

Contributions of IWIN National Programme to Hydrology in India *

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Abstract

Isotopic measurements of water constituents namely, oxygen and hydrogen ($\delta^{18}\text{O}$ and δD) have been used advantageously to study the hydrological processes operating over different spatio-temporal scales in many regions of the world and significant new insights have been generated. In India, a big push towards understanding the hydrological cycle has been given by successful implementation of a multi-institutional collaborative national research programme on isotope fingerprinting of waters of India (IWIN), funded jointly by the Department of Science and Technology (DST), New Delhi and Physical Research Laboratory (PRL), Ahmedabad. In this programme 14 leading research institutions and central agencies are collaborating, with the PRL as the nodal agency for implementation.

The broad scientific objectives of IWIN are to study:

1. origin and evolution of rain bearing vapor and meteorological influence on rainout;
2. partitioning of rain into groundwater recharge and stream flow generation;
3. rain-vapor interaction and vapor source identification;
4. movement and mixing of water/ vapor front across various hydrological boundaries;
5. identification of constituent components of river discharge; and
6. sea surface water dynamics.

As part of the IWIN programme, more than 30,000 new isotope data ($\delta^{18}\text{O}$ + δD) have been generated in the isotope ratio mass spectrometer (IRMS) laboratories at PRL (Ahmedabad), NIH (Roorkee), and NGRI (Hyderabad). The enormous stable isotope data generated in the past 4 years under IWIN programme far exceeds the data generated in India over past 3 decades and has provided important new insights about hydrological processes concerning various components of the hydrological cycle over India. Besides the new hydrological knowledge IWIN programme also contributed significantly to development of

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isotope analytical procedures for large throughput, students internship programme, human resource development and collaborative research.

Some of the important achievements and contributions from the IWIN programme, concerning the isotope hydrology research in India, are briefly presented in the following.

Introduction

Stable isotopes of oxygen and hydrogen are being advantageously used as tracers to study the hydrological processes since the sixties, when the physics underlying co-variation of ^2H (D) and ^{18}O in fresh waters was described, (Craig and Gordon, 1965; Dansgaard, 1964). Oxygen and hydrogen isotopic compositions are normally expressed in δ -notation ($\delta^{18}\text{O}$ and δD), as deviations of heavy to light isotopic ratios relative to an international standard of known composition, in terms of parts per thousand or per mil (denoted as ‰). The isotopic composition in terms of δ values can be calculated using following equation.

$$\delta(\text{in } \text{‰}) = \left[\frac{R_{\text{Sample}}}{R_{\text{Standard}}} - 1 \right] \times 1000$$

In the above equation, R_{sample} and R_{standard} denote the ratio of heavy to light isotope (e.g. $^{18}\text{O}/^{16}\text{O}$ or D/H) in the sample and standard respectively.

The observed linear relationship ($\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$) between oxygen and hydrogen isotopic compositions ($\delta^{18}\text{O}$ and δD) in fresh waters on a global scale, was known as the global meteoric water line (GMWL), which slowly emerged as a practically useful concept in the isotope hydrology (Craig and Gordon, 1965; Rozanski et al., 1993). Additionally, the slope of GMWL was advantageously used by Dansgaard (1964) to define another isotopic parameter, namely *d*-excess ($= \delta\text{D} - 8 \times \delta^{18}\text{O}$), which is diagnostic of evaporation or vapor recycling under lower humidity conditions (Clark and Fritz, 1997; Kendall and McDonnell, 1998). At regional scales, the observed divergence from GMWL emerged as a basis to discern the processes concerning the regional hydrology. Isotopic signatures of various physical processes (e.g. evaporation, condensation, rainout, recycling, etc) and geographic factors (e.g. altitude, distance from oceans, weather in vapor source region, etc) were also highlighted in several studies (Craig and Gordon, 1965; Dansgaard, 1964; Gat and Carmi, 1970; Gonfiantini, 1986; Jouzel and Merlivat, 1984). Over the years, numerous studies were undertaken to discern the hydrological processes using these isotopes (Clark and Fritz, 1997; Gat, 2010; Kendall and McDonnell, 1998).

