Environmental Isotope Hydrology

Environmental isotope hydrology is a relatively new field of investigation based on isotopic variations observed in natural waters. These isotopic characteristics have been established over a broad space and time scale. They cannot be controlled by man, but can be observed and interpreted to gain valuable regional information on the origin, turnover and transit time of water in the system which often cannot be obtained by other techniques. The cost of such investigations is usually relatively small in comparison with the cost of classical hydrological studies.

The main environmental isotopes of hydrological interest are the stable isotopes deuterium (hydrogen-2), carbon-13, oxygen-18, and the radioactive isotopes tritium (hydrogen-3) and carbon-14. Isotopes of hydrogen and oxygen are ideal geochemical tracers of water because their concentrations are usually not subject to change by interaction with the aquifer material. On the other hand, carbon compounds in groundwater may interact with the aquifer material, complicating the interpretation of carbon-14 data.

A few other environmental isotopes such as ^{32}Si *and* $^{238}U/^{234}U$ *have been proposed recently for hydrological purposes but their use has been quite limited until now and they will not be discussed here.*

Stable Isotopes of Hydrogen and Oxygen in the Hydrological Cycle

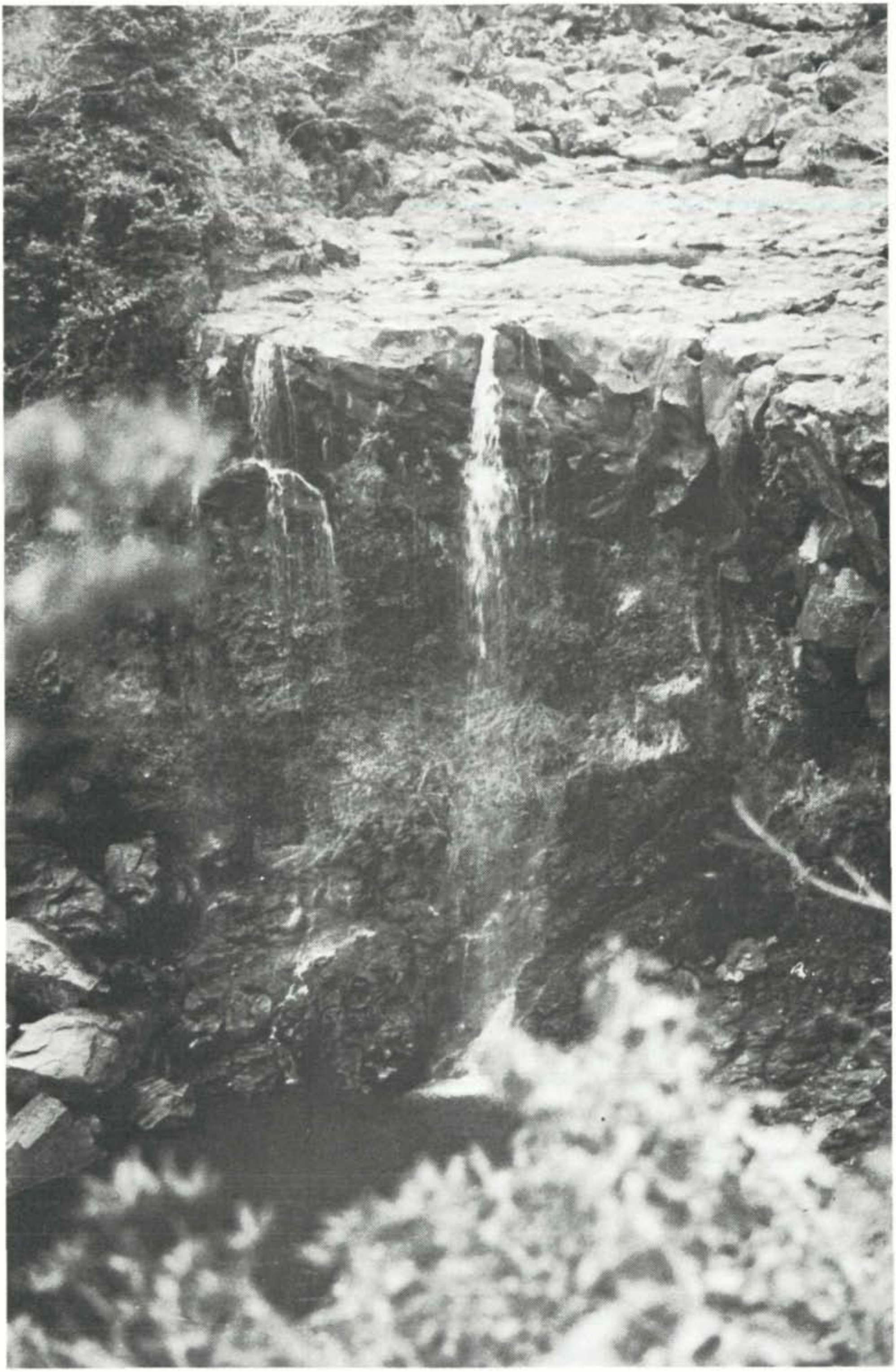
The variations of the isotopic ratios D/H and $^{18}O/^{16}O$ in water samples are expressed in terms of per mille deviation (δ‰) from the isotope ratios of mean ocean water, which constitutes the reference standard SMOW:

$$\delta‰ = \left(\frac{R_{\mathrm{sample}}}{R_{\mathrm{SMOW}}} - 1 \right) 1000$$

The isotope ratio, R, is measured using a special mass spectrometer.

The principal value of stable isotope data of a hydrological system is to identify its recharge area on the basis of general knowledge of the isotopic variations of precipitation and surface waters. The most important natural processes that cause variations of the stable isotopic composition of natural waters are evaporation and condensation. The light molecules of water, $H_2{}^{16}O$, are more volatile than the heavier ones, so on cooling of atmospheric moisture the heavy molecules condense preferentially, leaving a

Tracing water sources in the volcanic island of Cheju in the Republic of Korea . . . the Chungji Fall, Sampling Point No. 5. ▶



residual vapour more and more depleted in heavy isotopes. Such sequential condensation occurs as air masses move inland from the sea or rise to higher altitudes. Because the residual vapour requires a lower and lower temperature for further condensation, a relationship between temperature of condensation and isotopic composition of precipitation is observed; as the condensation temperature decreases, the heavy isotope content of the precipitation is lower.

This dependency on temperature produces (i) seasonal isotope variations of precipitation (winter precipitation is depleted in heavy isotopes with respect to summer precipitation), (ii) latitude variations (high latitude precipitation is depleted with respect to low latitude precipitation) and (iii) altitude variations (the heavy isotope content of precipitation decreases with increasing altitude). The last effect is especially important in regional hydrological studies, where for instance groundwaters deriving from recharge areas at different elevations may be differentiated.

When precipitation infiltrates to feed groundwater, mixing in the unsaturated zone smoothes the seasonal isotopic variations so that water in the saturated zone has a composition corresponding to the mean isotopic composition of infiltration in the area. Thus, *the isotopic composition of groundwater is related to that of precipitation in the recharge* region of the aquifer at the *time* of recharge and may serve to identify the area of recharge on the basis of altitude or distance from the sea. One must consider any climatic differences of the time of recharge that could have produced a different isotopic composition of the original infiltration from that occurring at the present time.

Groundwater recharge by lateral seepage from rivers and lakes or by vertical infiltration from ponded waters may be identified since such waters often have a different isotopic composition than local precipitation. Rivers may bring in water precipitated at high altitude, hence depleted in heavy isotopes. In ponds or lakes, the water may be considerably enriched in heavy isotopes through evaporation and they will deviate from the D-^{18}O relationship usual for precipitation.

Tritium in the Hydrological Cycle

Tritium is produced in the atmosphere by cosmic radiation and has been released in thermonuclear tests. Most of it is rapidly oxidized to HTO and incorporated in the hydrological cycle where it constitutes a very useful marker for water that has been in the atmosphere within the past 20 years. The great dilution by H_2O results in very low concentrations which can be measured only by means of tritium's radioactivity, usually after an isotopic enrichment treatment (IAEA Bulletin Vol. 15, No. 1 1973). The tritium content of natural waters is expressed in Tritium Units (TU). One Tritium Unit corresponds to a concentration of 1 tritium atom per 10^{18} hydrogen atoms.

