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ISOTOPES IN GROUNDWATER: INDICATORS OF CLIMATE CHANGES

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Abstract: Isotopes of the water molecule ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) are a well-used tool for investigating groundwater origin and history, i.e. tracing the recharge conditions over time, processes occurring during infiltration of the rain water towards aquifers and those issued from the water-rock interaction and mixing of different waters. This paper proposes a review of several large European aquifers (Portugal, France, UK, Switzerland, Germany, Hungary, Poland) investigated in terms of the recharge conditions and the story of the groundwater at large scale, involving recent, Holocene and Pleistocene components and eventually mixing between them.

Keywords : hydrogeology, stable isotopes, Groundwater, Recharge, Climate change

1 – Introduction

Since several decades the use of isotopic methods in groundwater investigations is of great acceptance among hydrogeologist and scientists scrutinizing groundwater resources and their evolution in aquifer systems [1, 2]. Well-established techniques mainly applying stable isotopes of the water molecule (hydrogen and oxygen) as tracers of water source have been applied in water resource investigations and thus isotope hydrology and isotope hydrogeology are great challenges since that time [3-6].

It is also clear and of great evidence either for scientists than end-users that groundwater is one of the endangered resources of Europe. Groundwater, the main source of fresh water in the majority of EU states, is under increasing threat from anthropogenic activities (industry, intensive agricultural practices, mass tourism etc.). Because of over-exploitation, present recharge cannot fully compensate for the increasing pumping, and groundwater resources are declining in many of the important aquifers of Europe. Climate projections for Europe show changes in precipitation and temperature patterns that are one of the key variables controlling formation of groundwater resources [6]. Substantial decreases of precipitation have been predicted for some parts of Europe while more rainfall is expected in the northern Europe. The climate of Europe is diverse and characterized by large variations from north south and east-west. In Southern Europe, global warming, will lead to a large reduction in recharge due to the decrease in precipitation. This may lead to impacts on the water quality. In Central Europe, continued depression of groundwater levels correlates with excessive use of water resources. In the Atlantic regions and in Northern Europe increase in precipitation and recharge and reducing of the unsaturated zone are expected as direct consequence of the climate change. Thus, because aquifers may be subject of the climate change effect, which is expected to decrease precipitation and recharge rates in large parts of Europe, there is no general agreement on how to maintain a sustainable development of European aquifers in the future [7]. The objective of this paper is to illustrate the past climates variations as well as recharge over time and water origins using isotopic methods in groundwater investigations, especially with stable isotopes of the water molecule ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). Major continental aquifer systems over Europe are used to illustrate complex stories of groundwaters from infiltration to the aquifer through the processes that can affect their original signal.

2- What is climate and climate changes?

We are all living in areas of regional climate corresponding to the average weather in a place over more than thirty years. The regional climate can be described by the temperatures over the seasons, how windy it is, and how much rain or snow falls. The climate of a region depends on many factors including sunlight amount, height above sea level, shape of the land, and distance to the oceans. On the other hand, considering the entire earth, global climate is a description of the climate as a whole including all the regional differences as average.

Climate variations and change, caused by external forcings, may be partly predictable, particularly on the larger, continental and global, spatial scales. Because human activities, such as the emission of greenhouse gases or land-use change, do result in external forcing, it is believed that the large-scale aspects of human-induced climate change are also partly predictable.

The climate system, comprising the atmosphere, the hydrosphere, the cryosphere, the land surface and the biosphere is an interactive system as defined in the IPCC Report [8, 9]. This system is forced or influenced by various external forcing mechanisms, the most important of which are the Sun and the direct effect of human activities. In the climate system, the atmosphere is the most unstable and reactive part of the system and its composition has changed with the evolution of the Earth. The most variable component of the atmosphere is water and because the transition between the various phases (vapour, cloud droplets, and ice crystals) absorb and release lot of energy, water vapour is central for climate variability and change. The hydrosphere is the component comprising all liquid surface and subterranean water, both fresh (rivers, lakes and aquifers) and saline water (oceans and seas). Fresh water runoff from the land to the oceans influences the ocean's composition and circulation but due to the large thermal inertia of the oceans, they act as a regulator of the Earth's climate as well

as a source of natural climate variability, in particular on the longer time-scales. The cryosphere, including the ice sheets, continental glaciers and snow fields, sea ice and permafrost, derives its importance to the climate system from its albedo, low thermal conductivity, large thermal inertia and its critical role in driving deep ocean water circulation. Because of the large water amount stored in ice sheets, their volume variations are a potential source of those of the sea level. Vegetation and soils control the Sun-atmosphere exchange of energy. Part of the exchange induces heating of the atmosphere as the land surface warms, part serves to evaporation processes inducing water returning back to the atmosphere. Because the evaporation of soil moisture requires energy, soil moisture has a strong influence on the surface temperature.

