ISOTOPE AND TRACER APPROACHES IN SNOW AND GLACIER STUDY

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Content of Today Lecture

- 1. What is Hydrology?
- 2. What are Isotopes?
- 3. What is Isotope Hydrology?
- 4. Processes controlling natural distribution of isotopes

5. Applications of Isotopes in Understanding the Hydrological processes of Snow and Glacier

6. Details of case studies

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What is Hydrology

Hydrology - Science of Water, It deals with the occurrence, circulation and distribution of water of the earth and earth atmosphere.

Hydrological Cycle



- Water in the atmosphere Meteorology, Climatology
- Water in the oceans Oceanography
- Water in lakes and rivers Limnology
- Water beneath the earth surface Groundwater – Hydrogeology/Groundwater Hydrology
- Water on surface in form of Glacier and Ice – Glacier Hydrology
- Water resources management, water supply, water quality

INTRODUCTION: ROLE OF GLACIER AND ICE WITHIN THE HYDROLOGICAL CYCLE

SNOW AND ICE: THE FIRST LARGEST FRESHWATER RESERVOIR OF THE HYDROLOGICAL CYCLE

Volume (Mm ³ x 10 ⁶) Oceans and seas 1 338 000 Glaciers and polar		% of the total water on the planet 97.5	% of total fresh water
Fresh groundwater	10 530	0.76	30.1
Freshwater lakes	91.0	0.007	0.26
Saltwater lakes	85.4	0.006	
Rivers	2.12	0.0002	0.006
Biomass	1.12	0.0001	0.003
Atmosphere	12.9	0.001	0.04

(Shiklomanov, 1997)

Development of Isotope Hydrology

In late 1940s/early 1950s

precise/sensitive nuclear techniques available to study

- fractionation of stable water isotopes (²H, ¹⁸O) and
- distibution of radioactive hydrogen isotope (tritium, ³H)

in atmosphere and hydrosphere*)

Since then,

- the use of stable and radioactive isotopes expanded (e.g. stable C and N isotopes, radioactive carbon, Cl, Kr isotopes)
- new insights into both atmospheric and terrestrial elements of the water cycle have been gained (e.g. recharge and flow regime of groundwater, climate in the past)
- new interdisciplinary scientific field came into being Isotope Hydrology

*Isotope Hydrology (Eds. Aggarwal, Froehlich, Gat, Gonfiantini) - Benchmark Papers in Hydrology, IAHS (2012)

What are isotopes

- Atoms consist of a nucleus surrounded by electrons. The dense concentration of matter of the nucleus mainly consists of two kinds of particles, neutrons and protons.
- The number of protons (Z), the atomic number, is equal to the number of electrons surrounding the nucleus.
- Protons and neutrons are called nucleons. The sum of the number of protons and neutrons (N) in a nucleus is the nuclear mass number:

 $\mathbf{A} = \mathbf{Z} + \mathbf{N}$

• The notation describing a specific nucleus (= nuclide) of element X is:



Α

What are isotopes: Isotopes of the water molecule: Isotopes of oxygen



What are isotopes: Isotopes of the water molecule : Isotopes of hydrogen



OXYGEN ISOTOPES

- $14 \mathbf{R} (T_{\frac{1}{2}} = 72 \text{ sec})$
- 15 − R (T_{1/2} = 120 sec)
- 16 **S** (99.759%)
- 17 **S** (0.037%)
- 18 **S** (0.204%)
- $19 \mathbf{R} (T_{\frac{1}{2}} = 29 \text{ sec})$
 - **R Radio-isotope S - Stable Isotope**

- ¹⁴O, ¹⁵O and ¹⁹O have very less half-life, hence are not useful for various hydrological studies.
- Abundance ratio of ¹⁸O/¹⁶O is used in hydrological studies.

HYDROGEN ISOTOPES

- 1 − S (99.985%)
- 2 **S** (0.015%)
- $3 \mathbf{R} (T_{\frac{1}{2}} = 12.34 \text{ y})$

- ¹H or H Protium
- ²H or D Deuterium
- ³H or T Tritium

D/H ¹⁸O/¹⁶O ratios is very important in many hydrological studies for example hydrograph separation, Identification of recharge zones and sources of aquifer, springs, leakage from reservoir and pollutant movement etc.

> ¹H¹H¹⁶O, ¹H¹H¹⁸O ¹H²H¹⁶O, ¹H²H¹⁸O, ¹H³H¹⁶O

ISOTOPES, ISOBARS, ISOTONES



The stable isotopes of water molecule (oxygen 18, deuterium and tritium) are the most used in hydrology

Chart of Nuclides



Most of the nuclides are unstable (radioactive) and are very short-lived. Only some unstable nuclides with longer life-time are of practical importance, e.g. ³H, ¹⁴C. Which are the most widely used isotopes in hydrology and why?