Cosmic radiation establishes a concentration of about 10 TU in temperate zone continental precipitation. Large amounts of man-made tritium have been released to the atmosphere by thermonuclear tests since 1953. Concentrations up to 10,000 TU were reached in northern hemisphere precipitation in 1963. Since then concentrations have decreased as a consequence of limitations on the explosion of thermonuclear devices in the atmosphere. Considerable seasonal and geographical variations of the tritium content of precipitation result from the location of the major releases (the northern stratosphere) and the mechanisms of transfer from the stratosphere to the troposphere to surface waters. The IAEA publishes data on the concentration of tritium in precipitation collected at stations around the globe, from which tritium deposition at most places may be estimated.

In hydrological studies, tritium measurements give information on the transit or turnover time of water within a system. In a confined groundwater system, tritium concentrations may be correlated with the known tritium deposition modified by considerations of seasonally-selected recharge and dispersive mixing effects within a granular aquifer. Qualitatively, concentrations of less than 2 or 3 TU at a northern continental site indicate that the water was recharged before the release of thermonuclear tritium, i.e. before 1953, whereas concentrations above 20 TU indicate a much more rapid flow of water through the system. In an open system, surface or subsurface, mixing of waters of different ages predominates and tritium concentrations are interpreted in terms of a Mean Residence Time in a mathematical model consisting of a mixing cell or combination of cells that are considered reasonable from the geohydrological standpoint.

Carbon Isotopes in the Hydrological Cycle

Like tritium, carbon-14 occurs in the environment as a result of cosmic ray irradiation of the atmosphere and release in nuclear tests. It is oxidized to carbon dioxide, mixes with the carbon dioxide of the atmosphere and enters the global carbon cycle. Its longer half-life (5730 y) makes it of interest in studying groundwater systems where transit times may be very long. Bomb carbon-14 is not normally of interest for hydrological studies since tritium is a much better marker for recent waters.

The use of ^{14}C for dating groundwater is based on the fact that soil zone carbon dioxide is of biogenic origin, resulting from the respiration of plant roots and plant decay and hence contains ^{14}C derived by plants from the atmosphere. This biogenic carbon dioxide dissolves in infiltrating water and is carried down to the groundwater reservoir. Its ^{14}C content decreases by radioactive decay and the fraction of the original remaining is a measure of the time since it was removed from the soil zone, i.e. the time since infiltration of the associated water.

^{14}C is measured relative to the total carbon content of the sample, so one must consider the origin of both the ^{14}C and the stable carbon of the sample. Not all of the stable carbon of groundwater carbonate is of the same origin as the ^{14}C. Infiltrating water, containing carbon dioxide dissolved from the soil zone, dissolves carbonate minerals in the soil. However, the carbon originating from limestone in general contains no ^{14}C, so that the water reaching the water table contains dissolved carbon (in the chemical forms of H_2CO_3, HCO_3^- and $CO_3^=$) with a ^{14}C content lower than that present in the soil biogenic CO_2. The evaluation of the dilution of soil CO_2 originally containing 100% of modern ^{14}C with ^{14}C-free carbonate to estimate the initial ^{14}C concentration in recharge water reaching the water table constitutes the most difficult problem in the ^{14}C age determination of water.

Experience has shown that 85% of modern ^{14}C is a good average value for the content of recent, prethermonuclear infiltrating water in central Europe. In an attempt to obtain a better estimate of this value at specific sites, the stable ^{13}C content of the groundwater carbonate sample may be studied. Since biogenic carbon dioxide has a significantly lower ^{13}C content than limestone, one could hope to estimate the proportions of biogenic and limestone carbon from the ^{13}C content of the groundwater carbonate. However, knowledge of the ^{13}C content of plants in the place and time (thousands of years ago) of recharge is usually very limited. Furthermore, it is recognized that the carbon isotope ratios can be affected by much more complicated groundwater chemistry than the simple carbonate system considered above.

The ^{14}C method can be used for waters younger than 30,000 years. In general, it is applied to study the movement of water in confined aquifers. Where recharge occurs only in the outcrop area and the water chemistry and isotopic composition of dissolved carbon species are relatively uniform, the age differences in space are *not* affected by the uncertainties which affect the absolute age determination of water. Thus, it is possible to determine the flow velocity of water, by determining the age differences between two sampling points at known distance. This proves the hydrologist with an estimate of the mean regional permeability. ^{14}C measurements, especially in association with tritium measurements, may also give information on mixing processes of waters of different ages within a given aquifer.

Examples of Application

These general principles have been put to practical use in many parts of the world during the past few years in projects supported by the IAEA at the request of the Member States in whose regions hydrological problems occured.

