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Investigation of $^{36}\text{Cl}$ distribution: towards a new estimation of groundwater residence times in the confined aquifer of the LCB?

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Abstract

$^{36}\text{Cl}$ measurements in groundwaters of the deep confined aquifer of the Lake Chad Basin (LCB) were performed in order to constrain groundwater geochemical ages and residence times. Twenty-seven wells were sampled in Nigeria, Niger and Chad in the southern parts of the large (700 000 km$^2$) multilayered aquifer of the LCB. $^{36}\text{Cl}/\text{Cl}$ values range between $11\pm1.10^{-15}$ to $148\pm8.10^{-15}$ at/at. The highest ratios are observed near the recharge zone of the Nigerian part of the Continental Terminal aquifer, while the lowest ones are found in wells located near the southern fringe of the present-day lake Chad. Chloride concentrations are low (below 100 mg/l) and not correlated to the $^{36}\text{Cl}/\text{Cl}$ values, indicating negligible dissolution of evaporites in most samples. Reliable $^{36}\text{Cl}$ ages can be calculated along the different flow paths investigated, suggesting residence times of the deep groundwaters larger than 300 000 years. These results are consistent with new AMS-$^{14}\text{C}$ data below the detection limit but are in contradiction with previous $^{14}\text{C}$ data obtained in the area.

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1. Introduction

Large sedimentary aquifers of northern and western Africa contain important groundwater resources [1]. In these semi-arid to arid regions, their use is expected to increase substantially to combat growing food insecurity. Improved knowledge of the hydrological behavior and recharge of these aquifers is essential to properly assess availability and sustainability of these resources. This is specially the case for the multi-layer aquifer system of the Lake Chad Basin (LCB) that remains poorly studied. Located in Central Africa, at the transition between Sahel and Sahara, the LCB is one of the greatest endorheic basins of the world. It encloses a multi-layered aquifer composed of two main aquifer units: an unconfined Quaternary aquifer and a deeper confined aquifer. The latter is subdivided into Lower (Continental Terminal formation) and Middle (early Pliocene formation) aquifer sub-units in the Nigerian part of the LCB [3,4]. For the sake of simplicity, they are undifferentiated in this study and both named Continental Terminal (CT). The CT is mostly artesian, but increasing withdrawal in the populated area of northeastern Nigeria leads to a significant pressure decline.

According to a comprehensive review of the rare hydrogeological study carried out on the Continental Terminal system [2], the waters flow from the South West of the Basin (present-day recharge zone) to the North East depression of the “Bas-Pays” (present-day outlet zone). Geochemical investigations in the Nigerian part of the Continental Terminal aquifer show waters recharged during humid periods $^{14}$C-dated around 20 or 40 ka [3,4]. However, these $^{14}$C-derived ages are questionable since $^{14}$C contents are within the range (0-10%) where classical techniques may be significantly biased by atmospheric contamination during sampling [5]. Moreover, the recharge periods are not fully consistent with paleoclimatic reconstructions, especially during the Last Glacial Maximum, 21 ka ago that is generally recognized to be an arid period in this part of Africa [6].

In this study, we propose to use, alternatively to $^{14}$C, another cosmogenic nuclide, the chlorine-36 to provide further constraints on groundwater dynamic in a large part of the Continental Terminal aquifer that extends over Niger, Nigeria and Chad. Chlorine-36 is a powerful tool in hydrological studies and in groundwater dating because of the conservative behavior of chorine and its half-life of $3.10^5$ a$^{-1}$. Although this tool was largely applied in many large aquifer systems around the world [7], it is the first time that $^{36}$Cl analyses were performed on LCB aquifers.

2. Method

![Piezometric map of the confined aquifer. The dots represent the water sample locations and the arrows three different groundwater flow paths. The Lake Chad Topographic Basin (LCB) is drawn on the map of Africa (DEM: blue=3000m; red=200m). Groundwater flows are represented on a SW-NE cross-section of the sedimentary basin [2]](image)

Groundwaters of twenty-seven wells from the Continental Terminal aquifer were sampled in the Nigeria, Niger and Chad parts of the Basin from 2008 through 2013. With the exception of two wells located near the recharge zone

(in blue in the Figure 1), all wells were artesian. $^{36}$Cl measurements were carried out at the French AMS National Facility ASTER, CEREGE following the procedure described in [7]. No spike was added to the samples to avoid $^{36}$Cl contamination. All samples have $^{36}$Cl/Cl ratios at least ten times above the chemical blank ratio ($5 \times 10^{-16}$ at/at) with a reproducibility of 8% [8]. Chloride concentrations were measured at HydroSciences Montpellier by Ion Chromatography. $^{14}$C-AMS analyses (Artemis-AMS facility) were performed on four samples originating from the Chadian zone investigated in this study. Because of the very low $^{14}$C contents measured in previous studies (<10 pmc), special care was taken to avoid contamination during $^{14}$C-dedicated water sampling and inox bottles with two entries were used. This device allows flushing air outside the bottle and ensuring no contact with the atmosphere.