- Environmental Isotopes (H, O, N, C, Cl, B, He, S)
- Other isotopes (Sr, Rn, U, etc)



 Isotopes used in hydrology are preferentially abundant in the hydrosphere and atmosphere

Isotope abundances, ratios, and delta notation (abundance)

- In nature out of every 100 atoms of Oxygen, 0.2 atoms would be ¹⁸O and the rest would be ¹⁶O
- Lighter isotopes are the most abundant in hydroshpere and atmosphere compared to the lithosphere
- Heavier isotopes tends to be fixed to the solid phases in the earth

ELEMENT	ISOTOPE	ABUNDANCE
HYDROGEN		
(Z=I)	^I H (Protium)	99.985
	² H (D, for Deuterium)	0.015
045501		
CARBON	10	
(Z=6)	¹² C	98.9
	¹³ C	1.1
NITROGEN		
(Z=7)	¹⁴ N	99.63
	¹⁵ N	0.37
OXYGEN		
(Z=8)	¹⁶ O	99.76
	¹⁷ O	0.04
	¹⁸ O	0.2

Isotope abundances, ratios, and delta notation

(ratio)

The determination of an isotopic abundance in a given system is very difficult. So it is easier to express isotopic abundances using the isotopic ratio R (R<1).

 $R = \frac{abundance \ of \ rare \ isotope}{abundance \ of \ abundant \ isotope}$

Stable Oxygen: R= (¹⁸O/¹⁶O) = (2005.2±0.45)-10⁻⁶



Isotope abundances, ratios, and delta notation (the delta notation for stable isotopes)

For practical reasons, instead of using the *isotope ratio* R, isotopic compositions are generally given as δ values, the relative deviations with respect to a standard value, as defined by:



The accepted standard for the isotopes in water is SMOW (Standard Mean Ocean Water). It provide an appropriate reference for meteoric waters, as the oceans are the basis of the meteorological cycle.

Subsequently, The IAEA prepared a standard water from distilled seawater that was modified to have an isotopic composition close to SMOW. This reference is identified as VSMOW (Vienna Standard Mean Ocean Water) and defining the value of $\delta = 0$.

SLAP and **GISP**

Standard Light Antarctic Precipitation (SLAP)

- $\delta^{18}O_{SLAP} = -55.50\% VSMOW$
- δD_{SLAP} = -428.0‰ VSMOW

Greenland Ice Sheet Precipitation (GISP)

- $\delta^{18}O_{GISP} = -24.76\% VSMOW$
- δD_{GISP} = -189.5‰ VSMOW

Isotope abundances, ratios, and delta notation (Standards)

δ - Notation

Average composition of O is:

 16 **O = 99.63%;** 17 **O = 0.0375%;** 18 **O = 0.1995%**

- Not convenient to use percentages to express slight differences in isotope composition
- Express stable isotope ratios using δ values in ‰ (per mil) relative to a standard
- O (and H): Standard = SMOW (Standard Mean Oceanic Water)



2.1. Abundance ratios and reference standards for some environmental isotopes.

Isotope	Ratio measured	Reference Standard	Abundance ratio of standard
²H	² H/ ¹ H	VSMOW	1.5575 - 104
³ He	³ He/ ⁴ He	atmospheric He	1.3 · 10*
⁶ Li	⁶ Li/ ⁷ Li	L-SVEC	8.32 · 10 ⁻²
"В	¹¹ B/ ¹⁰ B	NBS 951	4.04362
¹³ C	¹³ C/ ¹² C	VPDB	1.1237 · 10-2
¹⁵ N	¹⁵ N/ ¹⁴ N	atmospheric N ₂	3.677 · 10 ⁻³
¹⁸ O	¹⁸ O/ ¹⁶ O	VSMOW, or VPDB	$2.0052 \cdot 10^{-3}$ $2.0672 \cdot 10^{-3}$
³⁴ S	³⁴ S/ ³² S	CDT	4.5005 · 10 ⁻²
³⁷ Cl	³⁷ Cl/ ³⁵ Cl	SMOC	0.324
⁸⁷ Sr	⁸⁷ Sr/ ⁸⁶ Sr	Absolute ratio, or various materials	

Mathematically, the error between apparent and true ratios is cancelled.

