

The need and potential applications of a network for monitoring of isotopes in waters of India

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Meeting the water demand of a growing population in India requires large-scale engineering modification of the natural hydrological cycle that is bound to have significant environmental consequences. Therefore, it is essential to have a detailed understanding of the natural hydrological cycle in terms of processes controlling seasonal and spatial distribution of water. Some knowledge gaps in this context are: (i) quantification of sources of water vapour during different seasons; (ii) partitioning of incoming vapour into rain and its re-partitioning as evapotranspiration, soil moisture, stream flow and groundwater; (iii) quantification of interactions between these components; and (iv) identifying geographical and climatic factors that exercise major control over the entire hydrological cycle. With a view to address these issues comprehensively, a multi-institutional collaborative programme entitled 'Isotopes in Waters of India Network' is proposed. The strategy is to monitor spatial and temporal variations of isotopic composition in (i) atmospheric vapour phase, (ii) rain, (iii) major surface water sources and (iv) groundwater. This data and knowledge of isotopic fractionation process are then proposed to be used in conjunction with conventional data of fluxes and volumes to mathematically model and predict the water-related environmental consequences of planned development projects.

INDIA is well endowed with water resources, but increase in population and aspirations for a better quality of life are beginning to stress the available supplies in certain parts and seasons. Harnessing our water resources since independence has made the country self-sufficient in food production. New schemes involving harnessing of water at different scales, from local to inter basin transfer, are being launched in an effort to secure sufficient water of reasonable quality to meet the anticipated future requirements.

In this context, it is felt that an improved understanding of the controls (e.g. geographical and climate) on the seasonal and spatial distribution of water during rainy seasons and its redistribution during the non-monsoon periods will provide scientific inputs to plan a better water resource development strategy for the country. Some knowledge gaps in this context are: (i) identifying dominant sources of water–

vapour supply during different seasons; (ii) the partitioning of vapours into rain and re-partitioning of rain to various components as evapotranspiration, soil moisture, stream flow and groundwater; (iii) quantification of the extent and rates of interactions between these components, and (iv) the controls that geographical and climatic factors exercise over the entire hydrological cycle, both temporally and spatially.

Answers to some of the issues raised above are available partially as a result of the investigations that involved measurement and monitoring of atmospheric pressure, temperature, humidity, rainfall and wind velocities from ground level and airborne platforms conducted over almost a century by the India Meteorology Department (IMD) and other agencies involved in river (Central Water Commission) and groundwater (Central Ground Water Board) monitoring. However, identifying the vapour and water sources and their temporal evolution in response to changes in meteorological and geographical controls and to estimate the hold-ups in different reservoirs and their spatial distributions require tools that can trace water molecules through their annual hydrological cycle. This can be achieved through studies of stable isotopes of oxygen and hydrogen (^{18}O and ^2H) in the water molecules in different reservoirs together with other data pertaining to volume measurements and fluxes. The little sluggishness of the heavier isotopes (in comparison to ^{16}O and ^1H) results in their preference to concentrate in the denser phase during phase change (water to vapour or ice and vice versa). This causes isotope fractionation between the phases involved in the process. The known relationships between degree of phase change and the extent of isotope fractionation then provide the best tools for tracing the movements of water molecules through the various components of the hydrological cycle.

The surface waters of two oceanic vapour sources for India, namely the Indian Ocean/Arabian Sea and the Bay of Bengal, have different isotopic composition due to large difference in river water discharge. Oceanic vapours inherit these differences. Therefore, rains in the coastal areas derived from these vapour sources exhibit characteristic isotopic signatures. Farther inland, the isotopic composition of rain is altered by preferential rainout of heavier isotopes, evaporation from raindrops and the return flux into the atmosphere by means of evapotranspiration. The precipitated water at any location is further partitioned between surface

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run-off, infiltration into the soil and eventual groundwater recharge. The isotopic composition of these respective fluxes may differ from that of the precipitation due to the modification resulting from the partial evaporation of water and by the selective utilization in these different pathways of rain with different isotopic compositions. These hydrological processes impart a characteristic isotopic signature to different water sources and the differences can be used to study their extent and the mutual interactions between the respective fluxes.

Realizing the importance of stable isotopes in hydrology, the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) established a Global Network of Isotopes in Precipitation (GNIP), in which samples are collected regularly to monitor the $\delta^{18}\text{O}$ and δD of precipitation. The data produced by this network are essential for environmental isotope hydrology. They are available on the World Wide Web at <http://www.isohis.iaea.org>. Over the last three decades, the data have been useful in understanding the systematics of isotope hydrology as also in tracing large-scale atmospheric vapour transport systems. Unfortunately, long-term precipitation isotope data are available only for two Indian stations, namely New Delhi (1967–2000) and Mumbai (1960–78). No data on isotopes in precipitation from anywhere along the east coast of India exist.

There are few seasonal river-water isotopic measurements, except in the Ganga^{1,2}, Indus³ and Yamuna⁴ basins, to establish identity and origin of stream waters during different parts of the year. Even in these basins, the available data do not permit identifying the areas of effluent groundwater discharge and the volumes involved in different parts of their catchments.

Fairly large numbers of groundwater isotopic measurements in different parts of the country have been made by different workers. Using these data as a proxy for the precipitation isotopic data, efforts have been made to draw inferences about the influence of prevailing monsoon system^{5,6}, evaporation^{7,8}, recycling⁹ and for isotopic characterization of groundwater and river water^{10–13}. Using isotope data of groundwater as proxy, in the absence of precipitation data, is an unavoidable necessity and has limitations as discussed subsequently. The available isotopic data, together with ground-based and airborne meteorological data, are not enough to quantitatively describe the entire hydrological cycle in terms of exchanges and interactions among its various components, namely oceanic source, atmosphere, precipitation, surface water and groundwater.

In the following, after a relevant discussion on Indian monsoon dynamics and factors influencing the isotope signatures and interpretation of available isotope data, a case is made to initiate a study for spatial and temporal fingerprinting of water of India using stable isotopes to investigate seasonal evolution, interaction, geographic controls and climatic forcing. Towards this, a multi-institutional collaborative research programme, acronym IWIN

(Isotopes in Waters of India Network), has been conceptualized.

