ISOTOPIC INVESTIGATION ($\delta^{2}H$, $^{3}H$, $\delta^{18}O$, $\delta^{13}C$ AND $^{14}C$) ON RECHARGE, ORIGIN, RESIDENCE TIME AND DYNAMICS IN THE DOUALA/CAMEROON AQUIFER SYSTEM

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Abstract: A detailed stable ($\delta^{2}H$, $\delta^{18}O$, $\delta^{13}C$) and radiogenic isotopes ($^{3}H$, $^{14}C$) on Douala city has been led to understand the hydrogeochemistry and the functioning of the coastal sedimentary aquifer, for water supply and groundwater management resources. The environmental isotope show that the direct infiltration of rainfall is the most important process recharging the superficial and the intermediate aquifer system under a high humidity and a neglected evaporation. However mixing processes characterize the upper part of the intermediate aquifer. Groundwater of the system is modern and recent water. Ta radiocarbon isotopes reveal hundred and thousand ages.

1. INTRODUCTION
The sedimentary basin of Douala is a coastal aquifer characterized by more than 4000 mm/year of precipitation, the proximity of Mount Cameroon and a high humidity. But there are many problems of water supply and sanitation. The main goal of this project is to study and to understand isotope signature in a humid context for recharge, residence time and dynamics for water access and management.

2. METHODS
Two field campaigns have been realized on the intermediate season (December 2014) and on the rainy season (September 2016) from streams, springs, dug-wells and boreholes. 130 samples (Table 1) were carried out on the whole superficial aquifer namely Mio-Pliocene/Quaternary with 46 samples of $\delta^{2}H$ and $\delta^{18}O$, and 30 samples of $^{3}H$ respectively;
and the intermediate aquifer namely Upper Eocene/Oligocene (with 34 samples of δ²H and δ¹⁸O and 16 samples of ³H. The streams samples characterized the base flow and the run off, springs represent perched shallow aquifer while dug-wells depths range from 0.85 m to 20 m; all of them belonging to the Quaternary aquifer system. Samples collected from boreholes tapping at depths ranging from 20 m to 180 m representing the Mio-Pliocene/Quaternary and the Upper Eocene/Oligocene [1]. Unfiltered and unacidified samples were collected and cooled in tightly sealed 30 ml, 500 ml and 1 L polyethylene bottles for stable isotopes (δ²H, δ¹⁸O), tritium and radiocarbon (δ¹³C, ¹⁴C) isotopes respectively. Rainwater samples were downloaded from the IAEA/GNIP website (http://www-naweb.iaea.org/napc/ih/IHS_resources_isohis.html#wiser) of the Douala GNIP station (18 m altitude) from 2006 to 2016.

![Figure 1: Location of the study area](image)

Stable isotope of oxygen and hydrogen were analyzed using the laser-based spectroscopy (Picarro, L2120-i) at the Institute of Groundwater Ecology (Helmholtz Zentrum München/Germany. Both δ¹⁸O and δ²H values were determined relative to internal standards that were calibrated using Vienna-Standard Mean Ocean Water (V-SMOW). The data were normalized following [2]:

$$\delta = [(R_S/R_{V-SMOW}) - 1] \times 1,000$$

where R_S represents either the ¹⁸O/¹⁶O or the ²H/¹H ratio of the sample, and R_{V-SMOW} is ¹⁸O/¹⁶O or the ²H/¹H ratio of the V-SMOW. The analytical reproducibility was ±0.1‰ and ±1.0‰ for the oxygen and deuterium, respectively.

Tritium analyses were performed by electrolytic enrichment and liquid scintillation counting method [3] and values are reported in tritium units (TU) with an error of 0.55 UT [1].
The radiocarbon isotope ($\delta^{13}$C, $^{14}$C) were analyzed at the Gliwice Radiocarbon Laboratory Institute of Physics Silesian University of Technology of Krakow/Poland through benzene synthesis and liquid scintillation spectrometry [4]. The $\delta^{13}$C was measured using isotope ratio mass spectrometry and reported in ‰ versus PDB (American Belemnitella formation; North California, USA), with an analytical uncertainty < 0.10‰ VPDB. The measured $^{14}$C concentrations are expressed as percent of modern carbon (pmc) with an error ranging from ±0.20 to ±0.27 (pcm).

