtained by comparing the measured bomb-derived $^{36}\text{Cl}$ concentrations in groundwater with the background reference. Dating based on a $^{36}\text{Cl}$ bomb pulse may be more reliable and sensitive for groundwater recharged before 1975, back as far as the mid-1950s. The above $^{36}\text{Cl}$-background concentration was deduced by determining accurately the background corrected Dye-3 ice core data from the frozen Arctic Data, according to the estimated total $^{36}\text{Cl}$ resources, including bomb-produced $^{36}\text{Cl}$ fallout. Estimated residence time of $7.81\times10^4$ y is obtained from extrapolated flow velocity. $^{36}\text{Cl}$ concentration in groundwater does not reflect the input of bomb pulse $^{36}\text{Cl}$, and it belongs to the era before 1950.

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1. Introduction

In Saudi Arabia, the citizens usually use the groundwater as a main source of washing-water in houses, cities as well as in farms. The wells that supply the Al-Zulfi province with groundwater may differ; these depend on the situation of wells and nature of their basins, and the surrounding sources that replenish them from the seasonal rainfall through surroundings, mountains and valleys. We have to know how long it will take for the recovery of these well resources to be accomplished. The Al-Zulfi province is situated at the bottom of a valley between two huge dunes of red sands of special composition. The Surroundings Mountains of this valley play major effects on replenishing its groundwater aquifer. Our objective in this work is to make a complete view of how long the age of groundwater in Al-Zulfi province.

Making acquaintance with the isotopic of a selective isotope like $^{36}\text{Cl}/\text{Cl}$ ratios, which could be helpful in giving information about the groundwater age and its replenishing rate (Phillips et al., 2013). Previously, $^3\text{H}/^3\text{He}$ ratios were used to determine the groundwater age. Since large quantities of $^3\text{H}$ were produced during atmospheric thermonuclear testing, $^3\text{H}$ concentrations in precipitation reached a peak around 1963, resulting in a bomb pulse in the hydrological cycle. Tritium ($^3\text{H}$) has been one of the most useful environmental tracers for the dating of modern groundwater (age ~25 years) (Gates, 2013). Recently, several tracers have been successfully utilized; e.g., tritiogenic $^3\text{He}$ ($^3\text{He}$ produced by $^3\text{H}$ decay; $^3\text{H}/^3\text{He}$ method) (Gates, 2013), CFCs (Chlorofluorocarbons) (Han, 2007), $\text{SF}_6$ (Busenberg, 2008) and $^{85}\text{Kr}$ (Corcho Alvarado, 2007). Tritiogenic $^3\text{He}$ and CFCs, especially, are extensively used in groundwater studies. Comparison of methods for the detection and extrapolation of trends in groundwater quality, due to (1) statistical methods, (2) groundwater dating, (3) transfer functions, and (4) deterministic modeling was carried out by (Visser Ate et al., 2009). However, due to the relatively short half-life of $^3\text{H}$ (12.33 years), the $^3\text{H}$ bomb pulse has been attenuated significantly through radioactive decay. This leads to a need for another tracer or dating method applicable in modern groundwater studies. As an alternative, the application of bomb-produced chlorine-36 ($^{36}\text{Cl}$) was proposed by Kurth et al (Kurth et al., 2011). $^{36}\text{Cl}$ is a long-lived radioisotope of chlorine with a half-life of $(3.01 \times 10^5 \text{ years})$ (Baskaran, 2011). Natural $^{36}\text{Cl}$ is mainly produced in the following resources ways: (i) rain-out of $^{36}\text{Cl}$ from cosmic-ray induced spallation of atmospheric $^{40}\text{Ar}$. (ii) Capture of secondary cosmic-ray neutrons by $^{36}\text{Cl}$ in seawater and cosmic-ray spallation of $\text{K}$, $\text{Ca}$. (iii) Runoff of $^{36}\text{Cl}$ produced in situ in the continental crust and mobilized by weathering. (iv) Capture of neutrons by oceanic $^{36}\text{Cl}$ during nuclear weapons testing in the 1950s and 1960s (Keywood et al., 1998). Amongst these four sources, (1) cosmic-ray spallation in the atmosphere is the most natural source of $^{36}\text{Cl}$ in groundwater, in addition to significant amounts of $^{36}\text{Cl}$ which were produced by neutron activation of $^{35}\text{Cl}$ in seawater during thermonuclear testing on small islands or on barges, and this bomb-$^{36}\text{Cl}$ was injected into the atmosphere. The $^{36}\text{Cl}$ produced in the atmosphere is mixed with marine-derived stable chlorine (from sea spray) and falls onto the earth’s surface, with the greatest fallout occurring at mid-latitudes (Plummer et al., 1997). Fallout of this bomb-$^{36}\text{Cl}$ has been preserved in ice...
cores; for example, the Dye-3 cores from Greenland (Lecavalier, 2013), show a $^{36}\text{Cl}$ peak in the late 1950s (several years prior to the $^3\text{H}$ peak). The bomb-pulse $^{36}\text{Cl}$ is thought to have a latitudinal distribution with greatest deposition at mid-latitudes (Baskaran, 2011). Chlorine is geochemically conservative in hydrological cycle because it has a high electron affinity and it exists primarily as $\text{Cl}^-$ in the environment, except under low pH condition. This makes chlorine an ideal tracer in hydrology, and also makes sampling for $^{36}\text{Cl}$ very straightforward with these advantages and its long half-life.