Indian monsoon dynamics and annual hydrological cycle

The hydrology in India is largely controlled by precipitation during the summer (SW) and winter (NE) monsoons. The SW monsoon operates during the months of June–September and NE monsoon during the months of October–January. The causal mechanism^{14–16} for these monsoon systems is the seasonal reversal of temperature and pressure gradients and associated wind circulation following the annual northward and southward motion of the sun. These two seasonal circulation systems are part of the larger monsoon circulation of South Asia. Because of the geography of the continental drainage area, the river discharges into Arabian Sea (AS) and Bay of Bengal (BOB) differ by an order of magnitude. As a consequence, the surface waters of the BOB get more diluted by freshwater. In terms of average sea water isotopic composition, the BOB has been shown to be ~1‰ depleted in $\delta^{18}\text{O}$ with respect to the AS^{17,18} due to large influx of monsoon run-off from Himalayan rivers. As a result, the BOB is expected to have large seasonal changes in isotopic composition of its surface-water, similar to large seasonal surface-water salinity changes¹⁹.

The annual hydrological cycle begins with the onset of SW monsoon over Lakshadweep, Minicoy and Kerala, which brings copious rain over the Western Ghats. Slowly, the monsoon current advances over the southern peninsular region and crosses over to the east coast²⁰. This is the AS branch of the SW monsoon. Over the BOB, the monsoon current turns anti-clockwise and re-enters India across the central and northern parts of the east coast, giving rise to the BOB branch. During winter and spring, winds originating in the east and central Asia and moving towards the southwest direction pass over the BOB before entering the southeast parts of India in the form of NE monsoon^{13,15,21}. Roughly around the same period, the northern and north-western parts of the country receive rains due to western disturbances that originate over the Mediterranean and West Asia.

By the end of the rainy season in September–early October, the inflow of water vapour from the sea surface gradually decreases and the resident moisture within the country in different components continues to redistribute through evapotranspiration to the atmosphere, soil moisture drainage to the groundwater and effluent groundwater discharge to the rivers. Finally, with the beginning of summer in March–April, the evapotranspiration of the surface water and soil moisture becomes the dominant process controlling the hydrological cycle in the country until the end of May, when the yearly cycle begins afresh.

In the following, it is shown that extensive (spatially and temporally) measurements of stable isotopes of oxygen

and hydrogen through different components of the hydrological cycle can lead to quantitative estimation of vapour/water fluxes and residence times in different reservoirs.

Stable isotope systematics

Among all the methods used to understand hydrological processes, application of tracers—in particular isotope tracers—has been the most useful in terms of providing new insights. In particular, ^{18}O and ^2H (also known as deuterium; D) are integral parts of water molecules; hence they are ideal tracers to follow the movement of water.

Stable isotope compositions of oxygen and hydrogen are normally reported in δ -notation, as deviations relative to an international standard of known composition in units of parts per thousand (denoted as ‰). The δ values are calculated by

$$\delta (\text{in } \text{‰}) = (R_x/R_s - 1) \times 1000, \quad (1)$$

where R denotes the ratio of heavy to light isotope (e.g. $^{18}\text{O}/^{16}\text{O}$ or D/H) and R_x and R_s are the ratios in the sample and standard respectively. δD and $\delta^{18}\text{O}$ values are normally reported relative to SMOW (Standard Mean Ocean Water)²² or the equivalent VSMOW (Vienna-SMOW)²³ standard.

Isotopic fractionations are produced mainly by equilibrium isotopic exchange reactions and kinetic processes. Equilibrium isotope exchange reactions involve the redistribution of the isotopes between the products and reactants (or the two phases during phase change) in contact with each other. As a 'rule of thumb', among different phases of the same compound (e.g. H_2O), the denser the material, the more it tends to be enriched in the heavier isotope (D and ^{18}O).

In systems out of equilibrium, forward and backward reaction rates are not identical, and isotope reactions may, in fact, be unidirectional, if reaction products physically become isolated from the reactants reactions. Such reactions are called kinetic. A third reaction type where fractionation of isotopes occurs is the diffusion of atoms or molecules across a concentration gradient. This can be diffusion within another medium or diffusion of a gas into vacuum. Fractionation arises from the difference in diffusive velocities between isotopes.

Craig²⁴ showed that in spite of the great complexity in different components of the hydrological cycle, $\delta^{18}\text{O}$ and δD in freshwaters correlate on a global scale. Craig's global meteoric water line (GMWL) defines the relationship between $\delta^{18}\text{O}$ and δD in global precipitation as:

$$\delta\text{D} = 8. \delta^{18}\text{O} + 10 \quad (\text{‰ SMOW}). \quad (2)$$

It indicates that the isotopic composition of meteoric waters behaves in a predictable fashion. The line is global in application, and is the average of many local or regional meteoric water lines, which may differ from the global line due to

varying climatic and geographic parameters. Local Meteoric Water Lines (LMWLs) can differ from global lines in both slope and deuterium intercept. Nonetheless, GMWL provides a reference for interpreting the hydrological process and provenance of different water masses.

Adding the precision to Craig's GMWL, Rozanski *et al.*²⁵ compiled the precipitation isotope data from 219 stations of the GNIP. This refined relationship between ^{18}O and D in global precipitation is given by²⁵:

$$\delta\text{D} = 8.17 (\pm 0.07) \delta^{18}\text{O} + 11.27 (\pm 0.65) \text{‰ VSMOW}.$$

The evolution of $\delta^{18}\text{O}$ and δD values of meteoric waters begins with evaporation from the oceans, where the rate of evaporation controls the vapour-water exchange and hence the degree of isotopic equilibrium. Increased rates of evaporation impart a kinetic or non-equilibrium isotope effect on the vapour. Kinetic effects are influenced by surface temperature, wind speed (shear at water surface), salinity and, most importantly, humidity. At lower humidity, evaporation becomes an increasingly non-equilibrium process.