Many physical, chemical and biological interaction processes occur among the various components of the climate system on a wide range of space and time scales, making the system extremely complex. As an example, the marine and terrestrial biospheres have a major impact on the atmosphere's composition through the uptake and release of greenhouse gases by the biota. Similarly, the atmosphere and the oceans are strongly coupled and exchange, among others, water vapour and heat through evaporation. This is part of the hydrological cycle and leads to condensation, cloud formation, precipitation and runoff, and supplies energy to weather systems.

However, climate varies by region as a result of local differences in these interactions [10]. Thus, some of the factors that have an effect on climate are changes in the amount of solar energy, greenhouse gases, albedo of snow and ice and volcanic eruptions [11]. While the weather can change in just a few hours, climate changes over longer timeframes. Any change, whether natural or anthropogenic, in the components of the climate system and their interactions, or in the external forcing, may result in climate variations. Climate has changed

in the past, is changing nowadays and will change in the future. The time scale of climate change may vary from decades up to hundreds of million years.

3- Why stable isotopes can trace climate changes?

3.1 Trace the groundwater recharge

Recharge of aquifer is mainly done by direct infiltration of rainwater, surface water or by subsurface inflow, and thus primary originates from precipitation. In that way, it is necessary to first constrain the signature of the recharge, i.e. of the rainfall. For the hydrosphere, increasing global surface temperatures lead to changes in precipitation and atmospheric moisture [12] and impact the recharge of the aquifers. By the 1950's, it has been observed that stable isotopes of the water molecule in rainwater ($\delta^{18}\text{O}$ and $\delta^2\text{H}$, reflecting the ratio of heavy and light isotopes of ^{18}O and ^{16}O , and ^2H and ^1H respectively) depend on several climatic factors, including air temperature, rain amount, altitude and latitude of precipitations (e.g. [13]). Thus combining this relationship between isotope ratios and climate and the well established thermodependance, the isotopic signatures of the water molecule appear to be an appropriate tool to study the past climates in various continental and marines archives.

The spatial and temporal variability of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of meteoric water results from isotope fractionation effect accompanying evaporation/condensation processes. The laltitude effect reflects the rainout process based on the Rayleigh fractionation/condensation model that include two processes. Firstly, the formation of atmospheric vapour by evaporation in regions with the highest surface ocean temperature and secondly, the progressive condensation of vapour during transport to higher latitude. For coastal and continental stations in Europe, this latitude effect is about : $\Delta^{18}\text{O} \approx -0.6\text{‰}/\text{degree of latitude}$ (GNIP data network; [14]). The temperature is a key parameter that controls the $\delta^{18}\text{O}$ signatures (and thus $\delta^2\text{H}$), Yurstsever [15] established the folowing relation based on amount-weigthed means $\delta^{18}\text{O}$ for North Atlantic and European stations : $\delta^{18}\text{O} = 0.52 \text{ t} - 15\text{‰}$. The temperature effect thus mainly

controls the seasonal variations of the isotopic signal in rainwater. The continental effect, resulting in a progressive ^{18}O (and ^2H) depletion in rainwater with increasing distance from the ocean, also largely controls the isotopic signature of precipitations. Over Europe, from Irish coast to Ural Mountains, an average depletion of 7‰ is observed for $\delta^{18}\text{O}$, however the extent to which a continental effect occurs also depends on the prevailing direction of the movement of air masses. Finally, there is an altitude effect that is temperature-related, as the temperature drops when altitude increases. All these parameters controlling the isotopic signature in rainwater lead to the general relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$, defined as the GMWL (Global Meteoric Water Line, [13]) : $\delta^2\text{H} = 8 * \delta^{18}\text{O} + 10$. The isotopic signal of the recharge of aquifer, i.e. rainwater, over Europe is summarized as a map (Fig 1, [16]) reflecting well the continental and latitudinal effects. More detailed maps exist for European countries, reflecting especially the local altitudinal effects (e.g. France: [17]; UK : [18, 19]; Spain: [20]; Italy: [21,22]).