For example, a project in the Hodna region of Algeria concerns a study of the groundwater in two aquifers in the region of a dry salt lake, Chott-el-Hodna, where flood waters from the nearby mountains evaporate completely. The heavy isotope content of water in the deeper aquifer is lower than that in the shallow aquifer, despite the fact that the two aquifers are presumed to have been recharged from the same general area. However, carbon-14 measurements giving ages of the order of some 30,000 years for the deep aquifer, indicate that the difference in stable isotopic composition is most probably due to an age effect (climatic change since the time of recharge). The deep aquifer is connected with the shallow one through buried alluvial fan (revealed by geophysics). In this area, the ^{14}C *content of water in the deep aquifer increases together with the* ^{18}O *and C content. This is a clear indication of slow recharge from the shallow aquifer. In this study tritium measurements also demonstrated the occurrence of recharge of the shallow aquifer from wadis.*

Stable isotope and tritium analyses were used in the volcanic island of Cheju, Republic of Korea, to characterize groundwaters with respect to time and place of recharge and to determine the nature of mixing of the different groundwater sources and estimate their residence times. From a preliminary sampling of 14 springs, 8 wells and 2 streams from different parts of the island, nine points were chosen for periodic sampling. All the waters sampled contained appreciable amounts of thermonuclear tritium, thus indicating rapid circulation in the various groundwater systems. Upon the basis of their tritium content and stable isotopic composition, the waters were classified into a number of flow regimes.

This small well in Whasoon-ri was Sampling Point No. 7 in the Cheju isotope hydrology study. In the lower partitioned well, water is used for drinking, while the washing is done and stock is allowed to drink outside the enclosed area.

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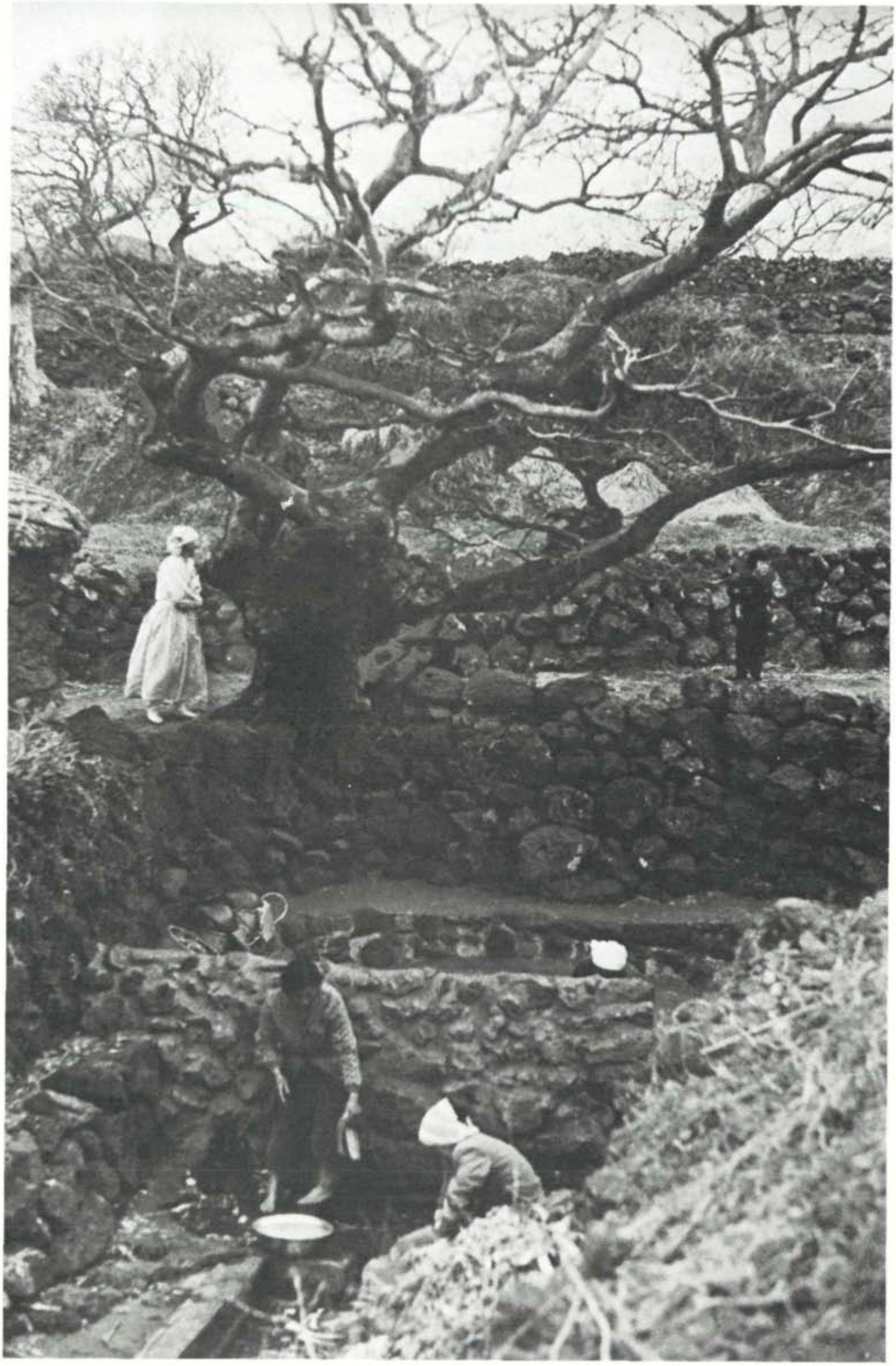