The most accepted model for non-equilibrium evaporation from a water body involves diffusion of water vapour across a hypothetical micron thin boundary layer (bl) over the liquid-water interface. The boundary layer has virtually 100% water saturation. This layer is in isotopic equilibrium with the underlying water column. Between the boundary layer and the mixed atmosphere above is a transition zone through which water vapour is transported in both directions by molecular diffusion. It is within the transition zone that non-equilibrium enrichment arises due to the fact that diffusivity of $^1\text{H}_2^{16}\text{O}$ in air is greater than that of $^2\text{H}^1\text{H}^{16}\text{O}$ or H_2^{18}O . The isotopic enrichment ($\Delta\epsilon$) due to kinetic fractionation at humidity (h) is given by the following two relationships²⁶:

$$\Delta\epsilon^{18}\text{O}_{\text{bl-v}} = 14.2 (1-h)\text{‰}, \quad (3)$$

$$\Delta\epsilon^2\text{H}_{\text{bl-v}} = 12.5 (1-h)\text{‰}. \quad (4)$$

The total enrichment between water column and open air is the sum of the enrichment factor for equilibrium water vapour exchange (ϵ_{v}) and the kinetic factor ($\Delta\epsilon_{\text{bl-v}}$) for diffusion through boundary layer. For ^{18}O , this would be

$$\delta^{18}\text{O}_1 - \delta^{18}\text{O}_v = \epsilon^{18}\text{O}_{1-v} + \Delta\epsilon^{18}\text{O}_{\text{bl-v}}. \quad (5)$$

This calculation represents the enrichment of water with respect to vapour. The depletion in vapour with respect to water is the negative enrichment. Under conditions of 100% humidity ($h=1$), the vapour is in isotopic equilibrium with sea water ($\Delta\epsilon^{18}\text{O}_{\text{bl-v}}=0$) and when humidity is low (e.g. $h=0.5$), the vapour is strongly depleted in ^{18}O compared to D. The global atmospheric vapour forms with an average humidity around 85% ($h=0.85$). Hence Craig's GMWL has deuterium intercept of 10‰.

Thus, formation of atmospheric vapour masses is a non-equilibrium process due to effects of low humidity and mixing of different vapour masses. However, the reverse process – condensation to form clouds and precipitation – takes place in an intimate mixture of vapour and water droplets with 100% humidity. Here equilibrium fractionation between vapour and water is easily achieved. The isotopic evolution of precipitation during rainout is largely controlled by temperature. Hence the slope of meteoric water line given by the ratio of equilibrium fractionation factors (α) for D and ^{18}O is

$$S \approx \frac{10^3 \ln \alpha_{\text{D/H}}}{10^3 \ln \alpha_{^{18}\text{O}/^{16}\text{O}}} = 8.2 \text{ at } 25^\circ\text{C}. \quad (6)$$

The actual slope will vary with average temperature of condensation from 9.2 to 8.0 for temperature between 0 and 30°C . It is thus seen that the meteoric relationship of ^{18}O and D arises from a combination of non-equilibrium fractionation from the ocean surface (at $\sim 85\%$ humidity) and equilibrium condensation from the vapour mass. However, it is Rayleigh distillation during rainout that is responsible for further partitioning of ^{18}O and D among different regions.

As an air mass follows a trajectory from its vapour source area to higher latitudes and over continents, it cools and loses its water vapour along the way as precipitation, a process known as rainout. Within the cloud, equilibrium fractionation between vapour and the condensing phases preferentially partitions ^{18}O and D into rain or snow. Along the trajectory of the air masses, each rainout condenses the heavy isotopes from the vapour. The remaining vapour then becomes progressively depleted in ^{18}O and D following Rayleigh process. Whereas each rainout gives isotopically enriched rain with respect to the remaining vapour, it will be depleted with respect to earlier rainout because the vapour from which it formed was depleted with respect to the vapour of the earlier rainout. In this process, the vapour mass also decreases progressively. One can model this isotope evolution during rainout according to Rayleigh distillation equation as below.

$$R = R_0 f^{(\alpha-1)}, \quad (7)$$

when R_0 is the initial isotope ratio ($^{18}\text{O}/^{16}\text{O}$ or D/H) in vapour and R would be the ratio after a given proportion of the vapour has rained out. The residual vapour reservoir fraction is denoted by f and α denotes the equilibrium water-vapour fractionation factor at the prevailing 'in cloud' temperature. When part of the rained-out vapour is returned to the atmosphere by means of evapotranspiration, then the simple Rayleigh law no longer applies. The downwind effect of the evapotranspiration flux on the isotopic composition of the atmospheric vapour and precipitation depends on the details of the evapotranspiration process.

Transpiration returns precipitated water essentially unfractionated to the atmosphere, despite the complex fractionation in leaf water^{27,28}. Thus transpiration reduces the effect of rainout process. Under such circumstances, the change in isotopic composition along the air mass trajectory measures only the net loss of water from the air mass, rather than being a measure of the integrated total rainout. On the other hand, evaporated vapour is usually depleted in heavy species relative to that of transpired vapour and is actually closer to the composition of the atmospheric vapour.

Since the kinetic fractionation for ^{18}O is more than for that D (see eqs (3) and (4)) the relative enrichment of the residual water for an evaporating water body is more for ^{18}O than for D. Correspondingly, in the resulting vapour the depletion is more for ^{18}O than for D. Thus the parameter d -excess or d defined below, represents the excess δD than 8 times $\delta^{18}\text{O}$ for any water body or vapour²⁹.

$$d\text{-excess} = d = \delta\text{D} - 8 \cdot \delta^{18}\text{O} (\text{‰}). \quad (8)$$

Because of relatively more enrichment of ^{18}O in the residual water, d -excess of the evaporating water body decreases and that of the resulting vapour increases as the evaporation proceeds. Thus, if the original water was meteoric in origin, the residual water not only enriches in heavier isotopes but also shows progressively lower d -excess values as the evaporation proceeds, i.e. its position on the $\delta^{18}\text{O}$ – δD plot will move below the LMWL. The resulting vapour on the other hand, shows the opposite effect. Further, since condensation and consequentially rainout is an equilibrium process (with slope ~ 8), it does not significantly alter the d -excess. Thus d -excess provides an additional handle on identifying vapours of different histories and their mixing. Due to the involvement of evaporation, most meteoric and subsurface processes shift the $\delta^{18}\text{O}$ – δD signatures of water to a position below the LMWL. It is rare to find precipitation or groundwater that plots above the line, i.e. showing higher d -excess. However, in low-humidity regions, re-evaporation of precipitation from local surface waters creates vapour masses with isotopic content that plots above the LMWL. If such vapour is re-condensed in any significant quantity before mixing with the larger tropospheric reservoir, the resulting rainwater will also plot above LMWL³⁰, along a condensation line with slope ~ 8 . It is however, important to recall that recycling of water back to the atmosphere in the form of vapour from soil moisture by plant transpiration, is a non-fractionating process and does not affect the d -excess.