3. RESULTS
The dataset results of both campaigns field (rainy season (RS) and dry season (DS)) of environmental isotopes ($\delta^{18}$O, $\delta^2$H, $^3$H) and radiocarbon isotopes ($\delta^{13}$C and $^{14}$C) are shown on table 1. These results represent in one hand water river (streams), shallow aquifer (springs and dug-wells) and samples of boreholes of the superficial unconfined and semi-confined aquifer system namely Mio-Pliocene/Quaternary; and in another hand the shallow aquifer (springs) and samples of boreholes of the intermediate semi-confined and confined aquifer system namely Eocene/Oligocene [5].
Table 1: Number of samples according to environmental and radiocarbon isotopes

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>Mesures</th>
<th>Periods</th>
<th>Aquifers</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mio-Pliocene / Quaternary</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oligocene / Eocene</td>
<td></td>
</tr>
<tr>
<td></td>
<td>December 2014</td>
<td>$^{18}$O, $^2$H, $^3$H</td>
<td>25</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>September 2016</td>
<td>$^{18}$O, $^3$H</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>September 2016</td>
<td>$^3$H</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>September 2016</td>
<td>$^{13}$C, $^{14}$C</td>
<td>00</td>
<td>04</td>
</tr>
<tr>
<td></td>
<td>Number of samples</td>
<td></td>
<td>76</td>
<td>54</td>
</tr>
</tbody>
</table>

A record dataset of 105 samples of precipitation used since 2006 to 2016 was plotted on a conventional $\delta^{18}$O versus $\delta^2$H diagram, with weighted mean of -2.73 and -11.84 for $\delta^{18}$O and $\delta^2$H respectively. The linear trend led to the equation: $\delta^2$H = (7.47 ± 0.17) $\delta^{18}$O + (8.95 ± 0.57) with $r^2 = 0.95$. This LMWL is closed to the GMWL defined by Graig (1961) and still slightly different from those found by [6, 7] and [8] respectively $\delta^2$H = 8.17 $\delta^{18}$O + 12.74; $\delta^2$H = 8 $\delta^{18}$O + 11.4 and $\delta^2$H = 7.86 $\delta^{18}$O + 11.13. The different observed on the slopes 7.47; 8.17; 8 and 7.86 on the intercept 8.95, 12.74, 11.4 and 11.13 can be attributed to local climatic conditions namely re-evaporation during rainfall, the seasonality effect, the origin of vapor mass and especially the convective activity and cloud types occurring in the study area.

The stable isotope values range globally from -5.5 to 2‰ and -25 to -5‰ respectively for $\delta^{18}$O and $\delta^2$H. The surface water values range from 3-‰ to -2.03‰ with a mean of -2.63‰ and -11‰ to -9.3‰ with a mean of -10.3‰ respectively of $\delta^{18}$O and $\delta^2$H. Their depleted values are observed upstream whereas enriched values signature are observed downstream, due the evaporation effect and mixing during run off. According to groundwater:

(i) Dug-wells values are between -3.54‰ to -2.26‰ with a mean of -2.73‰; and -16.14‰ to -7.64‰ with a mean of -10.47‰ respectively $\delta^{18}$O and $\delta^2$H. The springs show values between -3.25‰ to -2.68‰ with a mean of -3.02‰, and -13.11‰ to -10.58‰ with a mean of -11.65‰ respectively of $\delta^{18}$O and $\delta^2$H. While the boreholes values of the Mio-Pliocene/Quaternary aquifer range from -5.13‰ to -3.00‰ with a mean of -3.65‰; and from -27.35‰ to -10.48‰ with a mean of -14.74‰ for both $\delta^{18}$O and $\delta^2$H respectively. This aquifer system is characterized by depleted values of stables isotopes. Groundwater of this aquifer are more under evaporation processes, some climatic local effects and the origin of vapor mass as mentioned upper. The study area is surrounded by the Moungo, the Wouri and the Dibamba rivers; is near the Mount Cameroon and is opened to the Atlantic Ocean.