δ-Notation for expressing Isotopic Composition



Example

$$\delta (\%_0) = \left(\frac{\left[0.0020253 \right]_{\text{Sample}}}{\left[0.0020052 \right]_{\text{Standard}}} - 1 \right) \times 1000$$

$$\delta$$
 (‰) = (1.010000 - 1) x 1000 = 10 ‰

A δ^{18} O value of +10 ‰ signifies that sample has 10‰ (i.e. 1%) more ¹⁸O than the standard. VSMOW Standard: 2005.2 atoms of ¹⁸O /1000000 atoms of ¹⁶O (1% =20.052 atoms of ¹⁸O)

+10‰ \rightarrow Sample has 2025.252 atoms of ¹⁸O /1000000 atoms of ¹⁶O

-10‰ \rightarrow Sample has 1985.148 atoms of ¹⁸O /1000000 atoms of ¹⁶O

SMOW-SLAP Stretching Factor



End of defining isotopes



What is Isotope Hydrology

Isotope Hydrology uses stable and radioactive isotopes of water and its dissolved constituents to trace hydrological processes



CLASSIFICATION OF ISOTOPIC TRACERS

- 1. Conservative tracers
- 2. Non conservative tracers
- 3. Stable isotopes
- 4. Radio active isotopes
- 5. Any combination of the above
 - Conservative, stable isotopes (isotopes of water molecule)
 - Conservative, radioactive isotopes (tritium)
 - Reactive, stable isotopes (stable isotopes of carbon)
 - Reactive, radioactive isotopes (radioactive isotope of carbon)

Environmental Isotope: Since Available in Earth Atmosphere, naturally introduced in hydrological cycle, neither to buy nor to inject

Note: artificial tracers also exists (eg. dyes, salts, isotopes, etc)

Two fundamental principles (linking physical properties of isotopes to hydrology)

- Isotope fractionation
- Radioactivitiy- radioactive decay

• Animation link



Isotope fractionation (definition)

The partitioning of stable isotopes of an element among different coexisting phases is called FRACTIONATION and is a MASS and TEMPERATURE dependent process

Fractionation leads to variation in the natural abundances of stable isotopes expressed as differences in ISOTOPE RATIOS, R

ALWAYS: R = HEAVY ISOTOPE/ LIGHT ISOTOPE

THAT IS: R = RARE ISOTOPE / ABUNDANT ISOTOPE

e.g. D/H, ¹³C/¹²C, ¹⁵N/¹⁴N, ¹⁸O/¹⁶O, ³⁴S/³²S

The substituted molecule is slightly heavier, allowing a different partitioning of energy between translational, vibration and rotational states. Isotopic fractionation is a quantum mechanical effect.

Liquids (and solids) have additional vibration states due to intermolecular forces.

So, for the same energy more of the light isotopes can be liberated from a liquid surface. (as 25°C, 1 percent more). The liquid is enriched, the vapor is depleted.

Isotope fractionation definition

Isotope fractionation is the physical phenomenon which causes changes in the relative abundance of isotopes due to their differences in mass. This can occur as a change in isotopic composition by the transition of a compound from one state to another (example: liquid water to water vapour).

The (equilibrium) isotope fractionation factor α is defined by :

 $\alpha_{1-2} = R (phase 1) / R (phase 2)$

For example, for liquid/vapor equilibrium (25°C), the fractionation factor are : α ¹⁸O = (¹⁸O/¹⁶O)liq / (¹⁸O/¹⁶O)vap = 1,0092

 $\alpha^{2}H = (^{2}H/^{2}H) liq / (^{2}H/^{2}H) vap = 1,077$

Isotope fractionation and enrichment factors (temperature dependent)

Isotope fractionation factor

 $H_2O_{water} \leftrightarrow H_2O_{vapour}$

$$\alpha = \frac{R_{\text{reactant}}}{R_{\text{product}}} \qquad \alpha^{18}O_{\text{water-vapour}} = \frac{(^{18}O/^{16}O)_{\text{water}}}{(^{18}O/^{16}O)_{\text{vapour}}}$$

Isotope enrichment factor

$$\varepsilon^{18} \mathbf{O} = \left(\frac{{}^{18} \mathbf{O}/{}^{16} \mathbf{O}_{\text{vapour}}}{{}^{18} \mathbf{O}/{}^{16} \mathbf{O}_{\text{water}}} - 1\right) \cdot 1000 \text{ \%}$$

Isotope fractionation (types of fractionation in nature)



- Vapor pressure of water containing light isotopes > Vapor pressure of water containing heavy isotopes, therefore vapor is enriched in light isotopes (depleted in heavy isotopes)
- Kinetic fractionation-rapid phase changes increase fractionation because light isotopes diffuse more rapidly than heavy ones

- •Kinetic fractionation
- •Non equilibrium fractionation (kinetic)
- •Equilibrium fractionation
- Rayleigh distillation
- Isotope mixing

Non-equilibrium (kinetic) fractionation

Forward reaction rate is accelerated relative to backward reaction and opportunity for backward mixing diminishes



Isotope fractionation (Rayleigh fractionation-condensation)

Rayleigh fractionation occurs when a <u>substrate</u> mass is depleted during a physicochemical reaction and product is removed from system.