A small fraction of rain percolates down through the soil layer eventually to become groundwater. For many groundwater samples, the isotopic composition has been shown to equal the mean weighted annual composition of precipitation^{9,31–33}. However, significant deviations from precipitation are also found in certain cases. Such deviations from local precipitation are more pronounced in arid zones due to extensive evaporation from the unsaturated zone or

even evaporative losses from the water table^{34,35}. Considering that only a small percentage of precipitation actually reaches the water table in most landscapes, the meteoric signal in groundwater can be significantly modified. Isotope variations in precipitations are attenuated and seasonal biases in recharge can be imparted to the newly formed groundwater. This bifurcation of the hydrological cycle between precipitation and surface water on one hand and groundwater on the other, closes where groundwater discharges and rejoins surface run-off in streams and rivers. Environmental isotopes play a role in quantifying relative contribution of groundwater to stream flow and in understanding the hydraulic functioning of a catchment area.

With this basic knowledge about the systematics of isotopes, the understanding gained from the isotopic investigation of precipitation, surface water and groundwater in India is highlighted in the following.

Isotopic investigations in India

The GNIP/IAEA database (available at URL: <http://www.isohis.iaea.org>) is the largest available dataset of isotopes in precipitation. Other than New Delhi and Mumbai, precipitation isotope data of shorter length (1–5 yrs) are available from Kozikode, Allahabad, Shillong, Hyderabad and a few closely spaced stations in Lower Maner Basin. Recently, data for the year 1994 have also become available from Nainital³⁶. On the other hand, a large number of groundwater and stream water samples have been analysed in the country principally by the four active groups, viz. Physical Research Laboratory (PRL), Bhabha Atomic Research Centre (BARC), National Geophysical Research Institute (NGRI) and Nuclear Research Laboratory (NRL, IARI).

Precipitation

Spatial and temporal variability of stable isotope composition of precipitation in Southeast Asia and the Western Pacific region, with emphasis on China, based on the database of IAEA/WMO network has been explained in terms of meteorological and pluviometric regime of climatology and atmospheric circulation pattern by Araguas-Araguas and Froehlich³⁷. The variation of stable isotopes in monsoonal rains of Sri Lanka has also been studied³⁸.

The synoptic hydrology of India, based on the regional maps of amount-weighted monthly distribution of $\delta^{18}\text{O}$ and d -excess of precipitation, for different seasons over the Indian subcontinent, has already been described³⁹. It was shown that primary oceanic vapour influx areas along the west and east coasts, both during SW summer and NE winter monsoons, are characterized by d -excess in the 8–12‰ range. Due to continued aridity even during the period of summer monsoons, the rain-shadow zone of the Western Ghats, parts of southeast coast, central and north-west India, show clear indication of evaporation from falling

raindrops in the form of a low (<8‰) d -excess belt. The region over Bangladesh and the eastern states of Tripura and Manipur, and eastern Myanmar show high (>12‰) d -excess values in precipitation for most of the year, except at the beginning of May. From August onwards, the area covered by this high d -excess region progressively increases and spreads westwards, indicating evaporative recycling of vapour from the large area of wetlands and soil moisture during the monsoon and post-monsoon seasons. Another region of persistent recycled vapour of land origin lies over Afghanistan and Pakistan. It spreads to Jammu and Kashmir under the influence of western disturbances, as seen clearly in the high d -excess in August precipitation (12–16‰). This spread of land-derived vapour during winter–spring is not so clearly seen in enhanced d -excess over Jammu and Kashmir, as evaporation from the falling raindrops reduces their high d -excess to ~10‰. The lowering of $\delta^{18}\text{O}$ values in May seen in eastern India and Bangladesh indicates onset of vapour influx from the northern BOB. This is also indicated by a decrease in d -excess value of precipitation from the previous season (from >12‰ to ~10‰).

Thus, even with limited availability of data on isotopes in precipitation, it is possible to identify on regional scale, the origin of vapour fluxes and the dominant hydrological processes in different seasons. These interpretations can be sharpened and reasonably good quantitative estimates made, if systematically monitored data from a bigger network on both precipitation and vapour could be collected.

Groundwater

A large number of groundwater samples have been analysed in the country principally by the four active groups, viz. PRL, BARC, NGRI and NRL. These studies, spread almost over a quarter century, indicate the following:

Repeat measurements of isotopic composition of groundwater samples^{40,41} do not show significant temporal variation in several parts of the country, indicating mixing of soil water of several years before groundwater recharge. However, regions with secondary porosity and/or otherwise fast recharge, particularly during storm events⁴², have shown significant temporal variations in groundwater.

Groundwaters show a significant evaporation-related modification of isotopic signals of precipitation in large parts of the country, particularly in the western and central parts comprising Rajasthan, Gujarat, Haryana, Madhya Pradesh; on the eastern side of the Western Ghats in Maharashtra, Karnataka, parts of Andhra Pradesh and Orissa. In Lower Maner Basin of Andhra Pradesh, the extent of enrichment was found to vary with recharge characteristics of various soils and rock types in the basin⁴³.

In these regions, the groundwaters are enriched with respect to the precipitation in $\delta^{18}\text{O}$ and show^{4,6,9,44} lower values of d -excess. This indicates that there is little to significant kinetic evaporation of the precipitated water before groundwater recharge.

In a study of groundwater in Pushkar valley a decrease in $\delta^{18}\text{O}$ with depth of water table was observed⁴⁵, which may be due to stratification of groundwater with shallower zones being recharged from relatively modern rainfall.

Several other cases, particularly from Rajasthan and Gujarat in India, and in Bangladesh have indicated that older groundwaters have lower $\delta^{18}\text{O}$, suggesting a somewhat different past climatic regime with less aridity and/or increased precipitation^{12,46-48}.

Using the groundwater $\delta^{18}\text{O}$ values from the Kolkata-Delhi segment and departure from the expected continental gradient due to rainout⁸, it was estimated that atmospheric return back of precipitation by transpiration was as high as ~40%.

In southern India with dual monsoon influence, groundwaters from the regions dominated by NE monsoon showed distinctly depleted stable isotopic compositions compared to those dominated by the SW monsoon. The $\delta^{18}\text{O}$ - δD regression line slope of ~6 in the east coast region was lower than that expected for local precipitation, suggesting secondary evaporation⁵.