Several Indian researchers have employed the stable isotope tracer techniques for various hydrological studies in different parts of India (Bhattacharya et al., 2003; Bhattacharya et al., 1985; Chandrasekharan et al., 1992; Chidambaram et al., 2009; Dalai et al., 2002; Das et al., 1988; Datta et al., 1996; Datta et al., 1991; Deshpande et al., 2003; Deshpande et al., 2010a; Gupta and Deshpande, 2005a; Gupta et al., 2005; Jeelani et al., 2010; Kumar et al., 1982; Kumar et al., 2010; Kumar et al., 2008; Majumdar et al., 2005; Maurya et al., 2011; Nachiappan et al., 2002; Pande et al., 2000; Ramesh and Sarin, 1992; Sengupta and Sarkar, 2006; Shivanna et al., 2008; Singh et al., 2010; Somayajulu et al., 2002; Srivastava et al., 2012; Sukhija et al., 1987; Warriar et al., 2010; Yadav, 1997). A few researchers from overseas have also undertaken isotope hydrological studies in India (Breitenbach et al., 2010; Lambs et al., 2005).

In spite of the above isotopic studies undertaken during past four decades in India, to understand the hydrological and hydrometeorological processes, it was not possible to holistically characterize the water resources on a sub-continental scale. Further there remained knowledge gaps on certain aspects of hydrological cycle over India, remained. This lacuna was due to the fact that available isotope data were insufficient to address to those aspects which involved synoptic processes on a large spatial scale or region specific processes or subtle processes on a smaller time scales. For example, some of the topic on which there is only limited understanding are:

1. identification of rain bearing vapors originating from different sources (e.g. Arabian Sea, Bay of Bengal, and Mediterranean, local recycling) during different seasons and affecting the same or different regions of the country;
2. rain-vapor interaction and evolution of ground level vapor front;
3. quantitative identification of constituent components (including snow/ice melt) of river discharge;
4. meteorological influence on isotopic characteristic of precipitation;
5. spatio-temporal variation in isotopic composition of surface waters of the Arabian Sea and the Bay of Bengal and its relevance to river discharge.

With a view to address some of these issues, India, uniquely, initiated a multi-institutional¹ collaborative research programme to isotopically characterize all the components of its hydrological cycle. A National Programme on Isotope Fingerprinting of Waters of India (IWIN), funded jointly by the Department of Science and Technology (DST) and Physical Research Laboratory (PRL) was launched in 2007. Detailed information about the evolution and origin of the IWIN programme can be obtained from the published literature (Deshpande and Gupta, 2008; Deshpande and Gupta, 2009; Gupta and Deshpande, 2005b).

The IWIN now makes it possible to address to some of the above open-ended issues. The spatio-temporal characterization of various water sources of the country, based on the above data, has enabled identification of broad regions, in which hydrological and hydrometeorological processes/factors have imparted characteristic isotopic signatures governed by subtle interactions between atmospheric, surface and sub-surface components of hydrological cycle. Prior to IWIN, the isotopic studies were undertaken for a particular component (rain, river, groundwater) within certain geographical boundaries (e.g. part of a river basin, catchment, agro-climatic zone, rainfall zone, orographic zone, regional aquifer system, etc) to discern the effect of specific controlling factor (e.g. temperature, rainfall, altitude, distance from coast) on particular hydrological component (e.g. rain, river or groundwater). Since isotopes integrate effects of all the ongoing processes /factors, the corresponding isotopic signatures are simultaneously imparted to all the associated components of hydrological cycle. Therefore, a composite isotopic image of the water resources is now able to provide holistic understanding about the processes affecting it. A summary compilation of the contributions of IWIN programme has been published recently (Deshpande and Gupta, 2012).

The new scientific knowledge generated so far from the IWIN National Programme has been published in several peer reviewed research papers (Achyuthan et al., 2013; Deshpande and Gupta, 2012; Deshpande et al., 2013a; Deshpande et al., 2010a; Deshpande et al., 2013b; Maurya et al., 2011; Purushothaman et al., 2012; Krishan et al., 2011).

¹ Other institutions participating in the IWIN Programme arranged alphabetically are: Anna University (AU, Chennai); Bhabha Atomic Research Center (BARC, Mumbai); Center for Water Resources Development and Management (CWRDM, Kozhikode); Central Ground Water Board (CGWB, New Delhi); Central Pollution Control Board (CPCB, Delhi); Central Research Institute for Dryland Agriculture (CRIDA, Hyderabad); Central Water Commission (CWC, New Delhi); Indian Institute of Technology (IIT-Kharagpur); India Meteorological Department (IMD, New Delhi); National Geophysical Research Institute (NGRI, Hyderabad); National Institute of Hydrology (NIH, Roorkee); National Institute of Oceanography (NIO, Goa); Nuclear Research Laboratory (NRL)- IARI, New Delhi.