The stable isotopes of the water molecule ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) are generally measured using an IRMS mass spectrometer with a precision of 0.1‰ vs. SMOW for $\delta^{18}\text{O}$ and 0.8‰ for $\delta^2\text{H}$. Isotopic compositions are reported in the usual δ -scale in ‰ with reference to V-SMOW according to $\delta_{\text{sample}} (\text{‰}) = \{ (R_{\text{sample}} / R_{\text{standard}}) - 1 \} \times 1000$, where R is the $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ atomic ratios. During the past decade, the ongoing development and evolution of laser gas analyzers and laser spectroscopy presents an alternative to conventional IRMS and CF-IRMS analysis of water isotopes O and H. In particular, the laser-based method is conceptually simple [23] and may display some major advantages over the IRMS method: smaller sample sizes, direct measurement of isotope ratios in the water vapour, avoiding the time-consuming and sample preparations. On the other hand, the main disadvantage of laser spectroscopy compared to IRMS is the lowering analytical flexibility because of the single gas isotopic species of interest (e.g., water vapour, CO_2 , or CH_4). However, presently, if some studies tend

to demonstrate that laser technology for the measurement of liquid water isotopes yields comparable or better accuracy to conventional IRMS and CF-IRMS analysis [24], others highlight divergences and concern that exist about the capability of laser spectroscopy for the analysis of liquid samples other than pure water due to the presence of organic compounds [25].

3.2 What changes in the water molecule can be traced by O-H isotopes in aquifers?

The isotopic composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of the water molecule can change (isotopic fractionation) during its travel from the atmosphere, as rainwater, to groundwater, and sometimes within the aquifer. These potential changes are controlled by evaporation and exchange processes.

If the isotopic signatures are not affected by any process from surface to groundwater, the measured isotope ratio in the aquifer strictly reflects the origin of the water (location, period and process of recharge), i.e. the conditions prevailing at the moment of the recharge. Thus, as the isotopic signature are highly thermo-dependent, the climate prevailing at the moment of the recharge is preserved in the groundwater system, as a typical isotopic signature (under a colder climate, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values are depleted in heavy isotopes and are thus more negative). If the isotopic signatures change along the groundwater paths, this traces the history of the water, particularly the mixing, salinization and discharge processes [14]. Even if the isotopic composition of groundwater is mainly inherited from atmospheric signal, there is some cases where reactions between groundwater and the rock matrix or gases or surface-subsurface processes such as evaporation, can modify the original meteoric signatures [14, 4].

4 - Recharge and residence time assessment of groundwater in the Adour Garonne district (S.W. France) through stable isotopes of the water molecule

The Adour-Garonne district covers 116 000 km² (1/5th of French territory). It is limited by the Massif Central and Montagne Noire to the east, by the Armorican Massif to the north, by the Pyrénées Mountains to the south and by the Atlantic Ocean to the west (Fig. 2). In this district, the Eocene sands water body (a multi-layer system) constitutes a series of major aquifers used for drinking water supply (6.7 million inhabitants), agriculture irrigation and thermo-mineral water resource [26] and is composed by sandy Tertiary sediments alternating with carbonate deposits. The Eocene aquifer system presents a high permeability and a thickness of several tenths of meters to a hundred meters and is constituted by at least five aquifers: Paleocene, Eocene infra-molassic sands (IMS), early Eocene, middle Eocene, late Eocene. Groundwater recharge may occur to the east by the edge of the Massif Central, to the south by the edge of the Pyrénées and by inflow from the Paleocene aquifer.

The $\delta^{18}\text{O}$ values of the ground waters fall in the range -5.6 to -10.6‰ vs. SMOW, with the $\delta^2\text{H}$ values varying between -34.3 and -72.3‰ vs. SMOW [2]. There is no relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and the salinity with a correlation coefficient R close to 0.30 and 0.45 between salinity and $\delta^{18}\text{O}$ - $\delta^2\text{H}$ values respectively. All the analysed waters (Fig. 3) plot on or near the global meteoric water line GMWL [13].

The groundwater data present a wide range of stable isotopic composition ($\delta^2\text{H}$, $\delta^{18}\text{O}$) both between the different aquifers and within a single aquifer (Fig. 3). Comparing independently each aquifer level sampled in low and high flows of a same hydrological cycle, it appears:

Palaeocene aquifer collected NW-SE along the Pyrenees border presents a large variation in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signature, agreeing with that observed in the district. Such heterogeneity in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures for the Palaeocene aquifer reflects a variable recharge, either in space and time. The most depleted value correspond to a water recharged with a colder

climate than the present one ($> 10\,000$ y), the likeness in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures along the hydrological cycle confirms a homogeneous aquifer system without any water input with a different signature between the two periods. This means that the aquifer is mostly confined with no significant recharge.