However, in the coastal regions both along the west and east coasts, groundwater samples exhibited a reasonable correspondence with the precipitation isotopic data, suggesting only minor modification of the isotopic signal during groundwater recharge. One interesting aspect of groundwater data from coastal regions is that the average $\delta^{18}\text{O}$ of groundwater samples along the west coast is $-1 \pm 1\text{‰}$ as against a much lower $\delta^{18}\text{O}$ value ($-5 \pm 2\text{‰}$) from the east coast (Figure 1a). This large difference in $\delta^{18}\text{O}$ values in groundwater samples from the west and east coast samples confirms the inferred $\delta^{18}\text{O}$ difference in precipitation along the two coasts during principal rainy seasons⁵. It may be recalled that there are no direct precipitation isotope data from any station along the east coast of India and the isotopic signatures of precipitation on this coast have been interpreted from neighbouring stations of Hyderabad and Shillong in India and few stations in Sri Lanka, Myanmar and Thailand with data only of few years.

In terms of d -excess (Figure 1b), groundwater samples on the west coast exhibit a slightly lower value (0 – 5‰) compared to east coast ($10 \pm 5\text{‰}$). This is suggestive of some evaporative enrichment of soil moisture before groundwater recharge along the west coastal regions.

It has long been known that compared to the AS, the surface waters of the BOB are ~1‰ lighter in $\delta^{18}\text{O}$ due to large influx of surface run-off from surrounding continental areas^{16,17,49,50}. This would explain only a part of the above-mentioned observed difference in $\delta^{18}\text{O}$ of groundwater from coastal localities between the west and east coasts. As seen from Figure 1a, the offset of $\delta^{18}\text{O}$ between surface water of the AS and groundwater along the west coast is ~2‰. But the offset of $\delta^{18}\text{O}$ between surface water of the BOB and groundwater along the east coast is >4‰.

Possible mechanisms to account for the higher $\delta^{18}\text{O}$ offset between the BOB and the east coast, include contribution from the AS vapour depleted due to rainout over

the land area and lower $\delta^{18}\text{O}$ of surface water of the BOB during the SW monsoon season. It is known that the BOB during SW monsoon receives large run-off (~1500 km³) from the Ganga–Brahmaputra river system¹⁹. An additional mechanism related to both heavy evaporation and precipitation (~3 m) over the BOB during the rainy season (Figure 2), could also be a contributing factor. That a part of increased precipitable water and precipitation rate seen over northern BOB and eastern India is derived from the BOB, is indicated by the increased evaporation from the BOB during the SW monsoon¹⁹. Thus, there seems to exist a seasonally active regional hydrological cycle between the northern BOB and the Ganga–Brahmaputra river system. In this seasonal cycle, the northern BOB supplies the vapour that mixes with the cross-over vapour from the AS and precipitates inland over Himalayas and the Ganga plains. This is supported by data of storm tracks that originate in the northern BOB and travel inland approximately north-westward⁵¹. The river system then quickly returns a large part back to the BOB through run-off that spreads widely as a surface layer owing to low salinity (hence density) and re-evaporates to start the cycle.

A further indication of such a hypothesized seasonal cycle is provided by the limited number of stream-water isotopic measurements¹ from the Ganga river system during

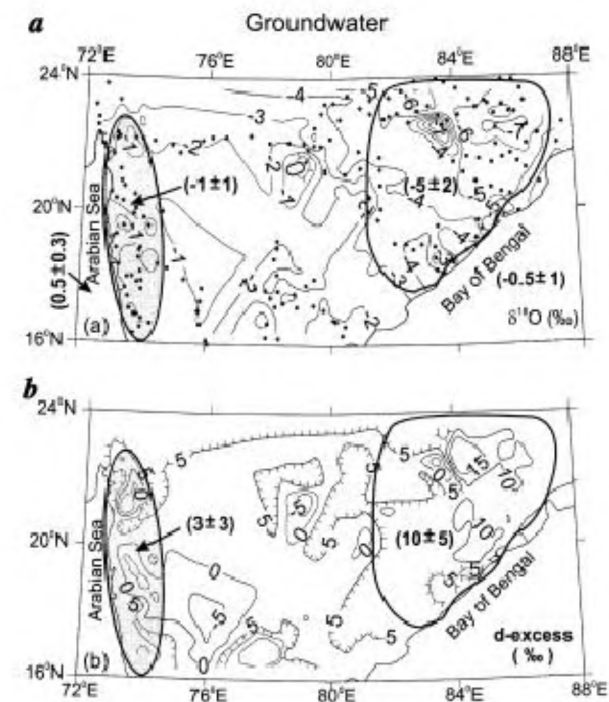


Figure 1. a, $\delta^{18}\text{O}$ of groundwater from Central Indian Peninsula. Offset of ~2‰ in $\delta^{18}\text{O}$ is observed between surface water of AS ($0.5 \pm 0.3\text{‰}$) and groundwater on the west coast ($-1 \pm 1\text{‰}$) and precipitation at Mumbai ($-1.4 \pm 1.1\text{‰}$). Coastal groundwater on east coast is depleted by >4‰ with respect to surface water of the BOB (0.5 ± 1.0). b, The d -excess of groundwater from west coast ranges between 0 and 5‰ and that from east coast is $10 \pm 5\text{‰}$.

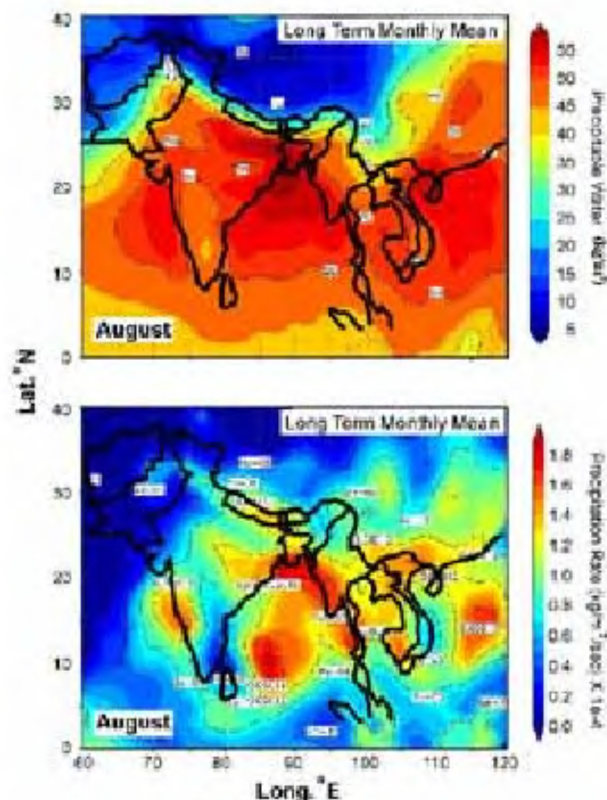


Figure 2. Long-term (1968–96) monthly means of (a) precipitable water and (b) precipitation rate for the month of August, i.e. during the middle of SW monsoon period, appropriately cropped from CDC-derived NCEP reanalysis product website (<http://www.cdc.noaa.gov/cdc/data.ncep.reanalysis.derived.html#surface>). A striking geographical correlation between the two is evident. Both evaporation and precipitation seen over the BOB may be responsible for part of the higher offset in $\delta^{18}\text{O}$ between surface water and east coast precipitation and hence groundwater.

