

Plate 6.2 Isotopes in the Water Cycle

Introduction

Most elements constituting matter are composed of a mixture of stable and radiogenic isotopes differing one from the other by their number of neutrons in the atomic nucleus. The mass difference leads to isotopic fractionation during physico-chemical processes. Here the lighter isotopes are generally more mobile than the heavier ones. Three isotope ratios are of special interest in water studies: the ratio of oxygen-18 and oxygen-16 ($^{18}\text{O}/^{16}\text{O}$), with 10 respectively 8 neutrons in their nuclei, the deuterium/hydrogen ratio ($^2\text{H}/^1\text{H}$) with 1 respectively 0 neutrons. Finally the tritium/hydrogen ratio ($^3\text{H}/^1\text{H}$) with 2 respectively 0 neutrons, the latter serving for age determination of water. These isotopes are present in all waters and represent ideal natural tracers for hydrologic processes.

Stable isotopes of the water molecule

One million water molecules (i.e. the same amount of oxygen atoms and double this amount of hydrogen atoms) normally contain 2000 oxygen-18 and 300 deuterium atoms. This composition is variable because of isotopic fractionation at phase changes. During evaporation, e.g., the molecules with lighter isotopes show a tendency to end up in the gas phase. As a consequence the remaining water will be enriched in the heavier isotopes. Inversely during the process of vapour condensation, the heavier isotopes show a preference for the condensate. In other words, the vapour phase gets depleted of heavy isotopes. The different isotope ratios for hydrogen and oxygen lead to a linear array of the analytical points (fig. 7). These points fall along the so called «meteoric water line» representative for the region under consideration. The deviation of the points representing meteoric waters from the line is evidence for complex processes as e.g. evaporation before infiltration, or of water exchanges with the aquifer host rock (e.g. thermal waters).

The extremely small variations of these isotope ratios are measured by mass spectrometry. The isotope ratios are given as delta values (δ) i.e. relative deviations in ‰ between a water sample and an international standard representing «standard mean ocean water» (VSMOW, cf. legend on the map). Most of the water on the earth's surface can be derived from this ocean reservoir by evaporation and are therefore depleted in heavy isotopes with respect to the standard, and yield negative δ values.

Climatic variations

As the isotopic fractionation at phase transitions is temperature dependent, the isotopic ratios of meteoric precipitation show a strong seasonality (fig. 3). During summer times meteoric precipitation is enriched in ^{18}O whereas during winter with the lower mean temperatures precipitation is depleted of heavy isotopes. In surface and subsurface waters, this phenomenon is damped by mixing processes (cf. map). The yearly distribution of isotopic ratios from precipitation during the last three decades is quite different from one year to another (fig. 2), but nevertheless shows a tendency of enrichment of the heavy isotopes with time (fig. 1). These findings could be related to a global warming of the climate, or to a change in the origin of precipitation. Figure 6 shows that these variations of the isotope ratios can also be observed at the scale of local heavy rains, here the data can be explained by the progressing depletion of certain parts of the cloud masses during the transition of a warm or cold front. Behind the weather front and beneath the central part of the cloud masses, the precipitation generally is isotopically depleted. The mean isotope ratios are also linked to regional climatic conditions as shown by the Locarno-Monti station (fig.1). The values close to zero reflect enriched water of Mediterranean origin and also the mild climatic situation.

Altitude effects

A cloud raising along a relief leads to a gradual depletion of precipitation in heavy isotopes (fig. 1, Meiringen–Guttannen–Grimsel). This depletion is a consequence of the lowering of the condensation temperature with decreasing pressure and of other minor influences, e.g. evaporation during the fall of the rain drops. Although a multitude of parameters influence all these phenomena, stable isotopes nevertheless define a more or less linear correlation with topographic elevation (fig. 4). Stable isotopes are therefore particularly apt for the determination of the mean altitude of a catchment in mountain areas (fig. 12), if the seasonality of isotope ratios of precipitation is taken into consideration, as well as areal and time variations of the altitude effect (fig. 4,5). Generally speaking, monthly average samples are sufficient for isotope analyses. The sampling frequency as well as the specific position of the pluviometers have to be adapted to the problem in question and the available budget. Differences in isotope ratios allow to distinguish the components building up a flood event: The more negative isotope ratios of river water reflecting higher mean elevation of its catchment area, are distinct from the local groundwater and rain of lower elevation that yield more positive isotope ratios (fig. 11).