3. Results

$^{36}$Cl/Cl ratios range between $11 \pm 1 \times 10^{-15}$ and $148 \pm 8 \times 10^{-15}$ at/at and chloride concentrations range between 2 and 117 mg/l (see Figure 2). The two samples characterized by the highest $^{36}$Cl/Cl values ($\sim 145 \times 10^{-15}$ at/at) and very low chloride content waters (below 5 mg/l) are close to the outcrop of the Continental Terminal formations. This $145 \times 10^{-15}$ value may reflect the initial $^{36}$Cl/Cl ratio of water recharging the aquifer system at this location. This value is however significantly lower that the $^{36}$Cl/Cl signature of the Holocene groundwaters of the Chadian part of the Quaternary aquifer that are characterized by a homogeneous pre-anthropic initial $^{36}$Cl/Cl ratio of $200 \times 10^{-15}$ at/at [9] that very likely reflects the initial $^{36}$Cl/Cl ratio of the southern part of the LCB. This significant discrepancy in "initial" $^{36}$Cl/Cl ratios between the Nigerian and Chadian parts remains elusive. Although it might be explained by spatial variations in $^{36}$Cl fallout and/or Cl- content in precipitation [10,11] over the LCB, we cannot rule out an "age effect" that would indicate older water in the near vicinity of the Nigerian CT outcrop.

![Graph showing $^{36}$Cl/Cl as a function of $[^{36}Cl]$](image)

Fig. 2. $^{36}$Cl/Cl as a function of $[^{36}Cl]$. The blue area depicts the $^{36}$Cl/Cl value of recharge zone while the yellow one the mean range of $^{36}$Cl/Cl ratio observed in the Quaternary aquifer [9]. The brown area is the secular equilibrium. The dot colors are the same as used on Figure 1 for sample location. Flow lines #1 and #2 can be associated with two radioactive decay lines. The arrows show the correction from potential dissolution of evaporites. The influence of evaporation and dissolution of evaporites on both the $^{36}$Cl/Cl and the $^{36}$Cl content are also represented.

The lowest $^{36}$Cl/Cl ratios (around 10 to $15.10^{-15}$ at/at, n=7) are measured in groundwaters from Chad and the eastern part of Nigeria. The equilibrium ratio found in sandstone formation similar to the Chadian formations is usually below $10 \times 10^{-15}$ at/at [12]. Although this requires complementary investigation, we hypothesize that these waters have not reached the secular equilibrium.
Low chloride concentrations and the absence of correlation between the $^{36}$Cl/Cl and [Cl] suggest the absence of dissolution of evaporites in most samples. Therefore the general decrease trend in both $^{36}$Cl/Cl and $^{36}$Cl observed along the two flow paths #1 and #2 (green and black points, Fig.2) can be explained by the radioactive decay of $^{36}$Cl. Assuming initial $^{36}$Cl/Cl ratio of $145.10^{-15}$ at/at, $^{36}$Cl ages can be estimated and lead to groundwaters older than 300,000 years for most of the samples (with the exception of 3 samples of the flow path #2 that are likely younger). For the samples situated at the end of the three flow paths investigated here and characterized by $^{36}$Cl/Cl ranging from 10 to $20.10^{-15}$ at/at, $^{36}$Cl ages attain 1 Ma.

These results are highly consistent with the four $^{14}$C analyses that are below the detection limit of Artemis-AMS facility (< 0.5 pmC). With the limitation of the small number of $^{14}$C-analyse samples, these data clearly indicate ages older than 50 ka, in agreement with the $^{36}$Cl-derived ages. These results, in contradiction with previous studies [3,4], give new insights to the paleohydrology of the survey area. It also confirms that special care is highly needed in the sampling of waters for $^{14}$C measurements [5].

4. Conclusions

$^{36}$Cl is a suitable tracer for groundwater dating in the deep confined aquifer of the Lake Chad Basin because of low chloride content of groundwaters compared to other large aquifers of northern Africa. Its application provides robust evidence that groundwater residence times are superior to 300 ka. Recent waters are not clearly evidenced even close to the recharge zone, indicating very limited active recharge of the system. These first results are pivotal for its sustainable water management.

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