the SW monsoon season, that indicate low values of $\delta^{18}\text{O}$ ($<-11\text{‰}$) and δD ($<-69\text{‰}$). This further suggests that the surface water of the northern BOB during at least the later part of the SW monsoon season (late July to September) can have significantly lower $\delta^{18}\text{O}$ (-3‰) to provide the required isotopically light source of vapour into the proposed seasonal hydrological cycle of regional dimensions.

It is thus seen that with the available isotope data on groundwater, isotopic modifications due to evaporation during rainfall and subsequent percolation through soil zone can also be understood, which may in turn, be useful to correlate the isotopic character of various components of the hydrological cycle. However, to make quantitative estimates, a much larger databank of isotopes in both precipitation and groundwater is required.

Surface water

There are few surface-water isotopic measurements in the subcontinent to establish the identity and origin of stream

water in any given part of the year to different parts of the catchments. Available data do indicate that during non-monsoon months most streams derive their base flow from local effluent groundwater discharge, which also indicates signatures of evaporative enrichment in isotopes⁴. Additionally, the following observations have also been made.

Data on isotopic composition of the headwaters of the Indus and its tributaries, surface ice in glaciers, saline and freshwater lakes and thermal springs in Himalayan and Kashmir region showed³ high d -excess that could be due to precipitation from western disturbances with unique signature of vapour source in the Mediterranean Sea⁵². All along the path of the western disturbance (Iran, Afghanistan, Pakistan and Kashmir) the precipitation is characterized by high d -excess⁵³. In this region the 'altitude effect' decreases with elevation.

In another study of the Ganges river system, high-altitude tributaries showed $\delta^{18}\text{O}$ – δD relationship close to GMWL, but streams from the lowland region showed a significant evaporation effect¹.

Seasonal variations in isotopic composition of the Yamuna and its tributaries were explained in terms of amount effect with most depleted values during the monsoon period and from high altitude samples⁴. The observed high d -excess during October was ascribed to the inherent signature of a source with a significant component of high d -excess vapour, possibly western disturbances.

In both Krishna and Godavari estuaries, δD was shown to behave conservatively during mixing between sea water and stream water⁵⁴.

Temporal variations in isotopic composition of Nainital Lake have been used to estimate subsurface components of the water balance to the lake³⁶.

From the knowledge gathered hitherto concerning application of isotopes in hydrology in India, it is clear that the observed isotopic variations are caused by meteorological, geographical and hydro-geological factors and it should be possible to quantitatively describe the entire hydrological cycle of the Indian subcontinent. However, at present, potential applications that will lead to water resource development and management options cannot be exploited because of a limited database. This situation can be remedied by establishing a country-wide network of stations for monitoring both temporal and spatial variations in different water sources, viz. atmospheric vapour, precipitation, surface and groundwater. This will provide a significant increase in the knowledge about natural transfer and movement of water within the country through its different pathways. An outline of the proposed multi-institutional collaborative research programme is discussed in the following.

Isotopes in Waters of India Network

The proposed investigation is formally entitled 'Spatial and temporal fingerprinting of waters of India using stable

isotopes to study seasonal evolution, interactions, geographic controls and climatic forcing' and is informally referred to by the acronym IWIN.

As a result of isotope monitoring and mathematical modelling, the IWIN is expected to achieve the following objectives:

- (i) Identify the dominant sources of water vapour over different regions of the country during different seasons and quantify these, *vis-à-vis*, AS, BOB and land-derived evapotranspiration.
- (ii) Quantify the partitioning of water vapour into rain, which subsequently re-partitions into evapotranspiration, soil moisture, stream flow and groundwater. Presently, estimates of evapotranspiration have large uncertainty, because these are either based on application of empirical formulae or on estimates of water-balance components being the difference between precipitation and groundwater recharge plus surface run-off.
- (iii) Quantify the degree and rates of interactions between these components seasonally. The interdependence of surface flow and groundwater exploitation is only now being realized as a result of large-scale decline in dry-season flow of streams around areas of groundwater pumping. Some indications of increased precipitation possibly due to enhanced evapotranspiration in command areas of Indira Gandhi Canal in Rajasthan have also been reported^{55,56}.
- (iv) Quantify the controls that geographical and climate factors exercise over the entire hydrological cycle, both temporally and spatially. The effect of orography, inland distance from the coast, vegetation cover, soil type, slope, temperature regime on rainfall, stream flow, infiltration and evapotranspiration is well recognized, but the combined effect of these in a given region can be estimated based on the degree of isotope fractionation among the different hydrologic components.

Identifying the dominant sources of vapour influx to India is also vital to improve the understanding of continental-scale hydrological circulation and land-ocean-atmosphere interaction, as the Indian monsoon is an important component of global atmosphere circulation and also the predominant source of freshwater to India. In terms of mathematical modeling it is, therefore, necessary to devise a programme of sample collection and analyses that is practical and at the same time rigorous enough to preserve the isotope record between sampling and measurement. Within the country annual variations in precipitation itself are fairly large, and this variation transcends to all other components of the hydrological cycle. Therefore, to be able to describe both the average features and the spatial variations associated with annual variations, a period of 3–5 consecutive years of monitoring at about 30–35 stations spread across the country may be required.