The groundwater ages of the samples had been estimated by the $^3\text{H}/^3\text{He}$ method (Corcho Alvarado, 2013). The bomb-produced pulse of ($^{36}\text{Cl}$) is more accurate due to the long-lived radioisotope of chlorine with a half-life of $(3.01 \times 10^5 \text{ years})$ of decays mainly by pure $\beta^-$ emission of $E_{\text{max}}=708.6 \text{ keV}$, $\beta^-$ decay intensity of 98.1% and EC decay intensity of 1.9 %. $^{36}\text{Cl}$ measurement is normally carried out by Liquid Scintillation Counting ($\text{LSC}$). In the case of the $^{36}\text{Cl}$ bomb pulse, the long half-life makes decay attenuation negligible on the time scale of several decades to centuries (in contrast to $^3\text{H}$). Thus, the $^{36}\text{Cl}$ bomb pulse provides a potential dating tool covering the last $\sim 25$ years. Few studies have investigated the application of $^{36}\text{Cl}$ as a dating tool (Corcho Alvarado, 2013). One approach to quantitatively investigate the potential use of $^{36}\text{Cl}$ is to reconstruct its fallout rates from measured $^{36}\text{Cl}/\text{Cl}$ ratios in groundwater. The $^{36}\text{Cl}$ fallout rates in Denmark, as reconstructed by (Alvarado et al., 2005), exceeded the estimates based on data from the Dye-3 ice core, Poland (Dowgielo et al., 1990). The authors attributed this discrepancy to the storage and recycling of chlorine in the biosphere (Scheffel, 1999). The $^{36}\text{Cl}$ fallout rates in Greenland, as reconstructed by Lecavalier (Lecavalier, 2013), were consistent with Dye-3 fallout data, suggesting that the successful application of $^{36}\text{Cl}$ is dependent of the conditions of the study site. To the best of our knowledge very few studies have used $^{36}\text{Cl}$ to quantitatively estimate the residence time of young groundwater. Several researchers used this technique to measure the isotopic ratios $^{36}\text{Cl}/\text{Cl}$ and identify the age of media in fossil rat urine as (Plummer et al., 1997). The main tool for analyzing these ratios is the Inductively Coupled Plasma Mass Spectrometry ($\text{ICP-MS}$) (Sturchio, 2009) and X-ray fluorescence ($\text{XRF}$) technique used for elemental analysis (Melquiades et al., 2013). The Arabic region $^{81}\text{Kr}$ and $^{36}\text{Cl}$ were previously used to reveal a one million year old groundwater in the Sahara (Plummer et al., 2012). $^{36}\text{Cl}$ has been applied to the dating of very old groundwater in such regions as Atlantic Coastal Plain, Maryland, USA (Plummer et al., 2012) and the Nubian Aquifer of Egypt (Sturchio, 2004). Although it has been applied $^{36}\text{Cl}$ studies to estimate recharge rates for the unsaturated zone (soil waters) (Phillips et al., 2013), there are studies applying the $^{36}\text{Cl}$ bomb pulse to groundwater (Corcho Alvarado, 2013).

Hydrogeology and groundwater chemistry of the central region have been previously investigated (Abdulaay Abdulrahman I., 1994) in which the groundwater of the region is characterized by high levels of $(\text{pH})$, $(\text{TDS})$, calcium, chloride, sodium, and sulfate. Some used numerical groundwater flow modeling to understand
and to manage the resource properly. To evaluate the impact of groundwater withdrawals from wells on future groundwater levels under different groundwater pumping scenarios using numerical techniques (Al-Salamah, 2000), radon levels were measured in eight water supply municipalities of the Central Region of Saudi Arabia (Alabdula'aly, 1999). An assessment of trace metals in the raw and product waters of 8 water treatment plants in Riyadh, Buraydah and Unayzah (Saudi Arabia) were carried out by Alabdula'aly (Alabdula'aly, 1998). The samples were analyzed by inductively coupled plasma spectrophotometer (ICP-MS) (Alabdula'aly, 1998). King Abdulaziz City for Science and Technology (KACST) has initiated a program to study the mobile drinking water treatment plant (MDWTP) in the central region of Saudi Arabia (Alabdula'aly, 1994). For the basin in the western part of Saudi Arabia (Wadi Yalamlam) (Subyani, 2006), Subyani used the classical and refined chloride mass balance (CMB) approach. The modified (CMB) method takes into consideration additional statistical parameters, which are variances and the correlation coefficient between variables concerned based on the application of the perturbation method. This refined method provides the recharge rate of groundwater and estimates the future need or adequacy. Due to rapid and comprehensive developments during the last three decades in the social, industrial, agricultural and construction sectors in the Eastern Provinces in Saudi Arabia, expansion of agricultural areas and excessive use of irrigation water has resulted in the formation and continuous rise of a shallow water-table. The shallow groundwater has continued to rise with the expansion of the irrigated agriculture. Chemical analyses of water samples indicate that the shallow groundwater table is contaminated with high concentrations of salts in addition to trace elements (Abderrahman, 2000).

2. Experimental procedures and calculation methods

2.1. Materials and methods

The study sites and groundwater sampling from Al-Zulfi province is a large polder (reclaimed land) area which is located in north central region Riyadh of Saudi Arabia. Coordinates of sampling points are located along the major groundwater flow direction presented in Table (1), at each point, groundwater samples were obtained from the well at outlet pipe that bring the water from the well directly. Seven aquifer wells were selected; all samples of volume (20 liters) were stored in polyethylene bottles, was kept refrigerated at 4°C until the results for Cl were received. This allowed calculation of the volume needed for 36Cl analysis. Each sample was slowly evaporated in clean environment was needed, yielding a final volumes of 200 ml.