Lower Eocene aquifer was essentially collected in the northern part of the district (Fig. 3). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures are less variable than those of the Paleocene aquifer and fall in the middle range observed as a whole. The values are consistent along the hydrological cycle and are more depleted compared to the present rainwater input in the Massif Central, reflecting an older recharge which could have occurred under colder climate. This means that the aquifer is probably semi-confined.

Middle Eocene aquifer has been largely sampled in the northern part of the district and presents a large range of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures among which the most enriched values, very close to that of the rain inputs observed in Dax, reflecting a modern recharge. Most of the samples show depleted values that reflect a recharge under colder climate. In between these two groups, a third group with intermediate values corresponds either to a mixture between the two previous groups or to close pockets (e.g. small confined part of the aquifer). The large variation of the point EM4 between the two surveys surely reflects hydrological conditions that differ from one survey to the other.

Upper Eocene aquifer was sampled in 4 locations in the northern part of the district along a NW-SE profile. Although having similar signature between the two surveys, they display either enriched or depleted values. ES-3 is enriched while ES-4 is depleted (recharge under colder climate) and ES-2 displays a signature close to present day rain water in the Massif Central.

Infra Molassic Sand aquifer was largely collected in the southern part of the district along a W-E profile and displays a large range of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures. SIM2 and SIM8 have a

signature close to those of rainwater in Dax and Massif Central. SIM2 is a shallow bore well (58 m) and a modern recharge is compatible with the observed values. On the contrary, SIM8 is a 1400 m depth bore well screened between 1030 and 1040 m and the water is the most saline of the district (TDS up to 2.5 g.L⁻¹). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signature, suggesting a modern recharge, may results in a rapid circulation of the groundwater in the system. As for the remaining points, they are depleted in ^{18}O and D compared to rainwater, reflecting a recharge under colder climate and a semi confined status for the aquifer.

Taken as a whole, the enriched samples clearly correlate with the present day recharge as measured in Dax and Massif Central. The most enriched waters (EM1, EM2, ES3) originate from the north of the area, in the vicinity of the Gironde estuary and present signatures quite similar to that of present day coastal precipitations (mean weighted rain in Dax). Samples SIM2 and 8 also show an enriched signature that can be related to the modern recharge. At the opposite, the most depleted sample (P3) originates from the Paleocene aquifer (860 m depth), and may reflect an old recharge as its signature is clearly lower than that of present-day precipitations from the Massif Central or Pyrenees. The groundwater presents a wide range of variation along the global meteoric water line which excludes significant evaporation of infiltrating waters and any continental effect on the stable isotope composition. These variations cannot be easily correlated with the data spatial location, and are probably mostly due to the period and location of the recharge of the aquifer. The most depleted sample of IMS (SIM4) is located in the eastern border of the basin and originates from 177 m depth, it may represent an old recharge (as the estimated age of some ground waters are close to 16–35 ka using ^{14}C , [26]).

5 – Stable isotope in some European large aquifers

Variations of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signature in the Eocene aquifer system from the Adour-Garonne district in SW France can be related to changes in the recharge over various climatic

periods, from present day to old (e.g. up to 35 ka). Similar behavior can be revealed by several studies of groundwaters in aquifers and such significant isotopic depletion of groundwaters may be due to a lower recharge temperature at the time of infiltration [27]. We will consider several cases of illustration in European aquifers as summarized in Figure 4 for which the authors have investigated groundwater as archive of climatic changes or as being a reflection of a more recent recharge period.

5.1. Aquitaine Basin

The Aquitaine basin considered in the study by Le Gal La Salle et al. [28] and Jirakova et al. [29]) occupies an area of 25,810 km² and extends essentially in the northern part of the Adour-Garonne area (Poitou-Charentes district) and is limited to the west by the Atlantic Ocean. Lower and Middle Jurassic carbonate formations make up the deepest aquifer of the northern part of the Aquitaine Basin investigated in these studies. Reported in the $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ graph (Fig.5), data plot in the upper range of values measured for the whole Aquitaine Basin (see this work, §4 and André [26]).