The equation describing **Rayleigh** processes is:

 $\mathbf{R}_{t} = \mathbf{R}_{0} f^{(1-a)}$

R and R₀ are the ratios at t and at t=0 *f* is the fraction remaining at t
a is the equilibrium fractionation factor



Condensation example - condensate is formed from a vapor mass and fraction remaining of original vapor declines Isotope fractionation (Rayleigh fractionation-evaporation)

Rayleigh fractionation describes the process of ISOTOPE FRACTIONATION as a liquid pool evaporates (e.g., ephemeral pond) or as a vapor mass condenses (e.g., rainfall)

Rayleigh fractionation creates differences in δ values between source and product masses (e.g., liquid and vapor)

Evaporation example - vapor is formed from the liquid and the fraction remaining of original liquid declines, as in an evaporating lake



Link with hydrology



Rainout and Rayleigh Distillation



Processes controlling natural distribution of isotopes



Environmental Isotopes

How Isotope is Linked with Hydrology

Processes controlling natural distribution of isotopes



Applications of Isotopes in Hydrology

- 1. Atmospheric water vapor and precipitation evaporation, condensation, and recycling processes
- 2. Surface water

river; lake, reservoir (dam); sea; estuary, ocean

3. Groundwater

surface-groundwater interaction; groundwater dynamics (recharge, flow, esidence time, mass transport); palaeogroundwater; arid-zone hydrology, geothermal fluids; groundwater pollution

4. Climate

Palaeoclimate, global warming, global change, climate phenomena (Monsoon, El Niño (ENSO), NAA etc)

Introduction: Isotope use in hydrology and hydrogeology

- 1. Isotopes are tracers of flow path and reactive processes
 - Identification source of vapor/precipitation
 - Origin and sources of (ground)waters
 - Origin of salinity and solutes in groundwaters
 - Scale of interaction between hydrologic compartments (eg. surface water-groundwater)
 - Sources of pollution
 - Recharge rates and mechanisms
 - Mixing ratio between hydrologic compartments
- 2. Isotopes are **indicators of timescale** of processes
 - Used as clocks
 - Used as signals

Isotope effects and hydrology

A number of interrelated isotope effects or processes due to which isotope ratios vary across hydrologic compartments

- Rainout effect (Rayleigh distillation)
- Continental Effect or Continentality
- Seasonal Effect or Seasonality
- Amount Effect
- Temperature Effect
- Altitude Effect
- Latitude Effect
- Paleoclimate
- Transpiration (no effect pumps water)
Rainout effect

 Every precipitation event deplete the vapor reservoir on stable isotopes than the previous one.

It correspond to a new decrease of condensation temperature.



Latitude effect



higher latitudes, precipitation tends to have more negative δ^{18} O values due to the strong relation between $\delta^{18}O$ content and temperature. The global map of δ^{18} O in precipitation illustrate this effect. The depletion in δ¹⁸O values with increasing latitude is clear while flat gradients are observed in the tropics regions.

Altitude and seasonality effect



At higher altitudes where the average temperatures are lower, precipitation will be isotopically depleted. For ¹⁸O, the depletion varies between about -0,15 and -0,5‰ per 100 m rise in altitude, with a corresponding decrease of about -1 to -4‰ for ²H.

➡ This altitude effect is useful in hydrogeological studies, as it distinguishes groundwaters recharged at high altitudes from those recharged at low altitude.

Altitude effect



Seasonality effect



Greater seasonal extremes in temperature generate strong seasonal variation in isotopes of precipitation. These variations in δ¹⁸O and δ²H give us an important tool to determine rates of groundwater circulation, watershed response to precipitation, and the time during the year when most recharge occurs

Continental Effect



As a vapor mass moves from its source region across a continent, its isotopic composition evolves more rapidly due to topographic effects and the temperature that characterize extremes continental climates. Continental stations are characterized by strong seasonal variations T, which in is a reflection of distance from moderating marine and latitude. precipitations Coastal are isotopically enriched, while the colder inner continental regions receive isotopically depleted precipitation with strong seasonal differences



Continentality effect: INDIA

Paleo-climatic Effect

Given the good correlation between isotopes in precipitation and groundwater, climate change should be recorded in fossil or paleogroundwaters. Temperate climates have experienced significant changes in temperature since late Pleistocene time. Such climate changes are manifested by a shift in the stable isotope content of precipitation, and in deuterium excess. This paleoclimatic effect is one the most important tools in identifying paleogroundwater. Late Pleistocene paleogroundwaters from temperate regions will be isotopically depleted with respect to modern waters and shifted along the GMWL towards negative values.