All samples for measurements of 36Cl were passed through 0.45 µm filters (JHWP04700, Millipore). The samples were then processed according to the preparation scheme shown in fig. (1). Water samples containing ~10 mg of Cl were acidified with 10 ml of 13 M of HNO3. Chloride was then precipitated as silver chloride (AgCl) by adding excess AgNO3, and was separated by centrifugation. The AgCl precipitate was dissolved once in 3 M of NH4OH, and saturated Ba(NO3)2 solution was added to the solution. The
solution was allowed to stand overnight in an oven at ~60 °C, to effectively precipitate SO$_4^{2-}$ as BaSO$_4$. This precipitate was removed by filtration with a 0.20 μm membrane filter (25HP020AN, Advantec), and the filtrate was acidified by the addition of 13 M of HNO$_3$ to precipitate AgCl again. The Ag$^{36}$Cl was then dissolved in the minimum volume of concentrated ammonia and diluting to 11 ml with water and added to 9 ml. ULTIMA Gold AB (part number 6013309).

![Chemical separation and counting sequences for $^{36}$Cl in water samples](image)

Figure (1) The chemical separation and counting sequences for $^{36}$Cl in water samples

Al-Zulfi is located at the north side of the Riyadh region, Al-Zulfi flows northward on the border between Riyadh and Qassim regions. Al-Zulfi is situated between to two huge mountains of duns that are called Al-Thuoyrat at the east and
Al-Tweeq at the west in the whole city of Al-Zulfi and it belongs to villages surroundings settled in this valley. Groundwater samples will be obtained from selected wells; sampling points are located along the major groundwater well sites distributed in Al-Zulfi province. At each site, groundwater samples were obtained from different wells dispersed in this site, water flow and velocities. The general features of the study area of groundwater samples from Al-Zulfi aquifers were collected along a SE–NW traverse in Al-Riyadh region. Al-Zulfi (sometimes said Az-Zulfi) is situated at 26.3° North latitude, 44.8° East longitude and 623 meters elevation above the sea level. Al Zulfi lies in the northern-central region of the Najd and to the south of the Sheayb Samnan (Samnan Valley), which is the longest valley in the Al-Zulfi province. It is surrounded by sand dunes to its north and west, which are known locally as the Al-Thoyr Sands. The Al-Sabalh woods are located to the north of the city. Next to Al-Zulfi is the Al-Kasar rain lake (or bohyrat Al-Kasar), which is considered an official part of the city. Al-Zulfi has three artificial lakes due to the problems of water salination. Al-Zulfi is noted for its many wells and fertile soils with many thousands of acres of land under cultivation. There are also coal reserves in the area, especially in the northeast near Qassim. The thickness of the deposits range from 5 to 50 meters and are spread over a vast area with some 66 coal mines discovered in the Qassim area in the early 1980s (Roy, 2006). The surface lowering of the investigated area on average is about 30 m above sea level. The area lies mainly below the sea water level, consequently and the rain water is permanently infiltrates into the shallow aquifer. The aquifer consists of fine to medium sized sands and the thickness is about 2–3 mm on the average, along the cross down banks of the area and recharged by rain water infiltration only. Seven groundwater samples were obtained from wells area in September 2013.

Table (1). Sample locations and distances from city center.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Coordinates: Latitude / Longitude</th>
<th>Distance from City Center (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>N26° 15' 35.04&quot;/E44° 44' 05.07&quot;</td>
<td>9.5</td>
</tr>
<tr>
<td>6</td>
<td>N26° 15' 32.45&quot;/E44° 43' 55.11&quot;</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>N26° 15' 25.44&quot;/E44° 43' 47.50&quot;</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>N26° 14' 14.03&quot;/E44° 40' 18.82&quot;</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>N26° 14' 47.72&quot;/E44° 37' 08.22&quot;</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>N26° 13' 08.30&quot;/E44° 36' 02.66&quot;</td>
<td>27</td>
</tr>
<tr>
<td>1</td>
<td>N26° 11' 07.42&quot;/E44° 30' 58.30&quot;</td>
<td>35</td>
</tr>
</tbody>
</table>