(ii) The springs have values between -3.28‰ to -2.73‰ with a mean of -3.0‰; and -12.73‰ to -10.24‰ with a mean of -11.80‰ for both $\delta^{18}$O and $\delta^2$H respectively. Whereas boreholes values range from -4.35‰ to -2.66‰ with a mean of -3.59‰; and -7.5‰ to -10.67‰ with a mean of -14.19‰ respectively for $\delta^{18}$O and $\delta^2$H. The samples of the Eocene/Oligocene aquifer show more different results with respect to the upper aquifer. The data scatter are parallel and in a lesser extend above the GMWL, indicating that recharge occurred without evaporation processes. Either those groundwater recharged at higher elevations, or old infiltrated water occurring probably during cooler and humid period in the past which has mixed with leakage from the shallow aquifer [6]; [8]; [1]. Moreover, graphs concerning $\delta^{18}$O versus Cl- $\delta^{18}$O versus NO$_3^-$ and $\delta^{18}$O and $\delta^{18}$O versus depth (not shown here) relative to the flow exchange indicate that groundwater samples downstream are more...
enriched chemically and exceed WHO guidelines. Also, groundwater are more depleted for boreholes which depths are upper to 80 m.

Tritium values of surface water range from 1.3 to 1.9 TU with a mean of 1.75 TU, those of the phreatic aquifer range from 0.40 to 2.30 TU with a mean of 1.31 TU while boreholes of the Mio-Pliocene/Quaternary aquifer have values which are between 0.7 to 2.2 TU with a mean of 1.34 TU; indicating recent and modern age. Groundwater samples from the unconfined aquifer that contains tritium for most of them are located near the recharge zones in the NE of the study area (Emvoutou et al., 2018). In contrast, boreholes of the Eocene/Oligocene aquifer range from 0.5 to 2 TU with a mean of 1.20 TU. These have tritium values below the detection limit (< 0.7 TU), attesting that these groundwater have recharged prior the atmospheric bomb tests; but some of them have been certainly mixed with more recent water according to the geological and hydrogeological contexts. The stable isotope content, the bulk of precipitation contents and the lower tritium content are consistent with recharge during a humid phase and perhaps also a lower temperature than in the current climate.

According to radiocarbon, there is no relation between 14C and carbonate contents. Radioactive decay is not probably in relation with the dissolution of "death carbon" of carbonates of the system. Moreover δ13C contents depend on bicarbonate contents in the study area. High values of δ13C are closely related to depleted values of carbonates, indicating a confined system, carbonic acid being used by weathering of silicate in the Eocene/Oligocene aquifer. In the light of this, Pearson and Evans methods displayed identical ages and have been adopted. The relative ages of the groundwater in the Eocene/Oligocene system (Table 2) range from hundred (160 years) to thousands (1760 years) [5].

Table 2: Results of residence time of radiocarbon isotope

<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>Aquifer</th>
<th>ΔH  (UT)</th>
<th>Δ14C (pMC)</th>
<th>Error</th>
<th>δ13C (‰ PDB)</th>
<th>pH</th>
<th>T (°C)</th>
<th>HCO3⁻ (meq/l)</th>
<th>Uncorrected Ages</th>
</tr>
</thead>
<tbody>
<tr>
<td>F‘11 Akwa Nord</td>
<td>RS</td>
<td>Eocene/Oligocene</td>
<td>90.30</td>
<td>0.20</td>
<td>-20.76</td>
<td>5.07</td>
<td>23.6</td>
<td>0.2</td>
<td>820</td>
<td></td>
</tr>
<tr>
<td>F‘22 Yaounde</td>
<td>RS</td>
<td>Eocene/Oligocene</td>
<td>98.01</td>
<td>0.26</td>
<td>-23.19</td>
<td>4.90</td>
<td>23.9</td>
<td>0.1</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>F‘6b Gétek Militaire</td>
<td>RS</td>
<td>Eocene/Oligocene</td>
<td>0.8</td>
<td>96.97</td>
<td>0.27</td>
<td>-21.25</td>
<td>4.7</td>
<td>28.4</td>
<td>0.1</td>
<td>250</td>
</tr>
<tr>
<td>F‘7b Gétek Militaire</td>
<td>RS</td>
<td>Eocene/Oligocene</td>
<td>80.35</td>
<td>0.25</td>
<td>-21.46</td>
<td>5.56</td>
<td>27</td>
<td>0.1</td>
<td>1760</td>
<td></td>
</tr>
</tbody>
</table>

4 CONCLUSIONS
The Mio-Pliocene/Quaternary aquifer receives and recharges through direct infiltration of precipitation and is characterized by recent and modern water. The Eocene/Oligocene is under mixing process in its upper part while the lower part is a confined aquifer system with old water. The global flow is from the NE (upstream) to SW (downstream) of the city/basin. Radioactive decay is not linked to the carbonate of the aquifer, they have been used during the weathering of silicate which is the main geochemical process occurring the system. Ages range from hundred to thousand years in the Eocene/Oligocene system.

REFERENCES