Paleo-climatic Effect

The paleoclimatic effect in arid regions is manifested by a depletion in stable isotopes with respect to modern waters. In arid regions like the Eastern **Mediterranean and North** Africa, the modern MWL is characterized by а deuterium excess value of 15 to 30‰. However, in the past, humid climates groundwaters tend to plot below the on or even **GMWL**.



Stable isotope signature of various paleogroundwaters from the middle East and North Africa shown with the GMWL

Paleo-climate effects

The depleted isotope composition of Continental Intercalaire aquifer is characteristic of palaeowaters in northern Africa. It is characteristic of old recharge occurring during the late Pleistocene period. Pleistocene age of this water is consistent with negligible radiocarbon content.



The δ^{18} O and δ^{2} H composition of groundwaters in Southern Tunisia compared with average of modern local precipitation and the GMWL.

Temperature effect

The $\delta^{18}O - T$ Correlation in Precipitation vs

The fractionation between isotopes is higher at low temperatures !



Fig.4.9 Weighted average annual values of ¹⁸δ in precipitation (pcpt) vs the mean surface air temperature, showing the variations from year to year (data from the GNIP network).

Source: IAEA

Amount effect



Heavy and intensive rainfalls tends to produce lighter rains than light rains

Amount effect in Bhagirathi Basin, Garhwal Himalayas, India; Rai et al 2013

Negative-relationship between amount of precipitation and isotopic composition is due to preferential removal of heavier isotopes during a rainfall event which increases with amount of rainfall



Meteoric Water Line/ Craig line

The intimate mixture of vapour and condensation in clouds tends to preserve isotopic equilibrium and the meteoric relationship between δ^{18} O and δ^{2} H. So, as the in-cloud temperature drops and rainout proceeds, the rain will have an isotopic composition controlled by equilibrium fractionation with the vapour and will plot on the MWL with slope close to 8.



The changes of ¹⁸O and ²H concentrations in meteoric waters were shown to be fairly well correlated so that in the (δ^2 H, δ^{18} O) graph the isotopic compositions of precipitation are aligned along a Global *Meteoric Water Line. (By Craig 1961)*

Craig Line was modified and now it is $\delta D = (8.17 \pm 0.1)^* \delta^{18}O + (11.27 \pm 0.6)$ GMWL by Rozanski et al., in 1993

Meteoric Water Line/ Craig line

GMWL is essentially a global average of many local meteoric water lines, each controlled by local climatic factors, including the origin of the vapour mass. These local factors affect both the deuterium excess and the slope. For regional or local investigations, it is important to compare surface water (snow and ice melt water) and groundwater data with local meteoric water line (LMWL).



The deuterium excess varies from an area to another according to the origin of air masses. The oceanic vapor gives rainwater whose deuterium excess is +10. In the Occidental Mediterranean the deuterium excess of rainwater increases and can reach +14.

Oxygen-18/ deuterium diagram of rainwater

Deuterium excess (d-excess)

$$d$$
-excess = $\delta D - 8 \times \delta^{18} O(\%)$

The observed intercept of the GMWL was advantageously used by Dansgaard, to define a parameter (*d*-excess), which can be calculated for individual pair of δ^{18} O and δ D using following equation.

The basic premise behind defining such a parameter is that whenever kinetic fractionation is involved, the net ratio of fractionation for deuterium to oxygen is different from 8.

 $\delta D = 8 \times \delta^{18} O + Excess Deuterium$

d-excess in vapour and Humidity

What does d-excess (= $\delta D - 8^* \delta^{18} O$) signify?



d-excess can be calculated for individual $\delta^{18}O-\delta D$ pair and it signifies the kinetic fractionation due to evaporation. On evaporation, *d*-excess of the residual water decreases and consequent vapour has correspondingly higher *d*-excess. The rain formed from such a vapour also has high *d*-excess.

Interpretation of Slope and Intercept of GMWL and LMWL

$\delta^{18}O-\delta D$ Regression line slope

- 1. If the slope of δ^{18} O- δ D regression line for a set of samples is less than that of GMWL it is an indication that the water under consideration has undergone certain degree of evaporation.
- 2. The intersection point of LMWL and GMWL is indicative of the average isotopic composition of precipitation at that location.
- 3. Intersection point of LMWL and $\delta^{18}O-\delta D$ regression line for groundwater/snow/ice is indicative of the average isotopic composition of the surface water from which the groundwater is formed.
- 4. If the $\delta^{18}O-\delta D$ regression line slope for groundwater is less than that for LMWL, considerable evaporation before recharge can be suggested.

<u>δ¹⁸O-δD Regression line Intercept</u>

1. If the slope of LMWL is ~8 and intercept is >10‰ it is an indication that precipitation is derived from vapour which is produced by kinetic evaporation under considerably lower relative humidity.