2.2. ICP and LSC measurements

Groundwater samples were analyzed for Cl⁻ and ³⁶Cl. All samples were filtered through 0.20 μm filter. The total Cl⁻ concentrations of aliquots were determined by (ICP-MS) (Hou et al., 2007). LSC used for radioactive ³⁶Cl (Bruyere and Cadwallader, 2012). Mass spectrometric measurements were performed using a double-focusing magnetic-sector field ICP-MS (Finnigan Element2, Bremen, Germany). Aqueous solutions were introduced into the ICP-MS with a SC-4 autosampler, an Apex nebulizing system connected to an ACM desolvator and a self-
aspirating PFA-ST-nebulizer (all from Elemental Scientific Incorporation, Omaha, USA). The sample was first introduced to an argon plasma torch using a nebulizer spray chamber. The argon plasma transformed all constituents to ionized elements. The ions were passed through a vacuum interface, a focusing lens and into the quadrupole mass separator. The ions were focused onto a detector that counts individual events at a particular charge-to-mass ratio. Commercial instruments have the capability of scanning the mass range from 1 to 240 atomic mass units (amu) in a few tenths of a second and achieving detection limits in the 0.1 to 1 ppb range during that time. This technique has potential isobaric interferences, resulting from combinations of abundant ions in the mass spectrometer. An instance of isobaric interference comes from a combination of $^{35}\text{Cl}$ and $^1\text{H}$ as a combined ion yielding a signal at mass number 36. $^1\text{H}$ would come from the water matrix. Thus, an interference correction must be applied. Because of the isobar $^{36}\text{S}$ (natural abundance, 0.02%) strongly interferes with $^{36}\text{Cl}$ measurements, the chemical reduction of sulfur is of major importance in preparing AgCl samples. The removal of sulfur (in the form of $\text{SO}_4^{2-}$) can be achieved by the precipitation of $\text{BaSO}_4$, by differential elution from an anion exchange resin, or by absorption onto a cation exchange resin (in the form of $\text{BaSO}_4$). The main part of sample preparation, including sulfur reduction, was performed in an air-conditioned room to prevent additional sulfur contamination and was performed under dark conditions to avoid the photolytic decomposition of AgCl. The sample was purified by repeated precipitation of AgCl with $\text{HNO}_3$ and dissolution in $\text{NH}_4\text{OH}$. To further exclude remaining impurities, the AgCl precipitate was washed with Milli-Q ultrapure water twice and with 99.5% $\text{C}_2\text{H}_5\text{OH}$ twice using ultrasonic vibration. The overall chemical yield of chlorine was typically about 80%.

The \textit{LSC} is well suited to detect the low energy beta particles emitted by tritium decay (Bruyere and Cadwallader, 2012). In this work we are using the (PerkinElmer Tri-Carb 2910 TR) ultra-low-level liquid scintillation \(\alpha/\beta\) spectrometer. Quenching effects of the measuring system were carefully examined and the results were corrected accordingly. The causes of quench, the types of quench, and the methods for quench correction have been widely studied (Chen and Lu, 2014). In a chemical quench, chemicals with negative electron affinity (e.g. chlorinated solvents) capture electrons transferring between solvents and solutes, reducing the energy intensity or terminating the energy transfer. The consequence of chemical quench is a shift in the pulse spectrum of the \textit{LSC} towards a lower energy range, resulting in decreased counts in a specific range of energy channels that have been set for optimal measurement conditions. Therefore, the counting windows must be adjusted to compensate for the pulse spectrum shift, and to reach optimal counting conditions (Gudelis et al., 2012). Disintegrations per minute (\textit{DPM}) is employed, and it is calculated with the formula given below:

\[
\text{DPM} = \frac{\text{CPM}}{(\epsilon \cdot I_e \cdot D_c)}
\]
Where, $CPM$ represents counts per minute, $\varepsilon$ represents the counting efficiency, $I_e$ represents emission intensity and $D_c$ represents decay correction. Tri-Carb® is a state-of-the-art liquid scintillation spectrometer that was described thoroughly by Tudyka and Pawlyta (Tudyka and Pawlyta, 2014). Tri-Carb® is a sophisticated liquid scintillation counting system for the measurement of a variety of low level radioactivity. The detector unit of Tri-Carb® has two photomultiplier tubes facing the counting vial with liquid scintillation cocktail (Ultima Gold® AB) for detecting the weak scintillation pulses caused by the decay of $^{36}\text{Cl}$ nuclides. LSC analysis was carried out by directly mixing 11 ml of the prepared Ag$^{36}\text{Cl}$ samples solution as described above and the quenching agent with 9 mL of the commercial cocktail, using FeCl$_3$ (III) as quencher. The minimum detectable activity (MDA) was evaluated using the following equation:

$$\text{MDA (Bq/L)} = L_d \left( \varepsilon T V \right)^{-1}$$

(2)

Where, $L_d$(counts) = 2.71 + 4.65$(BT)^{-0.5}$; $T$ represents counting time, $B$ represents background count rate ($s^{-1}$), $\varepsilon$ represents detection efficiency (~100%), and $V$ represents sample volume ($L$). The LLD for gross $\beta$ was 0.54 pCi/l for 500 min. of counting time, 11 ml of sample size, and 9 ml of cocktail. The calibration samples were prepared by adding the standard solutions ($\text{Na}^{36}\text{Cl}$) reagent and the quenching agent to the scintillation cocktail in glass vials.