Previous studies have shown that in most parts of the country, the seasonal and yearly variations in isotope cha-

racter present in the rainfall get obliterated during passage of soil water through the unsaturated zone and groundwater at a given location does not exhibit temporal variations seen in precipitation. But due to the highly variable nature of micro-meteorology and geography and the limited horizontal flow velocity of groundwater, the spatial variations get accentuated. It is, therefore, essential that the IWIN component for groundwater monitoring is designed to provide inputs to study this spatial variability across the 'atmosphere-groundwater continuum', river water-groundwater interactions, and lake or surface reservoir-groundwater interactions. Therefore, rather than collecting 1800 monthly groundwater samples from the same 30–35 stations, it is desirable to collect these from 1800 to 2000 stations spread across the various basins and sub-basins in the country, initially focusing on the shallow unconfined aquifers as these represent the most active phases involved across hydrological boundaries. Subsequently, samples from aquifers with palaeo-groundwater and those from special 'problem areas' can be taken.

As mentioned above, sample collection and storage ensuring no modification in their isotopic composition from collection to measurement is a major task of the programme. This can, however, be achieved easily if several agencies having their own network of water sample collection for a variety of hydrological monitoring programmes can be made involved in the IWIN programme. The India Meteorology Department (IMD)/Indian Agricultural Research Institutes (IARI)/Central Water Commission (CWC)/Central Pollution Control Board (CPCB)/Central Groundwater Board (CGWB) and other agencies have an established network and a regular programme of weather, water flow/water table/surface water or groundwater quality monitoring from well-established locations/stations. The IWIN programme needs to latch on with the programmes of the respective agencies to organize the sample collection programme. The required supplemental data that are already being collected are: weather data (precipitation, temperature, relative humidity, pan-evaporation, and wind velocities); volumetric flow data and groundwater table and quality fluctuations.

In terms of measurement capabilities, the country is poised for a major increase with new Stable Isotope Ratio Mass Spectrometer facilities coming up at Indian Institute of Technology, Kharagpur and National Institute of Hydrology, Roorkee in addition to functional facilities at PRL and BARC. In view of the practical importance of the programme in understanding the hydrological cycle on country-wide scale, it may also be worthwhile having another dedicated Stable Isotope Ratio Mass Spectrometer facility.

Other practical applications

The IWIN data could have several practical applications to various related disciplines at smaller regional to local scales. These are enumerated in the following.

Isotopes in catchment hydrology

Knowledge of the hydrological pathways by which water moves over land, and percolates and moves underground to re-emerge as streams, is important to understand the hydrogeology of a terrain. Stream-flow generation (drainage of water to streams and rivers) is a key component of the hydrological cycle. This fundamental knowledge, perfected by application of isotope technique, can be useful in designing computer models for streamflow prediction, that are important for land-use planning, flood-contingency planning and dam construction and operation. Another important application of the isotope technique is to understand the nature of water storage and drainage on hill slopes. This has important implications for slope stability, erosion and related aspects of geomorphology.

The isotopes of oxygen and hydrogen are among the most effective tools available for delineating and constraining hydrological flow paths in watersheds. The basis for this application of $\delta^{18}\text{O}$ and δD is the temporal variation in the isotopic composition of precipitation. It is well known that the isotopic composition of rainfall varies from storm to storm at a given site. Therefore, the rainfall in any one storm may differ isotopically from the water stored in the subsurface at the start of the storm. This contrast in isotopic composition has proved useful in the analysis of streamflow generation on 'storm event' timescales⁵⁷. The isotopic composition of precipitation also varies with season, leading to a variation of the isotopic composition of stream water on this longer timescale as well.

Thus, $\delta^{18}\text{O}$ and δD measurements can be useful in determining the contribution of rainfall to storm flow, the residence time of water on catchments and other aspects of watershed hydrology. The separation of contributions from event and pre-event (or 'new' and 'old') waters to storm flow adds a constraint on streamflow generation that hydrometric measurements could never do. The identification of large contribution of pre-event water to storm streamflow (often 70–80% of hydrograph volume and peak flow rate) is entirely consistent with importance of subsurface storm flow as documented by hydrometric studies on forested catchments before isotopes became widely used⁵⁷. In addition, isotopic studies clearly show that through some combination of mixing and displacement, pre-event water usually makes up the bulk of storm flow, even discharging to streams through macro pores and soil pipes⁵⁸.

In development of lumped-parameter hydrological models, stable isotopes have provided information that influenced the conceptualization of streamflow generation mechanisms and improved model calibration⁵⁸. Parameter identifiability was improved with tracers, keeping the model structures quite simple.

Isotopes in meteorology

In addition to meteorological observations and forecasting, an important mandate for meteorologists is to provide accu-

rate meteorological statistics required for agriculture, water resource management, industries and other nation-building activities.

Some previous detailed studies have interpreted the stable isotopic compositions of meteoric waters and their geographic variations, primarily in terms of temperature and orographic effects^{58,59}. Recently, investigators have considered all components of the hydrological cycle, including the important component of evapotranspiration⁶⁰. Quantifying evapotranspirational recycling is critical to the quantification of the hydrological cycle and is of great importance when considering natural or anthropogenic climate change, or effects of changing vegetation pattern on precipitation. The small geographical depletion (0.075‰ per 100 km) of the $\delta^{18}\text{O}$ of precipitation in the Amazon basin was shown⁶¹ to be a result of a large contribution of re-evaporated moisture to the basin's water balance. The ratio of evaporation to transpiration in the Amazon Basin has been estimated^{62,63} using a steady-flux model incorporating *d*-excess values. An increase of 3‰ in the *d*-excess of precipitation was reported across the Amazon Basin and attributed to an isotopically fractionated evapotranspirational flux to the water balance. This *d*-excess corresponds to 10–20% of the precipitation being evaporated, which represents an evaporative component of 20–40% of the total evapotranspiration flux. A decrease in δD of 3.3‰ per 100 km in winter precipitation and 1.3‰ per 100 km in summer precipitation in Central Europe has been observed. This was explained⁶⁴ by a ratio of winter precipitation to summer evapotranspiration.

Isotopes in pollution studies

In the rapid pace of urbanization and industrialization, the pollution watchdogs face the tough task of (i) ensuring appropriate treatment and disposal of industrial and domestic waste; (ii) monitoring and preventing the loading of pollutants in the atmosphere, soil and water; (iii) investigating the movement and mixing of natural (arsenic, fluoride, salinity, etc.) and anthropogenic pollutants from point sources (industrial or urban agglomeration), and most importantly, (iv) offering guidelines and solutions to the nation to protect the environment and also sustain development.