Groundwaters with a wide range of $\delta^{18}\text{O}$ values (-4.9 to -7.4‰) and $\delta^2\text{H}$ (-35 to -48‰) plot along the GMWL reflecting the meteoric origin (Fig.5, [28]). Some of the groundwaters are significantly enriched or depleted in comparison with modern waters ($\delta^{18}\text{O}$ around - 5.7‰ and $\delta^2\text{H}$ around -36‰). Considering the repartition of the values, Enriched stable isotopes in groundwaters in the southwest part of the area were evidenced while groundwaters are either depleted or similar to modern recharge northeastward [28]. The heterogeneity of the recharge conditions in the area are attested by the observed variations and may be due to climate, temperature or infiltration changes even if the authors do not preclude mixing with enriched waters (e.g. seawater) in the deeper part of the basin. However, groundwaters having a depleted value compared to the modern recharge plead in favor of a large palaeorecharge of

the aquifer that occurred during a colder period, possibly the last glaciation or deglaciation periods.

Considering a larger area in the Poitou-Charentes district, Jirakova et al. [29] show an entire range of stable isotope values from -7.7‰ to -4.9 ‰ for $\delta^{18}\text{O}$ and -52.3‰ to -29.6‰ for $\delta^2\text{H}$ that agree with the study of Le Gal La Salle [28] concerning the heterogeneity of the recharge conditions as demonstrated in the $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ diagram (Fig.5). Enlarging the area confirms the existence of depleted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and suggests lower temperatures during the recharge period. This type of waters represents the palaeorecharge under cold climatic conditions during the late Pleistocene period and was clearly separated from those of the Holocene. The modelling of the water residence time, using ^{14}C , showed Holocene waters with enriched values (around -6‰ and -38.5‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively) with radiocarbon ages up to 10 ka B.P. On the other hand, the groundwaters having depleted values (around -7.4‰ and -48‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively) have radiocarbon ages between 20 and 15 ka B.P. that corresponds to the cold recharge.

5.2 Paris Basin

Moving north of the Aquitaine Basin, the Paris basin is the second major sedimentary basin in France with an extend of around 600 km in diameter and more than 3000 m of sediment deposits. The Dogger aquifer (200-300 m, predominantly limestone), confined between the Liassic and Upper Callovian marls was studied by Matray et al. [30]. The Cretaceous Chalk aquifer (700m of fine grained limestone) either confined or unconfined is extensively exploited for drinking water and irrigation and was studied by Kloppmann et al.[31].

Groundwater samples from the recharge zone of the *Dogger aquifer* mimic the stable isotope composition of the present day rain waters, indicating a recent meteoric origin (Fig.5). The rest of the groundwater plot on the right the meteoric water line with low variations in the $\delta^2\text{H}$

and $\delta^{18}\text{O}$ (range -40 up to -30‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the range -6 up to -3‰). In this part of the basin, the water temperature and salinity are high but seem to have no impact on the stable isotope signatures. The authors discussed the possible isotope exchange with the carbonate matrix for oxygen, and with H_2S for deuterium, but they argued that such processes cannot be the major one controlling the groundwater isotope values. Important mixing processes are responsible of both the stable isotope composition and salinity of the groundwater in the Dogger aquifer and successive mixings between sedimentary brines with several meteoric waters led to the observed isotope compositions of the groundwater. The authors argue for percolation of meteoric water, dissolution of halite in the Triassic aquifer that generate a brine that mixed with a residual primary brine, then migrated via vertical faults into the Dogger aquifer.

Stable isotopes in the confined groundwaters of the Paris Basin *Chalk aquifer* plead in favour of a recharge during Holocene time with a water component related to Pleistocene ages in the deepest confined part of the aquifer. The observed depleted values in the confined part of the aquifer can be related to a lower recharge temperature at the time of infiltration. On the other hand, the influence of the continental effect affects the stable isotope composition of Chalk groundwaters. The observed depletion of the stable isotopes in the unconfined groundwaters from west to east mimics the one that could be observed in rainfall when air masses penetrated a continental area. Long term changes in the input function related to climatic evolution yield to the lowermost $\delta^2\text{H}$ - $\delta^{18}\text{O}$ values in the confined aquifer as well enriched values in the unconfined aquifer originates from fractionation processes due to variation in the recharge signal (e.g. the rain input).

5.3 London Basin

In United Kingdom, the Chalk aquifers were studied by Hiscock et al. [32] in the Norfolk area (eastern England), by Dennis et al. [33] in the London Basin (SE England) and by Elliot et al. [34] in the London and the adjacent Berkshire Basin (east of the London Basin). The geology consists of Cretaceous Chalk overlain by Tertiary clastic deposits with a thickness of more than 400 m in the Norfolk area and up to 250 in the London Basin.