In the following, abstraction of important contributions from IWIN programme to isotope hydrology research in India is enumerated.

Sampling and Isotope Analyses

Innovative sampling procedures for vapor and rain

A new, simple and cost effective method of complete cryogenic trapping of moisture from the stream of ambient atmospheric air has been designed, developed and tested successfully. This method circumvents the requirement of elaborate pumping lines and vacuum pumps but requires only liquid nitrogen. Besides this cryogenic trapping method, another simple and cost effective method of sampling ambient atmospheric water vapour by condensing it on ice-cooled conical surface has been designed, developed and tested. The kinetic isotope fractionation occurring in this method can be corrected by an empirical formula relating (i) the degree of super-saturation during condensation; (ii) the measured isotopic composition of vapour (though fractionated); and (iii) its true value determined by cryogenic trapping. A simple, robust and cost effective method of collecting fortnightly accumulated rainwater sample has been designed, developed and tested which minimizes the evaporative losses and maximizes the sample collection. Details of sampling protocols can be downloaded from the IWIN website <http://www.prl.res.in/~iwinoffice/>. Reference is also made to (Deshpande et al., 2010b; Deshpande et al., 2013b; Purushothaman et al., 2012; Krishan et al., 2011) for details of the above sampling methods.

Large throughput of isotopic analyses with accuracy

A state of the art Isotope Ratio Mass Spectrometer (IRMS) laboratory has been set up at PRL, Ahmedabad for analysing oxygen and hydrogen isotopic composition of water and vapour samples. Robust laboratory and analytical protocols have been developed after extensive experimentation and standardized with international standard reference materials (Maurya et al., 2009). Towards this, four secondary laboratory standards were prepared and used for ensuring large throughput of accurate isotopic analyses. An inter-laboratory calibration exercise for various isotope mass spectrometer laboratories (PRL, NIH, NGRI, IIT-Kgp, CWRDM) collaborating in IWIN programme was undertaken with calibration measurements of four secondary laboratory standards done at the International Atomic Energy Agency (IAEA), Vienna. Approximately 10500 $\delta^{18}\text{O}$ and 8500 δD analyses of IWIN samples have been made in this IRMS laboratory at PRL and equally large number of analyses at other IRMS laboratories (NIH, NGRI, IIT-Kharagpur and CWRDM) participating

in IWIN, which together sums up to more than 30,000 new isotope data ($\delta^{18}\text{O}$ + δD) in the country.

Research and development in laboratory procedures

Specific R&D efforts have also been made to enhance the throughput of an IRMS laboratory by optimizing analytical parameters such as equilibration duration, equilibration temperature, laboratory ambient temperature, volume of water sample to be used for equilibration, flush-filling duration, flush-filling sequence (i.e. before or after introduction of water sample). To optimize cost of analyses and minimise down time, an additional metallic needle guide for guiding and protecting the analyses needle was designed and developed. This component has been attached to the auto-sampler which has prevented accidental misalignment, collision and breakage of needle reducing the cost of analyses. An indigenous contraption for de-clogging the analyses needle has been designed and developed in which acetone in a glass bottle is pressurised by helium gas and is passed through the analyses needle. Clogged needles are routinely retrieved using this method, reducing the cost of analyses.

New Scientific Knowledge

As a result of successful implementation of IWIN programme, a large dataset on oxygen and hydrogen isotopic compositions of various components of hydrological cycle is generated. Using this dataset, season-wise spatial distribution maps of isotopic composition of precipitation, groundwater and river waters across the country have been prepared (Deshpande et al., 2011; Deshpande and Gupta, 2012). Important diagnostic tests such as plots of δD vs. $\delta^{18}\text{O}$, d -excess vs. $\delta^{18}\text{O}$, $\delta^{18}\text{O}$ vs. rainfall, $\delta^{18}\text{O}$ vs. temperature etc. have been performed on temporally and spatially segregated datasets. Efforts have been made to recognize any conspicuous pattern specific to some region or season and to discern its controlling factors. From these analyses of the IWIN isotope data new and interesting insights about the hydrological and hydro-meteorological processes is available.

