

Isotopes in groundwater as indicators of climate changes

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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 rainwater towards aquifers and those involved in the water-rock interaction, and mixing of different waters).

This review covers several large European aquifers (Portugal, France, UK, Switzerland, Germany, Hungary, and Poland), which were investigated in terms of their recharge conditions, and the story of the groundwater at a large scale, involving recent, Holocene and Pleistocene components and their eventual mixing.

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1. Introduction

For several decades, the use of isotopic methods in groundwater investigations has been readily accepted by hydrogeologists 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 sources, have been applied in investigations, so isotope hydrology and isotope hydrogeology have been great challenges since that time [3–6].

It is also clear and really evident to scientists and end-users that groundwater is one of the endangered resources of Europe. Groundwater, the main source of fresh-water in the majority of European Union (EU) states, is under increasing threat from anthropogenic activities (e.g., industry, intensive agriculture, and mass tourism). 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 key variables controlling formation of groundwater resources [6]. Substantial decreases in precipitation have been predicted for some parts of Europe,

while more rainfall is expected in northern Europe. The climate of Europe is diverse and characterized by large variations from north, south, east and 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 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 reduction of the unsaturated zone are expected as a direct consequence of climate change.

Thus, because aquifers may be subject of the effects of climate change, 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 article is to illustrate past climatic variations, recharge over time and water sources using isotopic methods in groundwater investigations, especially with stable isotopes of the water molecule ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). We use major continental aquifer systems from all over Europe to illustrate complex histories of groundwaters from infiltration to the aquifer through the processes that can affect their original signature.

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2. What are climate and climate changes?

We are all living in areas of regional climate corresponding to the average weather in that place over more than 30 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 the amount of sunlight, the height above sea level, the lie of the land, and the distance to the oceans. However, considering the entire Earth, global climate is a description of the climate as a whole, including all the regional differences in the average.

Climate variations and change, caused by external forces, may be partly predictable, particularly on the larger, continental and global, spatial scales. Because human activities (e.g., emission of greenhouse gases or land-use change) result in external forces, 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 influenced by various external forces, 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 (vapor, cloud droplets, and ice crystals) absorbs and releases lot of energy, water vapor is central for climate variability and change. The hydrosphere is the component comprising all liquid surfaces and subterranean waters, both fresh (rivers, lakes and aquifers) and saline (oceans and seas). Freshwater run-off from the land to the oceans influences ocean composition and circulation, but, due to the large thermal inertia of the oceans, they act as a regulator of the Earth's climate and a source of natural climate variability, in particular on 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 critical role in driving deep ocean-water circulation. Because of the large amount of water stored in ice sheets, their variations in volume are a potential source of variations in sea levels.

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 leads to evaporation processes inducing water to return 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 over wide ranges of space and time scales, making the system extremely complex. As an example, the marine and terrestrial biospheres have a major impact on the composition of the atmosphere through uptake and release of greenhouse gases by the biota. Similarly, the atmosphere and the oceans are strongly coupled and, for example, exchange water vapor and heat through evaporation. This is part of the hydrological cycle and leads to condensation, cloud formation, precipitation and run-off, 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 forces, may result in climate variations. Climate has changed in the past, is changing nowadays and will change in the future. The timescale 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 aquifers is mainly done by direct infiltration of rainwater or surface water or by subsurface inflow, so primarily originates from precipitation. In that way, it is necessary first to obtain 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 aquifers. By the 1950s, it was 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) depended on several climatic factors, including air temperature, amount of rain, and altitude and latitude of precipitations (e.g., [13]). Thus, combining this relationship between isotope ratios and climate and their well-established thermo-dependance, the isotopic signatures of the water molecule appeared 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 the isotope-fractionation effect accompanying the processes of evaporation and condensation. The latitude effect reflects the rainfall process based on the Rayleigh fractionation/condensation model that includes two processes:

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