2.3. Estimates of Residence Time

To estimate the groundwater residence time based on bomb-produced $^{36}\text{Cl}$, the measured $^{36}\text{Cl}/\text{Cl}$ ratios were converted to above-background (bomb-derived) $^{36}\text{Cl}$ concentrations (Cook, 2005) by (1) subtracting the background $^{36}\text{Cl}/\text{Cl}$ ratio from measured ratios, and multiplying by the $\text{Cl}^-$ concentrations to derive the above-background $^{36}\text{Cl}$ concentrations (atoms/l). Reference $^{36}\text{Cl}$ data are also required to estimate the residence time. These data were obtained as follows: (1) reduction of Dye-3 fallout data using the background $^{36}\text{Cl}$ flux at the Dye-3 site (Baskaran, 2011) to derive a time series of the above background $^{36}\text{Cl}$ flux; (2) linear scaling of the above-background $^{36}\text{Cl}/\text{Cl}$ flux using the estimated total bomb-produced $^{36}\text{Cl}$ fallout in seawater (Argento et al., 2010) after correcting for the difference resources of precipitation amount; (3) conversion of the scaled above-background $^{36}\text{Cl}$ flux to the above-background $^{36}\text{Cl}$ concentration by Argento et al. (Argento et al., 2010). The background $^{36}\text{Cl}/\text{Cl}$ ratio was assumed to be $(48 \pm 0.33) \times 10^{-15}$ (Argento et al., 2010). Table (2) lists $^{36}\text{Cl}/\text{Cl}$ ratios range after subtracting this value from the $^{36}\text{Cl}/\text{Cl}$ ratios measured for the samples. These values were multiplied by each $\text{Cl}^-$ concentration to obtain the above-background $^{36}\text{Cl}$ concentration. In contrast, yearly values of bomb-produced $^{36}\text{Cl}$ fallout (values above the background level) at the Dye-3 site were deduced by subtracting the natural background $^{36}\text{Cl}$ flux (20 ± 6 atoms/m$^2$/s) from the original Dye-3 fallout data. These values were then scaled with a scaling factor obtained in the manner described below:
In order to account for the effect of the Cl⁻ variation, we considered a two-component mixing process, assuming the Cl⁻ concentrations of the initial waters (i.e. before mixing) to be 27 mg/l. Extension of the mixing line through water infiltration that provides a Cl⁻ source along the path ended having a $^{36}\text{Cl}/\text{Cl}$ ratio of about $(61 \pm 4) \times 10^{-13}$ and an assumed Cl⁻ concentration of 92.05 mg/l. We calculated the initial $^{36}\text{Cl}/\text{Cl}$ ratio for each sample. After accounting for the effect of chloride concentration variation, the $^{36}\text{Cl}/\text{Cl}$ ratios were converted into $^{36}\text{Cl}$ fallout rates by using the mass balance equation below (Cook, 2000). The number of $^{36}\text{Cl}$ atoms can be expressed using the elapsed time $T$ for the groundwater residence time as follows:

$$^{36}\text{Cl} = R_m \cdot C_m = R_o \cdot C_l \cdot \exp \left( -\lambda_{36} t \right) + R_{eq} \cdot C_l \cdot \exp \left( t - \lambda_{36} t \right) + R_{eq} \cdot (C_l(T) - C_l)$$  \hspace{1cm} (3)

Where, $^{36}\text{Cl}$ is the $^{36}\text{Cl}$ concentration (atoms $^{36}\text{Cl}$/l), $C_l(T)$ is the total chlorine concentration in groundwater at time T; $C_l$ and $R_o$ are the initial recharging value of the chlorine concentration and the initial $^{36}\text{Cl}/\text{Cl}$ ratio, respectively, in rainwater infiltrated in the recharge zone; $R_{eq}$ is the secular equilibrium $^{36}\text{Cl}/\text{Cl}$ ratio in the water wells; $\lambda_{36}$ is the decay constant of $^{36}\text{Cl}$ ($2.31 \times 10^{-6}$ y⁻¹). We can rewrite Eq. (4) as follows:

$$^{36}\text{Cl} = C_l \cdot \left( R_o - R_{eq} \right) \cdot \exp \left( -\lambda_{36} \cdot t \right) + R_{eq} \cdot C_l(T)$$  \hspace{1cm} (4)

Using the subscript m to signify measured values and assuming $C_l(T)=C_{lm}$ and $^{36}\text{Cl}=R_mC_{lm}$, we can rewrite Eq. (5) as follows:

$$\left( R_m - R_{eq} \right) \cdot C_{lm} = C_l \cdot \left( R_o - R_{eq} \right) \cdot \exp \left( -\lambda_{36} \cdot t \right)$$  \hspace{1cm} (5)

We can rewrite Eq. (6) to solve for $T$ as follows:

$$\left( \frac{R_m - R_{eq}}{R_o - R_{eq}} \right) \cdot \left( \frac{C_{lm}}{C_l} \right) = \exp \left( -\lambda_{36} \cdot t \right)$$  \hspace{1cm} (6)

$$T = \frac{-1}{\lambda_{36}} \cdot \ln \left( \left( \frac{R_m - R_{eq}}{R_o - R_{eq}} \right) \cdot \left( \frac{C_{lm}}{C_l} \right) \right)$$  \hspace{1cm} (7)

We can estimate elapsed time $T$ from the groundwater flow velocity and position on the flow path. If we assume that groundwater flows with a constant velocity $V$ from the recharge zone to the discharge point (sampling water wells) along the flow path, we can derive the elapsed time as $T = L/V$, where $L$ is the distance along the selected flow paths. We can then rewrite Eq. (8) as follow:
Fig. (2) shows the data set of $L$ vs. $f$, from which we could estimate from the slope of the resulting line a constant velocity $V (m/y)$ of underway water from recharge zones to discharge area along the flow path. The residence time derivation along the flow path could be extracted using Eq. (9). We extrapolate groundwater velocity $V$ by correlating parameters of $^{36}Cl/Cl$ ratio and $Cl$ concentration and flow distance $L$ along the flow lines to the groundwater samples, as listed in Table (2). The estimated slope was -0.0116 for the flow path. The extrapolated velocity was $(2.68 \pm 1\%) \times 10^{-5} m/y$ along flow path. From the velocity and the flow distances extrapolation to zero, the estimated residence time of $7.81 \times 10^4 y$ is obtained. The given estimated ages for the dating of groundwater from flowing wells based on a $^{36}Cl$ bomb pulse may be more reliable and sensitive for groundwater recharged before 1975 and back as far as the mid-1950s.