Discovery of kinetic fractionation during condensation under supersaturated condition

A kinetic isotope fractionation effect occurring during liquid condensation under supersaturated condition was discovered in course of the atmospheric water vapour condensation experiments. As a result of this kinetic effect the liquid condensed at 0°C from ambient water vapor was found to be isotopically depleted in ^{18}O (contrary to expected equilibrium enrichment). The liquid was also found to be less enriched in ^2H compared to

equilibrium fractionation. Consequently, the liquid had unusually high *d*-excess. Additionally, it was discovered that this type of kinetic fractionation also occurs during dew formation when super-saturation is attained under natural environmental condition. Prior to this work such a kinetic fractionation was reported only for ice condensation and not for liquid condensation. Therefore, this finding has now added another dimension to investigation and interpretation of isotopic characteristics of water in the ecological water pool and also of rainwater formation under extraordinary weather conditions. An important research paper has been published discussing this kinetic fractionation and its implications (Deshpande et al., 2013b).

Interaction between rain and vapor

From the isotopic investigation of the ground level vapour (GLV) and rain at Ahmedabad it was observed that during a rain event, GLV rapidly interacts with raindrops and tends to move towards isotopic equilibrium but is not in isotopic equilibrium. On cessation of rain, the $\delta^{18}\text{O}$ and δD of GLV returns to the typical baseline value. Therefore, use of isotopic composition of monthly rainfall for estimating average monthly isotopic composition of GLV, as practiced by some researchers, can lead to erroneous results. Another important observation was that the *d*-excess of GLV increases suddenly and persistently almost a month before the first monsoon rains at Ahmedabad. This observation indicates that new vapor sources arrive well before the onset of monsoon and offers up the possibility of using isotopic composition of GLV as a tracer of these vapor sources. These observations, inferences based on them and their implications are discussed in (Deshpande et al., 2010b).

In addition to the above study, important new insights about the atmospheric water dynamics are also available from the isotopic investigation of ground level water vapor (Krishan et al., 2012; Rao et al., 2012).

Glacial Melt Contribution to Ganga River at Rishikesh

Contributions from various constituent components (Groundwater, surface runoff and glacial ice-melt) to Ganga River discharge at Rishikesh were quantitatively estimated using a three component mixing model. The contribution of glacial ice-melt to the Ganga River discharge at Rishikesh peaks during summer monsoon, reaching a maximum value of $\sim 40\%$ with an average of 32% which drops to $\sim 8\%$ during winter (Dec-Mar). The fraction of groundwater discharge varies within a narrow range ($15\pm 5\%$) throughout the year. The

contribution of surface runoff peaks to 70-90% during winter, due to near zero contribution of glacial ice-melt and essentially represents the melting of surface snow from the catchment.

An important implication of this study is related to the fact that peak d -excess value of $\sim 20\text{‰}$ in Ganga River at Rishikesh, in the monsoon month of August, cannot be accounted by isotopic mass balance of the known isotopic composition of the constitute components. Therefore, a source with very high d -excess is necessary to explain the observed high d -excess values. This source could be Himalayan Glaciers. The implication of this finding is that the Himalayan Glaciers receive the contribution of snow from western disturbances, more than believed so far; or snow received during winter disturbances is better preserved than that received during summer monsoon. Detailed discussion on this study is presented elsewhere (Maurya et al., 2011).

Surface water dynamics of the Bay of Bengal

Surface water mixing in the Bay of Bengal has been inferred from spatio-temporal distribution of $\delta^{18}\text{O}$ and salinity based on synthesis of 194 new samples together with earlier published data. This study on surface water dynamics of the Bay of Bengal highlights that the seasonal distribution of $\delta^{18}\text{O}$ and salinity over the northern Bay of Bengal is dominantly governed by the spatial and temporal variation in the $(P+R-|E|; \sim 4000 \text{ km}^3 \text{ a}^{-1})$ in spite of the fact that both Summer Monsoon Current and Winter Monsoon Current transfer more than 80 times water between the two basins, the Arabian Sea and the Bay of Bengal, of the northern Indian Ocean. This confirms the formation of a shallow stratified layer of meteoric water over the Bay of Bengal that restricts vertical mixing. Earlier studies have indicated that formation of this stratified meteoric water layer is important to maintain the threshold SST over BOB for charging the cloud-base air-mass with the required moist static energy for sustenance of large scale deep convection in the atmosphere during the summer monsoon. Significant holding back of continental runoff in response to societal requirements or melting away of glaciers due global warming therefore may limit the formation of this stratified meteoric water layer leading to undesirable consequences for rainfall over south Asian region. This aspect needs to be further investigated.