The radioactive isotope of the water molecule

Tritium is the only radioactive isotope of hydrogen. It disintegrates with a half-life of 12.43 years, emitting an electron. It is this β^- decay, that by means of a scintillation counter allows to quantify the minute amounts of tritium present in water in nature. For tritium measurements in water a specific unit was introduced, the tritium unit (TU, cf. map legend).

Natural tritium is produced through interaction of cosmic radiation with atmospheric nitrogen, normally yielding around 5 TU, whereas a good proportion of the present tritium is of anthropogenic origin. Between 1952 and 1963 the radioactive fallout of tritium in precipitation was increased by a factor of 1000 by nuclear tests. Since the signature of the ban on nuclear tests in the atmosphere in 1963, the amount of tritium has been gradually decreasing (fig. 8), but the industrial non military use of tritium has replaced the military production.

Certain industrial regions of Switzerland show important tritium emissions, this is the case for the Jura (watch industry), as well as for Berne and for Teufen in the Canton of Appenzell (luminescence light bulbs). The nuclear power plants Gösgen, Leibstadt, Beznau, and Mühleberg, as well as the Paul Scherrer Institute (PSI, Villigen in the Canton of Aargau) also contribute to the anthropogenic input of tritium to the water cycle. This overall human activity leads to higher tritium concentrations in water in the close vicinity of the forementioned plants [14]. Prior to the federal law on radioprotection of 22nd June 1994 household or industrial waste dumps were often contaminated by tritium. Here tritium could be used as tracer to quantify the contamination of the groundwater (fig. 10).

Determination of the residence time for groundwater

For a sustainable management of subsurface water, an age determination is indispensable. For water with an age of some tens of years at maximum, the radioactivity of tritium is particularly suitable for age determination. The effects of the hydrogeological system on the tritium concentration is simulated by mixing models. Figure 9 shows how the residence time of groundwater can be estimated.

The federal observation network of isotopes

Since 1992, the Swiss National Hydrological and Geological Survey (SNHGS) in collaboration with the University of Berne (Department of Physics) and the University of Lausanne (Department of Mineralogy and Petrography) has been monitoring an observation network in order to provide serial measurements for daily practice and the scientific community. These isotope measurements are the base for the interpretation of isotope data on water [10,11]. The isotope analyses are performed by the above mentioned departments. The Swiss stations of the world-wide network of the International Atomic Energy Agency (IAEA) and of the World Meteorological Organisation (WMO), partly in use since 1966, have been integrated into the Swiss federal network. At present the Swiss network includes 18 stations, of which 11 are used for precipitation, 6 for rivers, and one recent station for groundwater (the Lutry spring in the Burdigalian Molasse of Jorat, station of GEOLEP). All these data are stored centrally at the SNHGS and made available to the interested public. Presided by the SNHGS, a group of experts («Isotopes and Environment») supervises the observation network. A compilation of the principal Swiss observation stations for isotopes in the water cycle for the period 1986–1998 was realised by the SNHGS, in collaboration with the Federal Institute of Technology of Lausanne (GEOLEP) (cf. maps, table). The inventory may be consulted through the SNHGS (CDS, Catalogue of Data Sources).

Conclusions

Although the isotopes of oxygen and hydrogen are not the only isotopes used in hydrology (also carbon, sulfur, nitrogen, lead, uranium, thorium, strontium, argon, radon, and krypton isotopes are used), nevertheless hydrogen and oxygen constitutes the water molecule. They are therefore the only true conservative tracers in hydrology. The isotopic methods yield a polyvalent and performing tool for hydrogeologists and hydrologists, the possibilities of which reach far beyond the few examples cited above [1,2]. The present work has been realised on demand of the SNHGS. From the SNHGS-side, the project was supervised by J.-P. Tripet, P. Buttet, D.A. Grasso, T. Herold and R. Kozel.

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