3. Results and discussion

Table (2) lists $Cl$ concentrations, and $^{36}Cl$ data for the municipal water, and groundwater wells samples. The $Cl$ concentration increases from ~27.0 mg/l to ~92.05 mg/l with distance from the Al-Zulfi. One possible cause of the increase is mixing between the infiltrating of the surface water and groundwater. Although the unconfined aquifer is essentially an underway flow down of about 37 m, the groundwater is recharged to some extent by infiltration through the unsaturated zone by 115–150 mm/year. The $Cl$ concentration in the infiltrating water would be 0.93–3.18 mg/l. These values were calculated from 434 mm of mean annual precipitation (1951–1980) (Scheffel, 1999) with 0.34–1.1 mg/l of $Cl$ concentration . The mixing rate of the infiltrating water would be 74–65%, when the infiltration is responsible for all of the reduction in $Cl$ due to raising of mean annual recharge rate. However, the mean annual recharge rate 115–150 mm/year is considerable compared to the
thickness of the aquifer ~30 m and wide spread of surrounding dunes that collect the infiltrating rains, accordingly. The mixing of 74–65% of the infiltrating water should have occurred. Other phenomena such as the changes due to evaporation rate may have caused the variation in Cl concentration of the Al-Zulfi. This kind of variation has no effect on $^{36}\text{Cl}/\text{Cl}$ ratio. The possible mixing rate of the infiltrating water would be ~35% as calculated from 70 mm/year of recharge rate for 25 years and 37 m of the thickness of the aquifer. In this case, Cl derived from the infiltrating water is only 0.8–3% of total Cl in the groundwater (Scheffel, 1999). This contribution would not cause serious effect to the original $^{36}\text{Cl}/\text{Cl}$ ratio. Therefore, any influence of the Cl concentration variations on the $^{36}\text{Cl}/\text{Cl}$ ratios of groundwater samples does not appear to be a significant driver of the observed variations of the $^{36}\text{Cl}/\text{Cl}$ ratios of the eight samples.

To allow comparison of these data to the fallout history of bomb-1 produced $^{36}\text{Cl}$, the $^{36}\text{Cl}/\text{Cl}$ ratios of the Al-Zulfi samples were converted into fallout values using the following equation (Quevauviller, 2010):

$$R = \frac{F \cdot 3.15 \cdot 10^7}{P \cdot 10^{-15} \cdot C_p \cdot 6.022 \cdot 10^{23} / 35.45}$$  \tag{9}

where, $R$ is the measured $^{36}\text{Cl}/\text{Cl}$ ratio (in unit of $10^{15}$), $F$ is the $^{36}\text{Cl}$ fallout (atoms m$^{-2}$ s$^{-1}$), $P$ is the mean annual precipitation (mm), and $C_p$ is the Cl concentration in the precipitation (mg/l). The mean annual precipitation ($P$) was assumed to be 150 mm. The estimated fallout values from Al-Zulfi samples and measured fallout values at Dye-3 (Baskaran, 2011) are plotted together in Fig. (3). The ages assigned to the Al-Zulfi groundwater samples are from the $^{36}\text{Cl}/\text{Cl}$ ratio ages table (2) using 2014 as year zero.