In spite of the broad geographical correspondence between $\delta^{18}\text{O}$ and Salinity during different seasons, all available data pairs considered together show no significant relationship between $\delta^{18}\text{O}$ and Salinity in x-y plot; though such relationships for different seasons and

sub-regions of the BOB have been observed by earlier workers. Detailed discussion of this study is presented elsewhere (Achyuthan et al., 2013).

Mystery of ice-stones (megacryometeors) falling from clear sky

In a strange and unexpected atmospheric hydrological event, four unusually large ice-stones (megacryometeors) weighing several kilograms fell in Western India during October-November 2010. Samples were retrieved from three fall events. To investigate the origin and formation of these megacryometeors, $\delta^{18}\text{O}$, δD , chemical composition and γ -activity were measured. The range of $\delta^{18}\text{O}$ - δD is similar to the local meteoric water, suggesting origin from local atmospheric water vapour. The relative humidity at ~ 4 km altitude was higher during a few days before and after the fall. No γ -activity from cosmogenic radionuclides such as ^{26}Al could be detected in the inherent dust. These investigations indicate terrestrial origin of these megacryometeors. Detailed discussion of this study is presented elsewhere (Deshpande et al., 2013a).

Meteorological controls and Vapor source identification for rains at Ahmedabad

Factors governing variations in the $\delta^{18}\text{O}$, δD and d -excess of 120 daily rainfall events sampled at Ahmedabad in Western India, over a 4-year period, were examined statistically using 120-hours backward wind trajectories, at 6-hourly intervals, converging at a typical cloud base attitude of 2.5 km. As a scientific outcome of the IWIN programme it was earlier indicated that observed isotopic variations in the daily rainfall at Ahmedabad may be related to variation in vapor sources (Arabian Sea, AS; Bay of Bengal, BOB; continental recycling). Important inferences from this study are: (i) the amount of rainfall, temperature, Rh or the possible extent of evaporation have limited influence on the observed isotopic variation in daily rainfall; (ii) the amount weighted monthly average $\delta^{18}\text{O}$ values progressively decrease from June to September i.e in the later months of monsoon; (iii) the contribution of vapors originating from three major sources, to the rainfall at Ahmedabad, is estimated as 62.5% from the AS; 17% from the BOB; and a minimum of 12.6% from the land-derived vapor through recycling. There is 72% probability that a rain event with mean ($\pm 1\sigma$) values of $\delta^{18}\text{O}$ and d -excess, derives vapor principally from the AS. In view of relatively lower contribution of vapor from the BOB to rainfall at Ahmedabad, it may be simplistically inferred that possible change in the surface water temperature due to changed surface water dynamics of the BOB, and associated change in the number of cyclonic storms, may not be of much concern for rainfall at Ahmedabad.

Isotopic compositions ($\delta^{18}\text{O}$ and δD) and salinity (S) of 683 surface water samples from the Arabian Sea (AS) collected during 2008-2011, were measured to understand the spatio-temporal distribution and to discern the controlling factors. From the distributions of $\delta^{18}\text{O}$ and salinity (S), and the relationships between $\delta^{18}\text{O}$ – δD and $\delta^{18}\text{O}$ –S, following inferences have been drawn: (1) there is a general correspondence between the distributions of the $\delta^{18}\text{O}$ and S; (2) in spite of a large scatter, a statistically significant $\delta^{18}\text{O}$ –S relationship can be identified in much of the investigated part of the AS; (3) the $\delta^{18}\text{O}$ – δD regression line for all samples clumped together has a slope of 3.2 (± 0.16), much lower than that for the global ocean surface water (7.37) which in case of the AS is seen only for samples with salinity <33; (4) the linear relationship between $\delta^{18}\text{O}$ and δD breaks down completely in the months of March-May; (5) contrary to the adjoining Bay of Bengal (BOB), both $\delta^{18}\text{O}$ and S progressively increase from 0°-10°N; (6) the $\delta^{18}\text{O}$ – δD and the $\delta^{18}\text{O}$ – d -excess relationships indicate strong kinetic fractionation due to evaporation from surface waters of the AS throughout the year, with enhancement in summer months.

Ongoing activities

In addition to the studies summarised above, analyses and interpretation of other isotope datasets, pertaining to various hydrological components in different geographical regions of India, is carried out by different IWIN collaborators. New insights are also expected to emerge in due course of time from these ongoing studies.

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