Interpretative Significance

$\delta^{18}O$ and δD values

- 1. Depending on the geographical location of the station, lower (isotopically depleted) values of both δ^{18} O and δ D could be associated with: either higher altitude, greater distance from vapour origin region, considerable rainout or rainfall during NE winter precipitation.
- 2. Higher (isotopically enriched) values of both δ^{18} O and δ D could be associated with evaporation from falling raindrops in small rain events, proximity to vapour source region,

d-excess values

- 1. Lower than average *d*-excess of a particular rainwater sample could be due to evaporation from falling raindrops or it could as well signify considerable rainout from original marine vapour parcel.
- 2. Higher (than average) *d*-excess in a particular rainwater sample signifies either formation of marine vapour parcel under lower (than average) relative humidity (for e.g. from Mediterranean Sea) or contribution of recycled vapour from continental areas for that particular event.

Local Evaporation Line

Relation between ¹⁸O/¹⁶O and ²H/¹H in Evaporating and Non-evaporating Water



Evaporated water bodies in a given region plot along a local evaporation line whose slope is function of humidity

Water isotope fractionation and exchange in groundwaters



Isotopes in hydrologic cycles studies-towards interpreting/using stable isotope data

- Each site has its own LMWL (Local Meteoric Water Line)
- Need to collect all the rain for 2-3 years at a site to get a good average value for recharge.
- Do not interpolate LMWL or averages from the data for the closest IAEA or other station.
- There is lots of spatial and temporal variation in the isotopic compositions of rain.
- The GMWL or LMWL is *nota tight line –they are lines through an ellipse of data points.* Evaporation causes samples to plot below the MWL.
- Sublimation enriches the isotopic composition of snow and ice at the surface, it causes sample to fall below the LMWL.
- Recharge water can be very different from average rainfall.
- Samples easily fractionate in poor quality bottles; use ones with polyseal caps.
- Samples archive well; collect more samples than you need and analyze them in groups
- Evaporation prior to recharge enriches the recharging water
- Groundwaters recharged at higher altitude tends to be depleted in heavy isotopes compared to localy recharged groundwaters at low altitude
- Transpiration processes pumps groundwater into the atmosphere without leading major changes in isotopic composition
- Salt dissolution increases the total dissolved solids but stable isotope content does not change during dissolution
- The length of Local Evaporation Line corresponds with the degree of evaporative water lose
- Isotope exchange between CO2 gas and H2O leads to depletion of water with heavy isotopes while high temperature exhange of Oxygen from silicates or carbonates with oxygen of water leads to enrichment of d19O in water without affecting the d2H.

DEMONSTRATION OF ISOTOPE TO UNDERSTAND HYDROLOGICAL PROCESSESS

Development of LMWL Hydrograph Seperation Discharge Measurement



Sampling Sites in Bhagirathi River Catchment



Variation of Isotopic Signature of Rainfall and meltwater



Development of Indian Meteoric Water Line



Development of Indian Meteoric Water Line



ESTIMATION OF DIFFERENT COMPONENT OF MELTWATER USING ISOTOPIC: Hydrograph Seperation Technique



HYDROLOGIC FLOWPATHS



Water joining to stream through the different hydrological processes i.e., rainfall-runoff, throughflow, baseflow (groundwater), glacial melt etc.

What is Hydrograph



A **hydrograph** is a graph showing the rate of flow (discharge) versus time past a specific point in a river, or other channel or conduit carrying flow. The rate of flow is typically expressed in cubic meters or cubic feet per second (cms or cfs).

Therefore, hydrographs display the change of a hydrologic variable over time. So, the hydrograph gives information of hydrological processes in a catchment

Component of Hydrograph

MAJOR COMPONENT OF RIVER DISCHARGE

For example: River originating from the Himalays having the three major component in a river runoff. These three components are

- 1) Storm flow/ Rainfall-runoff
- 2) Snow/Glacial melt water
- 3) Base flow/groundwater

Hydrograph with Two Component

Hydrograph with Three Component



USE OF HYDROGRAPH SEPARATION

Hydrograph Separation help us to understand the mechanism of stream flow generation in a catchment

- How much contribution is from groundwater/ snow/ glacial melt?
- How does the groundwater/snowmelt component change with catchment scale?
- How important are geographically unique areas such as Glacial zone contributing to stream flow?

DIFFERENT TECHNIQUES TO SEPARATE A HYDROGRAPH



WHYISOTOPICTECHNIQUESFORHYDROGRAPH SEPARATION

The recharge, storage and discharge characteristics of a watershed is reflected its behavior during rainfall and baseflow. Surface runoff resulting from events is of major concern to engineers responsible for routing of water through channel, drainage systems and natural waterways. To assess the volume of runoff from a storm or continuous drainage from a given basin, empirical models have been developed that satisfy engineering needs but do not provide an actual understanding of the processes involved.