Applying isotopic tracers in conjunction with other chemical analyses and flow-path modelling can help determine origin, movement, mixing and flushing of various pollutants particularly in soils and groundwaters. Even the limited application of stable isotopes of oxygen and hydrogen can help in accurately estimating the travel time for pollutants through surface and subsurface pathways from the source to the surroundings. Tracing the movement of isotopically tagged water offers insights into the movement of pollutants that travel along with this parcel of water. Offering such information can be vital for planning and setting up industrial units at appropriate locations.

Prediction of chemical impacts of non-point source pollutants also requires an understanding of the different pathways through which water moves on its way to the stream, because different pathways provide different opportunities for contact with organic detritus, soil and rock.

Isotopes in ecology and agricultural studies

When water is transported between the roots and shoots within a plant, its isotopic composition remains unaltered until it reaches tissues or organs such as leaves or young unsuberized stems that are losing water to the external atmosphere. Evaporative process causes significant enrichment of heavier isotopes (D or ^{18}O) within the xylem-sap. The magnitude of isotopic enrichment is a function of leaf transpiration rate, the humidity gradient between the site of water loss and atmosphere as well as δD or $\delta^{18}\text{O}$ of the atmospheric water. In order to understand and document patterns of water use, uptake and transport by plants, it is important to understand distribution of isotopes within the hydrological components both on temporal and spatial scales. It has been shown that the vegetated land cannot be treated as freely evaporating surface⁶⁵. Plants do exert a significant degree of control over the patterns and rates of evaporative water loss. This has been referred to earlier^{27,28}.

It has also been well documented that the upper soil layers are commonly enriched in heavier isotopes in water due to evaporative fractionation from the upper soil surface⁶⁵. Below an isotopically unstable zone, the isotopic composition of water changes markedly with depth, often converging to a relatively stable value. When plants are growing in the soil, further modification of soil-water isotopic composition can result from the pattern of water uptake and water loss from plants rooted at different depths. In the simplest case, we might expect the magnitude of change in isotopic composition of soil water to be different between a tilled and fully planted crop field, or between a forested and deforested catchment⁶⁵.

Plants may utilize many potential water sources depending, first, upon the plant and secondly, upon the spatial and temporal properties of the soil and climate in a particular region. In order to know which one of these potential sources a plant may be using, it is necessary to collect waters and determine their stable isotope composition (δD and $\delta^{18}\text{O}$). These values are then compared with those of water extracted from xylem (water transport) tissues of plants growing in the same environment. This information also provides an indirect method for determining the rooting depth of a plant when clear differences in source water δD and $\delta^{18}\text{O}$ can be identified^{66,67}.

Other important components of most catchments are the trees that grow in the variable source area adjacent to streams. These so-called riparian trees are important because they sit at the interface between the terrestrial and aquatic portion of the catchment and thus influence the surface and subsurface fluxes of water and other substances

linked to water (e.g. nutrients and dissolved organic carbon). It is often assumed that these trees utilize the surface stream waters. Using isotopes, it has been shown that only smaller trees use stream waters, while mature trees use little or none of this water⁶⁸. Eucalyptus trees inhabiting the semiarid floodplains along the River Murray in Southeast Australia have been found to use groundwater and not surface stream water⁶⁹. Riparian trees have been found to seasonally switch water sources, using water in the surface layers during the early growing season and then switching to the deep water during draught period⁷⁰. These studies demonstrate that regardless of whether plants inhabit arid, semiarid or mesic regions, there can be strong relationship between water source and water-use pattern. At catchment scale, this information has many important applications. First, it means that more water moves through the 'soil-plant(s)-atmosphere' continuum than would be otherwise expected. Secondly, a hydraulically lifted water source could have a strong influence on the distribution and abundance of all plant species and in turn on the amount of water movement within a catchment or forest stand. Thirdly, estimates of evaporation and transpiration are 1.5 to 3-fold higher for large trees 'mining' deep water sources⁶⁵.

Summary and conclusion

Increase in population and aspirations for a better quality of life are beginning to stress the available water supplies in certain parts and during certain seasons in India. In an effort to secure sufficient water of reasonable quality to meet the anticipated future requirements, new schemes involving harnessing of water at different scales, from local to inter basin transfer, are being launched. An improved understanding of the controls (e.g. geographical and climate) on the seasonal and spatial distribution of water during rainy seasons and its redistribution during the non-monsoon periods will provide scientific inputs to plan a better water resource development strategy for the country. Additionally, this understanding is likely to be useful in modelling air-sea-land interaction at the beginning of monsoon and help in better predicting the advance of monsoon through more focused knowledge-based monitoring of the various parameters. This objective however, requires data that can trace water molecules through their annual hydrological cycle. This can be achieved through systematic studies of stable isotopes of oxygen and hydrogen in the water molecules in different reservoirs.

The knowledge gathered from the limited isotopic investigations of rain, groundwater and surface water carried out so far in India has already demonstrated that oxygen and hydrogen isotopic data can be potentially applied for a complete description of the hydrological cycle. However, available isotopic data are not enough to quantitatively describe the entire hydrological cycle in terms of exchanges and interactions among its various components. Therefore, it is imperative to initiate a project for spatial and

temporal fingerprinting of water of India using stable isotopes to study seasonal evolution, interaction, geographical controls and climatic forcing. In view of this, a multi-institutional collaborative project, IWIN, has been conceptualized.

It is planned to monitor spatial and temporal variations of isotopic composition of water in all its phases, namely atmospheric vapour; precipitation; surface flows and groundwater. A strategy of systematic sample collection and analyses has been formulated. To describe the temporal variations, monthly collection of samples of all the four hydrological forms of water is planned from about 30–35 stations. About 14,400 isotopic analyses are expected to be made as part of this project.

Sample collection and storage is the backbone of this project. Therefore, various agencies such as IMD, CRIDA, CWC, CPCB, CGWB, etc. have agreed to help in this task. The sample collection procedures for rainwater, groundwater and surface water have been identified from existing practices. The atmospheric vapour collection system has been developed 'in-house' and tested successfully.

A successful completion of this project is expected to lead to a significant increase in the knowledge about natural transfer and movement of water within the country through its major routes (vapour, rain, stream flow and ground water) in temporally and spatially distributed manner. In addition to being purely academic quest, this knowledge would help an efficient water resource management to meet existing challenges and those anticipated. Several practical applications of detailed isotopic studies to catchment hydrology, meteorology, agro-ecology and pollution studies have been pointed out.

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