Springs at medium and high altitude exhibited a relatively high tritium concentration and a wide spread of stable isotopic composition. This was interpreted as the water having a short transit time with poor mixing, in general agreement with the hydrogeology of the area. On the other hand, large coastal springs had a much lower tritium concentration, but with a similar spread in stable isotopic composition. This suggested a similar source as for the high altitude springs, but involving a somewhat longer transit time. Small springs and wells near the east coast of the island had a similar tritium concentration but, at the same time, somewhat higher heavy isotope content. The latter appeared to reflect the somewhat lower terrain in the eastern part of the island.

Although the period covered by the tritium analyses was relatively short, an estimate was made of the mean transit time of the waters. A well-mixed reservoir model was adopted assuming that recharge was only effective for monthly precipitation values in excess of 100mm. Values of from 2 to 8 1/2 years were estimated, the longer times being associated with waters discharged from an extensive well-mixed fresh water lens.

A project in the coastal plain of Nicaragua concerns the study of recharge mechanism to a phreatic aquifer. The project area is sub-rectangular in shape, having approximate dimensions of 30 × 55 km, oriented to NW-SE. The SW boundary is the Pacific Ocean, and the drainage divide of the volcanic chain, La Cordillera de Marrabios, constitutes the NE limit of the area. Across the short dimension, elevations rise uniformly to about 200 m above sea-level at about 20 - 25 km from the ocean (Chinandega Plain), and abruptly thereafter to the Cordilleran crest which has an average elevation of about 1000 m and a maximum of 1745 m. The plain is covered by Quarternary "tobas", ash deposits and the stratigraphic sequence of the Tertiary. Stable isotopes and tritium have been employed to study the problems associated with the recharge mechanism to the groundwater system in the area with particular emphasis on the importance of low plain recharge versus the elevated slopes of the Cordillera. Periodic sampling at 5 precipitation stations and two springs, all located at different elevations enabled experts to establish the relation between the elevation and stable isotopic composition of recharging water. Both shallow and deep wells in the plain are sampled periodically to determine the isotopic composition of local recharge as well as that of the deeper groundwater. The rather shallow wells on the plain with most enriched stable isotopic composition and highest tritium content were good indices for the isotopic composition of local recharge. The rather uniform stable isotopic composition of drilled wells, together with the known isotopic composition of local recharge on one hand and the stable isotopic composition of the water recharging from elevated slopes, enabled the study of the relative importance of plain recharge versus the recharge from elevated slopes. It was found that a much higher proportion of recharge to the groundwater system occurs from the elevated slopes with a mean altitude of about 500 m. The tritium content of wells in the plain enabled the study of the transit time involved in the recharge to groundwater and it was concluded that the water in the shallow wells had been recharged locally no more than 3 years ago and the water tapped by the drilled wells had a mean transit time in the order of 20 years.

Similar hydrological studies are at present being continued in Austria, Brazil, Bolivia, Canary Islands, Colombia, Crete, Jamaica, Katar, Lebanon, Mexico, Senegal, Turkey and Yugoslavia.