$\delta^{18}\text{O}$ - $\delta^2\text{H}$ values fall within the range of -8‰ to -6.6‰ and -55‰ to -43‰ respectively and all data plot on, or close to the global meteoric water line as illustrated in Fig.5.

Both studies argue that the evolved Chalk waters typically show enriched isotopic signatures that might be compared to the recharge temperatures determined through noble gas investigations. This may reflect the mixing of relatively young groundwater in the fissures with older groundwater in the matrix. The $\delta^{18}\text{O}$ - $\delta^2\text{H}$ variation along the meteoric water line was related by all studies to the complexity of the recharge over time and mixing processes in the aquifer. The conceptual model for the Chalk aquifer suggests that the water evolved from connate Cretaceous marine water repeatedly mixed with fresh meteoric water since the Late Tertiary. The present day conditions reflect such mixing with palaeowater recharged during a cold period.

5.4 Lorraine Basin

Moving eastward of the Paris Basin, the lower Triassic in eastern France is mainly represented by sandstones and conglomerates and the extent of the Triassic aquifer reaches 3000 km² for the unconfined and 25,000 km² for the confined part. In the $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ graph (Fig.5), data are scattered between two extreme values, the most enriched values correspond to recent waters close to the recharge zone and reflect the values of modern rainfall [35]. On the other hand the depleted values may correspond to a cooler recharge regime during the Holocene.

5.5 Germany: Gorleben and LaeGERdorf Basins

Moving more eastward, the salt structure of Gorleben–Rambow in Germany, crossing the Elbe river about 100 km upstream of Hamburg has been investigated in detail since past decades with around 400 boreholes [36]. In this frame, all analysed fluids plot on the global meteoric water line. The shallow groundwaters show $\delta^{18}\text{O}$ values of -8 to -8.5 ‰ and $\delta^2\text{H}$ of -56 and -60 ‰ (Fig. 5), in the typical range of meteoric waters and have been identified as modern on the base of their ^{14}C and ^3H contents. Most saline waters are depleted with respect to shallow groundwater by up to 20 ‰ in ^2H and 2 ‰ in ^{18}O . The lowest observed values are -72 ‰ ($\delta^2\text{H}$) and -10.3 ‰ ($\delta^{18}\text{O}$) for samples with salinities around 50 g/l. A group of highly saline groundwaters show stable isotope contents in the range of shallow freshwaters. The depletion of most of the deep saline groundwaters can be explained by a significant contribution of Pleistocene recharge probably through meltwater infiltration during or shortly after the last glaciation, this interpretation being in agreement with radiocarbon data. Intermediate stable isotope contents are due to mixing between Holocene and Pleistocene components leading to the large scatter of the reported values.

Also in Germany, Kloppmann et al.[31] presented isotope data in chalk groundwater (Fig. 5). The LaeGERdorf Chalk outcrop (Campanian- Maastrichtian) is exploited up to a 90 m depth. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values plot along the meteoric water line but with higher values than in Gorleben. Kloppmann et al. [31] related the most depleted values in LaeGERdorf to a temperature effect.

5.6 Pannonian Basin

Moving more eastward, the Pannonian Basin is a large area formed mainly during the late Tertiary and Quaternary periods and covering 100,000 km² in southeast Hungary. The

hydrogeological system is a multilayer aquifer system with an intermediate flow regime in the Pleistocene sediments that concerns local to regional scale and a deeper system, lower than 2500 m that concerns the regional scale.

Groundwaters plotted in a $\delta^2\text{H}$ and $\delta^{18}\text{O}$ graph define 2 groups (Fig.5, [37]). One group, corresponding to the deeper part of the aquifer (500 – 2500 m, $T > 40^\circ\text{C}$) shows a weak range in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and plots close to the global meteoric water line. This suggests that infiltration occurred during the same and probably the last cold period that occurred between 70,000 and 12,000 years BP. The other group of waters plots to the right of the global meteoric water line and the shift of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ is not related to an evaporation process but to mixing between old waters with water enriched in heavy isotopes [37]. The origin of the enriched waters is suspected to be from oil field water, squeezed from the Pannonian layers underlying the aquifer.