![Fig. (3). Comparison of measured $^{36}\text{Cl}$ fallout values from Dye-3 ice core and the estimated fallout values from the Al-Zulfi groundwater samples, the estimated fallout values were calculated using Eq. (3).](image)
In fig. (3) the estimated $^{36}\text{Cl}$ fallout rates are compared with the Dye-3 data and mid-latitude background data (Baskaran, 2011; Massmann, 2003). According to fig. (3) the trends of the estimated fallout values and the Dye-3 values are in fair agreement. With this consideration, the estimated $^{36}\text{Cl}$ fallout rates are in fair agreement and very close to mid-latitude background data and the natural background $^{36}\text{Cl}$ flux values. The $^{36}\text{Cl}/^{35}\text{Cl}$ ratios in the Al-Zulfi basin which extends from far well towards the central city (i.e. from location N26° 15'/E44° 44' to N26° 11'/E44° 30'), through this path the ground is descending in the same way, the water flow this path and ended with the city central at the bottom of the valley where Al-Zulfi city located. The $^{36}\text{Cl}/^{35}\text{Cl}$ ratios varies from 61.0 to 190.0×$10^{-14}$ (mean = 155 ± 1.1, 1 σ). This means that $^{36}\text{Cl}/^{35}\text{Cl}$ ratios obtained do not belong to the pre-bomb pulse period which was about (5.1 ± 2.2)×$10^{-15}$ (Baskaran, 2011), while the peak pulse value was 2–4×$10^{-13}$ for the years 1959–1961 (Priller et al., 1990). Their results have been interpreted as reflecting the $^{36}\text{Cl}/^{35}\text{Cl}$ ratios of soil waters in each sampled year. On the basis of (Baskaran, 2011; Priller et al., 1990) results and the concordance between Dye-3 and (Argento et al., 2010) results (and if dispersion and mixing effects are negligible), the results obtained in this study suggest that the groundwater $^{36}\text{Cl}$ bomb peak does not appear in Al-Zulfi. The highest sample (on the order of $10^{-13}$), which was taken at a distance of ~35 km from the Al-Zulfi does not belong to the peak $^{36}\text{Cl}/^{35}\text{Cl}$ ratio value. The raise in the $^{36}\text{Cl}/^{35}\text{Cl}$ ratios are due to different processes acting on the groundwater $^{36}\text{Cl}/^{35}\text{Cl}$ ratios, these four parameters will affect differently. Thus, evapo-transpiration will increase both chloride and $^{36}\text{Cl}$ concentrations, but will have no effect on the $^{36}\text{Cl}/^{35}\text{Cl}$ ratio. Radioactive decay of $^{36}\text{Cl}$ will reduce both the $^{36}\text{Cl}$ concentration and $^{36}\text{Cl}/^{35}\text{Cl}$ ratio, without changing the chloride concentration. Conversely, the fact that increases the $^{36}\text{Cl}/^{35}\text{Cl}$ ratio in groundwater implies a largely stratospheric source for the $\text{ClO}_4^-$ excluding anthropogenic synthesized $\text{ClO}_4^-$ salts, as any near-surface $\text{ClO}_4^-$ production mechanism, where, perchlorate $\text{ClO}_4^-$ is a stable oxyanion consisting of four $\text{O}^{2-}$ ions bonded in tetrahedral coordination with a central $\text{Cl}^{7+}$ ion, $\text{ClO}_4^-$ present in groundwater at concentration ranging from background levels of about 0.01 to > 100 $\mu$g/l in some arid regions where perchlorate has been concentrated by evaporation (Lybrand et al., 2013; Parker et al., 2008; Rajagopalan, 2009). A major production mechanism for natural perchlorate apparently involves reactions of atmospheric Cl species with ozone ($O_3$) (Catling et al., 2010; Kounaves et al., 2010; Rao et al., 2012). Subsurface production will increase the $^{36}\text{Cl}$ concentration and $^{36}\text{Cl}/^{35}\text{Cl}$ ratio, but again leave the chloride concentration unchanged. Mixing of groundwater with different chloride and $^{36}\text{Cl}$ concentrations may also occur. A special case of mixing is the addition of dead chloride from formation salts within the aquifer or from the rock matrix itself. Mixing can also be treated, provided that the end-members can be identified and characterized.
Table (2). $^{36}\text{Cl}/\text{Cl}$ ratios and Cl$^+$ concentrations for the municipal water, and groundwater wells.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distance (km)</th>
<th>$C^+$ (mg/l)</th>
<th>$^{36}\text{Cl}$ (µCi/l)</th>
<th>$^{36}\text{Cl}$ (atoms/l) $(10^{12})$</th>
<th>$^{36}\text{Cl}/\text{Cl}$ Ratios $(10^{-14})$</th>
<th>$^{36}\text{Cl}$–Age (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Zulfi ($p_0$)</td>
<td>0</td>
<td>92.05</td>
<td>7.90</td>
<td>4.00</td>
<td>61 ± 4</td>
<td>4.32E+04</td>
</tr>
<tr>
<td>$p_7$</td>
<td>9.5</td>
<td>67.42</td>
<td>8.89</td>
<td>4.50</td>
<td>101 ± 6</td>
<td>9.42E+04</td>
</tr>
<tr>
<td>$p_6$</td>
<td>11</td>
<td>55.88</td>
<td>7.77</td>
<td>3.94</td>
<td>110 ± 7</td>
<td>3.62E+04</td>
</tr>
<tr>
<td>$p_5$</td>
<td>13</td>
<td>47.17</td>
<td>7.02</td>
<td>3.56</td>
<td>122 ± 11</td>
<td>8.03E+03</td>
</tr>
<tr>
<td>$p_4$</td>
<td>18</td>
<td>38.98</td>
<td>6.74</td>
<td>3.42</td>
<td>131 ± 13</td>
<td>2.53E+04</td>
</tr>
<tr>
<td>$p_3$</td>
<td>25</td>
<td>31.61</td>
<td>6.54</td>
<td>3.31</td>
<td>133 ± 12</td>
<td>3.85E+04</td>
</tr>
<tr>
<td>$p_2$</td>
<td>27</td>
<td>27.74</td>
<td>6.01</td>
<td>3.04</td>
<td>139 ± 9</td>
<td>7.53E+04</td>
</tr>
<tr>
<td>$p_1$</td>
<td>35</td>
<td>27.00</td>
<td>6.89</td>
<td>3.49</td>
<td>215 ± 19</td>
<td>1.57E+04</td>
</tr>
</tbody>
</table>

The estimated residence times of these groundwater samples fell within the range of $(1.57-9.42)\times10^4$ years. Fig. (4) shows the $^{36}\text{Cl}/\text{Cl}$ ratios plotted against the distance from the Al-Zulfi. Although the $^{36}\text{Cl}/\text{Cl}$ ratios of Al-Zulfi samples do not capture the most diagnostic portion of the $^{36}\text{Cl}$ fallout pulse, the results clearly suggest that the distribution of $^{36}\text{Cl}$ in the Al-Zulfi groundwater corresponds to pre-bomb pulse. Fig. (5) shows the initial variations in $C^+$ concentrations with distance from the Al-Zulfi (i.e., along the major groundwater flow direction).