Traditional models for storm runoff oftem assume that baseflow from groundwater to river decreases during high water stages.

Isotope techniques show that such is not the case and provide some basic insights into the runoff process

TRACERS IN MIXING MODELS

- Choice of tracers will determine type of interpretation
- Chemical tracers often delineate flowpaths
 - Reacted
 - Un-reacted
- Isotopic tracers delineate water sources
 - Event (snowmelt)
 - Pre-event (pre snowmelt)
Isotope Tracer Fundamentals

- ¹⁸O is a constituent part of the water molecule
 it is the water molecule
- Tracer that is applied naturally during precipitation events
- Conservative in reactions with matrix materials at ambient temperatures
- Only mixing can alter the concentration

HYDROGRAPH SEPARATION: ASSUMPTIONS

Each techniques has assumptions

Isotopic Techniques

Time based separation/Source based separation

- Temporal and spatial variation of isotope concentration is known
- Stable end-members for source based separation
- Conservative tracers
- Only advective transport, no lateral diffusion/dispersion
- All components have significantly different concentrations for at least one tracer;

CONVENTIONAL METHODS FOR BASE FLOW SEPARATION



HYDROGRAPH SEPARATION USING ISOTOPES ----THE MIXING MODEL

- 2-Component Mixing Model
- 3-Component Mixing Model

Streamflow

"Old" Water (Groundwater)

"New**" %**ater

(Snowmelt)

Tracer = δ^{18} O

- One Conservative Tracer
- Mass Balance Equations for Water and Tracer



DERIVATION OF TWO COMPONENT MIXING EQUATION

Say we want to know the contribution of "new" rain water and "old" ground water to an observed hydrograph.

We know that the total flow, Q_t , should be equal to the sum of the flows of old (Q_o) and new (Q_n) water:

 $\mathbf{Q}_{t} = \mathbf{Q}_{o} + \mathbf{Q}_{n}$

If the new and old waters have different concentrations of a tracer in them, then the total amount of tracer is the sum of the new and old flows times their respective concentrations of tracer:

 $\mathbf{Q}_{t}\mathbf{C}_{t} = \mathbf{Q}_{o}\mathbf{C}_{o} + \mathbf{Q}_{n}\mathbf{C}_{n}$

We can re-write this expression to solve for either one of the water sources, old or new. Here's how we solve to get the <u>new water flow:</u>

$\mathbf{Q}_{t}\mathbf{C}_{t} = \mathbf{Q}_{o}\mathbf{C}_{o} + \mathbf{Q}_{n}\mathbf{C}_{n}$

Re-arrange:

 $\mathbf{Q}_{n}\mathbf{C}_{n} = \mathbf{Q}_{t}\mathbf{C}_{t} - \mathbf{Q}_{n}\mathbf{C}_{n}$

We can also re-write Q_0 in terms of Q_t and Q_n (to get rid of one of the unknowns) $\rightarrow Q_0 = Q_t - Q_n$ $\mathbf{Q}_{n}\mathbf{C}_{n} = \mathbf{Q}_{t}\mathbf{C}_{t} - (\mathbf{Q}_{t}-\mathbf{Q}_{n})\mathbf{C}_{o}$ $\mathbf{Q}_{n}\mathbf{C}_{n} + (\mathbf{Q}_{t} - \mathbf{Q}_{n})\mathbf{C}_{o} = \mathbf{Q}_{t}\mathbf{C}_{t}$ $\mathbf{Q}_{n}\mathbf{C}_{n} + \mathbf{Q}_{t}\mathbf{C}_{o} - \mathbf{Q}_{n}\mathbf{C}_{o} = \mathbf{Q}_{t}\mathbf{C}_{t}$



Gather more terms:

 $\mathbf{Q}_{n}(\mathbf{C}_{n}-\mathbf{C}_{o})=\mathbf{Q}_{t}(\mathbf{C}_{t}-\mathbf{C}_{o})$ $\frac{(\mathbf{C}_{t} - \mathbf{C}_{o})}{(\mathbf{C}_{t} - \mathbf{C}_{o})}$

So now, we have a formula that lets us "back out" the amount of new rainwater that contributes to the hydrograph.

And if we know the amount of new water, we can easily determine the amount of old water, too.

Why?