5.7 Poland Basin

The Malm aquifer (limestones, sandstones and marls) in southern Poland around Cracow is the most eastward of the investigated aquifers we illustrate in this study. This aquifer is intensively exploited and this aquifer serves as a major strategic reserve of potable water for the 1 million inhabitants of Cracow. The Malm aquifer is driven by numerous faults, graben and horsts and as a consequence of this complex geology, flow pattern and ages of water are poorly constrained. Based on several tools like nobles gases, tritium and carbon isotopes, Zuber et al. [38] defined a range of water ages on the confined and unconfined part of the aquifer from modern period to glacial waters, and glacial waters partly mixed with older water (e.g. before 15ka BP).

In the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ graph illustrated in Fig. 5 groundwaters plot along the GMWL. Modern waters show enriched $\delta^2\text{H}$ - $\delta^{18}\text{O}$ values, in agreement with the mean annual precipitation.

They are either from present day (e.g. containing tritium) or from pre-bomb time (e.g. free of tritium). More the waters are old, more they plot with depleted $\delta^2\text{H}$ - $\delta^{18}\text{O}$ values and their status (glacial-Holocene transition period waters and glacial waters) is constrained by the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ values and noble gases temperatures. The older waters show the largest $\delta^2\text{H}$ - $\delta^{18}\text{O}$ depleted values and are related to other recharge areas, or deeper origin than the glacial waters [38].

5.8 Portugal

Moving south-westward Europe, in the south Portugal, the Sado sedimentary basin is made of Eocene (sandstone and carbonate), Miocene (conglomerates, limestones and sandstones) and Pliocene (conglomerates and sands) sediments [39]. Within the Sado basin the Plio-Miocene and the Eocene are the two identified aquifer systems. The two aquifers have similar $\delta^2\text{H}$ - $\delta^{18}\text{O}$ values with as example -5.0 to -4.0‰ in the Eocene aquifer and -5.0 to -4.6‰ in the Plio-Miocene aquifer for the $\delta^{18}\text{O}$ (Fig. 5). Values are depleted along the flow path is observed as shown by the Plio-Miocene, which is more depleted near the northern limit of the basin when compared to the southern. According to the range in the ^{14}C ages for the groundwater and the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ values in the Plio-Miocene and Eocene aquifers, Galego-Fernandes and Carreira [39] argue for infiltration processes of the Eocene waters under climatic conditions different from the modern ones.

5.9 A highly complex aquifers system: the Switzerland example

In the middle of the Europe, the northern Switzerland is composed of three main sedimentary stratigraphic groups from Tertiary to Permo-Carboniferous that include large aquifers, potentially locally connected through tectonic accidents. These sediments contain several aquifers, it is composed of sandstone (Tertiary-Malm group) and Malm limestones; the upper

Muschelkalk consist of limestones and dolomites; and the lower Triassic-Permian group consists of clastic sediments. The two other aquifer systems are the Quaternary cover, largely impacted by anthropogenic activities, and the crystalline basement where water circulations in the crystalline basement are mainly controlled by tectonic fractures [40]. The synthesis present waters sampled in the beginning of the 80's (Fig. 5). Waters from Quaternary, Tertiary and Malm aquifers are not considered as most of the samples present typical values of modern recharge from the northern Switzerland. The Keuper aquifer level mainly contain young groundwaters, with detectable tritium contents, defining a relatively small range of stable isotopic signatures, from -10.5 to -8.7‰ and -74 to -63‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively.

The Muschelkalk layer first contains young waters ($^3\text{H} > 20$ TU) plotting on the meteoric water line and reflecting superficial waters of the upper and middle Muschelkalk, and also mixed superficial and deeper waters of the upper Muschelkalk. Samples with low tritium contents ($^3\text{H} < 20$ TU) present different stable isotopes signatures, some are identical to the modern samples while others are depleted in heavy isotopes or enriched in ^{18}O only. The ^{18}O enriched samples correspond to hot springs, that could originate from mixing of depleted deep water with enriched water in both ^2H and ^{18}O by evaporation, or by isotope exchange with the rock matrix. Depleted samples in both ^2H and ^{18}O have different stories and surprisingly the most depleted one, that normally must reflect an old recharge, was identified modern or younger than 1 ka with dating tools. This sample, close to the Rhine River, seems to reflect a recharge from the Rhine with similar signature than those of the Alpine precipitations. Some other samples have signatures consistent with a recharge in cooler conditions as they were estimated to older than 15-30 ka. Finally, some Muschelkalk samples probably reflect a recharge in higher altitude in the adjacent Black Forest.