![Fig. (4). The $^{36}\text{Cl}/\text{Cl}$ ratios were measured as a function of distance from Al-Zulfi city center.](image1)

![Fig. (5). The $C^+$ ions were measured as a function of distance from Al-Zulfi city center](image2)
4. Conclusions

In this study, $^{36}\text{Cl}/\text{Cl}$ distribution was investigated in groundwater aquifers in Al-Zulfi, Al-Riyadh, Saudi Arabia. The $^{36}\text{Cl}$ fallout values estimated from the $^{36}\text{Cl}/\text{Cl}$ dated Zulfi samples show fair agreement with $^{36}\text{Cl}$ fallout data from the Dye-3 ice core. This agreement provides support for the variations of $^{36}\text{Cl}$ in groundwater and does not reflect the input of bomb pulse $^{36}\text{Cl}$ if it takes place. Hence, the variations of $^{36}\text{Cl}/\text{Cl}$ in modern groundwater should reveal groundwater ages and flow systems in a region. In the utilization of $^{36}\text{Cl}$ in groundwater dating studies, the possible effects of dispersion on the $^{36}\text{Cl}$ concentrations and $^{36}\text{Cl}/\text{Cl}$ ratios in the groundwater should be correlated.

The distribution of $^{36}\text{Cl}$-based residence times is basically consistent with the estimated residence times from extrapolated velocity. The relatively low derived fallout rate of Al-Zulfi groundwater samples in comparison to measured $^{36}\text{Cl}$ fallout values from Dye-3 ice core reflect the agreement and it was very close to min-latitude base line. We estimated groundwater flow velocity for the regional groundwater flow paths based on $^{36}\text{Cl}$-dated water samples and their distance from the recharge area along the flow paths. The estimated residence times confirm that this groundwater is isolated from running water or lakes or watersheds, etc., of renewable water at short intervals and that this water is formed on long periods during which it largely accumulated. It must be that there is a balance between groundwater consumption rate and the rate of groundwater accumulation. Groundwater in Al-Zulfi does not contain radioactive bomb pulse that recorded and belongs to the era before 1950, and it is clear that groundwater belongs to the era before the experimental test activities, i.e. pre-1950’s to 1960’s AD.

Finally, we can extend this method by utilizing $^{36}\text{Cl}$ in such studies, which requires spatially extended sampling in order to map out the $^{36}\text{Cl}$ bomb pulse in the regional groundwater. Because of its geochemical behaviour, $^{36}\text{Cl}$ can be utilized in studying both unsaturated and saturated zones. $^{36}\text{Cl}$ is used in extensive research to review the volume of fresh water added annually to the groundwater, to make periodically and estimate the total volume of groundwater. In the nearest future we may expand investigation by studying spatial distribution of groundwater wells, and intense sampling on different depths, so as to add new measured factors to form a complete picture about groundwater flow pathways that describe patterns of Al-Zulfi carrying basin, and to know the extent which these pathways contact, infiltrate, and mix.

Acknowledgements

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References


[21] Han, L., Hacker Peter, Gröning Manfred, 2007. Residence times and age distributions of spring waters at the Semmering catchment area, Eastern Austria, as inferred from tritium, CFCs and stable isotopes. Isotopes in Environmental and Health Studies 43, 31-50.


[27] Lybrand, R.A., Michalski, G., Graham, R.C., Parker, D.R., 2013. The geochemical associations of nitrate and naturally formed perchlorate in the...
Mojave Desert, California, USA. Geochimica et Cosmochimica Acta 104, 136-147.


تطبيق تقنية الكلور-36 في تحديد عمر المياه الجوفية الحديثة بمحافظة الريفي

عنوان:
قسم الكثير العلمي، كلية التربية بالرياض، جامعة الأولى، مبنى 255، الرياض.
المملكة العربية السعودية
قسم الفيزياء النووية، مركز البحوث النووية، هيئة الطاقة الذرية، القاهرة، مصر

تعداد في 15/1/2014، قبل من رشح مياه الأغاطس. تقدر زمن

البحث:
36
هذه الدراسة تهدف إلى تقدير زمن بقاء المياه الجوفية اعتمادًا على تتبع النشاطات
36
التي تنتج من الانشطارات نتيجة التفجيرات النووية. عينات المياه تم تجميعها من بعض الآبار المختارة حول
Cl/CI
محافظة الريفي، المملكة العربية السعودية، النسبة بين
36
Cl/Cl
باستخدام المطيافية الكثلى المستحثة بالبلانزما وكذلك العد الوهمي للسائل. وقدرت النسبة

حوالي 0.2 - 10.

المياه الجوفية في المنطقة يتم استخذاها من رشح مياه الأغاطس. تقدر زمن

البقاء:
36
تتراوح زمن تقدير الكلور-36 (تظام) من المكونات المتفجرة النموية في المياه الجوفية على
Cl/CI
تحديث العصر بواسطة تقديرات هذه الدراسة إلى تقدير زمن بقاء المياه الجوفية على أساس
36
Cl/Cl
قائمة من الانشطارات النووية. تم جمع عينات المياه من بعض الآبار الموجودة حول محافظة
الريفي، المملكة العربية السعودية. نسبة

مئات
(36)
Cl/Cl
في عينات المياه، والتي تم

ICP-MS
تحذيرًا على المطيافية الكثلى بالبلانزما.

البقاء:
36
موردي المياه الجوفية في المنطقة أساسًا من تسر مياه الأغاطس المتوقعة. تم الحصول على تقديرات زمن
Cl/Cl
بالبقاء لهذه المياه من خلال تقديرات التكوينات المكافئة في المياه الجوفية عن مثابرة المراقب. تحديد زمن البقاء من

1955
على نشاطة الفتيلة
36
فمن أكثر موثوقية وحساسية للمياه الجوفية وإعادة شحنة قبل

1955
100
كلمات استبلالية: الكلور-36/ المطيافية الكثلى/ الريفي/ المياه الجوفية/ التجربة