Most of the waters from the Buntsandstein, Permian and Crystalline basement are in the same range for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ than samples of the other upper aquifers. The 4 most depleted samples from tunnels in the Alps present signatures consistent with recharge from precipitation in high altitude, and thus do not reflect old waters recharged under cooler climate. Enriched waters in ^2H and ^{18}O or only in ^{18}O group tritium free samples and waters with $^3\text{H} > 20$ TU as well as more or less mineralized waters. They reflect a specific story, from isotope exchange due to water-rock interaction to mixing of highly evaporated seawater with meteoric waters similar to young waters found currently in the upper crystalline of northern Switzerland. This example in Switzerland, mainly in the context of large sedimentary aquifers, illustrates well that signatures of stable isotopes of the water molecule can reflect long and complex stories and processes and not only climate variation through time, even when samples plot along the meteoric water line. It thus evidences that isotopic data always need to be jointly interpreted with chemical data in the general and local hydrogeological context.

6 – Summary

Based on the literature and recent investigations in the SW France, this study highlighted the use of the isotopic methods in groundwater investigations applying stable isotopes of the water molecule (hydrogen and oxygen) as tracers of water source, recharge over time and past climates variations in various continental aquifers. Parameters controlling the isotopic signature in rainwater (e.g. continental, altitude effects...) lead to the general relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$, defined as the GMWL (Global Meteoric Water Line) and groundwater generally fall along this line. If no processes affect the water molecule from surface to aquifers, groundwater conditions prevailing at the moment of the recharge are preserved. Thus the isotope signature may reflect recent recharge with hydrogen and oxygen isotope values in the range of rainwaters or recharge under colder climate.

Starting from the recent study of the a multi Eocene sands layer system (five aquifers: Paleocene, Eocene infra-molassic sands, early Eocene, middle Eocene, late Eocene) in the Adour-Garonne district (1/5th of French territory), this study explore the recharge conditions over different aquifer systems over Europe (Portugal, France, UK, Switzerland, Germany, Hungary, Poland) and highlights the recharge conditions and the story of the groundwater at large scale, involving recent, Holocene and Pleistocene components and eventually mixing between them.

The Adour-Garonne district highlights the story of the recharge over different climatic conditions with enriched samples in ¹⁸O and ²H that clearly correlate with the present day recharge while the most depleted sample reflect an old recharge. Such processes of variable recharge in aquifers over different climatic periods are also evidenced in the Aquitaine basin, in the Paris Basin Chalk aquifer and in the Lorraine, Poland and Portugal Basins. Depleted values in the confined part of this aquifer can be related to a lower recharge temperature at the time of infiltration corresponding to Pleistocene ages.

In addition to this processes, the conceptual model issued from the Chalk aquifer in the London Basin shows the complexity of the recharge over time and mixing processes. The water evolved from connate Cretaceous marine water repeatedly mixed with fresh meteoric water since the Late Tertiary, leading to the observed $\delta^{18}\text{O}$ - $\delta^2\text{H}$ variation. Such complex recharge-mixing processes are also evidenced in the Germany case, in the Pannonian Basin and more particularly in the example in Switzerland.

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Figure 1. Contour map of amount-weighted mean annual $\delta^{18}\text{O}$ values (‰) in precipitation derived from the GNIP database, for stations reporting as of 1997 (adapted from IAEA, [16])

Figure 2. General setting of the Adour Garonne district (SW France) and schematic map of the Total Dissolved Solids (TDS, mg/l) in the IMS aquifers (adapted from [2]).

Figure 3. $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot for the ground waters collected in the Eocene sand aquifers (adapted from Négrel et al., [2]). The Global Meteoric Water Line is defined as $\delta^2\text{H} = 8 * \delta^{18}\text{O} + 10$ [13].

Figure 4. Location map of the main European aquifers summarized in this study.

Figure 5. $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot for the groundwaters from European aquifers; Global Meteoric Water Line as in Figure 3: *Aquitaine Basin* [26, 28, 29 Data from the ground waters collected in the Eocene sand aquifers are in the greyed field. Chalk aquifer from the *Paris Basin* (data from [30, 31]. Chalk aquifer from the *London Basin* (data from [32-34]. *Gorleben* and Laeگردof aquifers(Germany; [31, 36). *Poland* aquifer (data from [38]). *Pannonian Basin* (data from [37]). *Portugal* aquifer (data from [39]). *Switzerland* (data from [40] and reference therein). *Lorraine* aquifer (Eastern France; [35]).