Because $Q_0 = Q_t - Q_n$

MIXING MODEL: 3 COMPONENTS (Using Specific Discharge)

- Two Conservative Tracers
- Mass Balance Equations for Water and Tracers

Simultaneous Equations

 $Q_{1} + Q_{2} + Q_{3} = Q_{t}$ $C_{1}^{1}Q_{1} + C_{2}^{1}Q_{2} + C_{3}^{1}Q_{3} = C_{t}^{1}Q_{t}$ $C_{1}^{2}Q_{1} + C_{2}^{2}Q_{2} + C_{3}^{2}Q_{3} = C_{t}^{2}Q_{t}$

Solutions

$$Q_{1} = \frac{(C_{t}^{1} - C_{3}^{1})(C_{2}^{2} - C_{3}^{2}) - (C_{2}^{1} - C_{3}^{1})(C_{t}^{2} - C_{3}^{2})}{(C_{1}^{1} - C_{3}^{1})(C_{2}^{2} - C_{3}^{2}) - (C_{2}^{1} - C_{3}^{1})(C_{1}^{2} - C_{3}^{2})}Q_{t}$$

$$Q_{2} = \frac{C_{t}^{1} - C_{3}^{1}}{C_{2}^{1} - C_{3}^{1}}Q_{t} - \frac{C_{1}^{1} - C_{3}^{1}}{C_{2}^{1} - C_{3}^{1}}Q_{1}$$

$$Q_{3} = Q_{t} - Q_{1} - Q_{2}$$

Q - Discharge

C - Tracer Concentration

Subscripts - # Components

Superscripts - # Tracers

MIXING MODEL: 3 COMPONENTS (Using Discharge Fractions)

- Two Conservative Tracers
- Mass Balance Equations for Water and Tracers

Simultaneous Equations

 $f_{1} + f_{2} + f_{3} = 1$ $C_{1}^{1}f_{1} + C_{2}^{1}f_{2} + C_{3}^{1}f_{3} = C_{t}^{1}$ $C_{1}^{2}f_{1} + C_{2}^{2}f_{2} + C_{3}^{2}f_{3} = C_{t}^{2}$

Solutions

$$\begin{split} f_1 &= \frac{(C_t^1 - C_3^1)(C_2^2 - C_3^2) - (C_2^1 - C_3^1)(C_t^2 - C_3^2)}{(C_1^1 - C_3^1)(C_2^2 - C_3^2) - (C_2^1 - C_3^1)(C_1^2 - C_3^2)} \\ f_2 &= \frac{C_t^1 - C_3^1}{C_2^1 - C_3^1} - \frac{C_1^1 - C_3^1}{C_2^1 - C_3^1} f_1 \\ f_3 &= 1 - f_1 - f_2 \end{split}$$

- f Discharge Fraction
- **C** Tracer Concentration
- Subscripts # Components

Superscripts - # Tracers

REQUIREMENT OF DATA Basic Requirement

1.Isotopic signature of river, rain, snow and groundwater2.Discharge Data3.Water Quality Data (Few conservative tracers)

Sampling Frequency

For Himalayan rivers, Daily sampling during April to Sept and weekly for rest of the month of the year

Rain on daily basis

Snow on daily basis

Ground Water sample of hand pump and spring at least premonsoon and post monsoon

Discharge data on daily basis

Exercise of Hydrograph Separation

ESTIMATION OF RAIN DERIVED RUNOFF CONTRIBUTION IN MELTWATER STREAM CASE -1







CASE –2



Site 2 Before Rain = -14.48After Rain= -20.06Rain = -30.26RC % = 35%Rainfall =8.9 cum Sn/Glacier = 16.75 cum CASE –3



Site 3 Before Rain = -14.8 After Rain = -20.54 Rain = -30.26 RC % = 38% RC =17.25 cum Snow/Glacier = 28.15 cum

Site 4 Before Rain = -14.9After Rain = -19.71Rain = -29.13RC % = 34%S



Variation in Isotopic Composition of Meltwater





d18O(‰)



Runoff Contribution at Gaumukh



DISCHARGE WITH MEAN TEMPERATURE



RADIOTRACER TECHNIQUES FOR THE MEASUREMENT OF MELTWATER/LOWFLOW

RADIOTRACER TECHNIQUES ARE BASICALLY THE DILUTION TECHNIQUES

CONVENTIONAL METHODS FAIL DUE TO HIGHER DEGREE OF TURBULENCE IN MOUNTAINOUS REGIONS

HIGHERDEGREEOFACCURACYISREQUIRED FOR SOME SPECIFIC PURPOSES

PRINCIPLE

•TO MIX A SUITABLE TRACER WITH THE FLOWING WATER AT A POINT AND TO OBSERVE ITS DILUTION AT SOME OTHER APPROPRIATE DISTANCE AFTER ITS HOMOGENEOUS MIXING WITH RIVER/STREAM WATER

CONDITIONS

• NO LOSS OF TRACER IN THE WAY AND FLOW CHARACTERISTICS NEAR TO WAY

 NO ANYINLET OR OUTLET BETWEEN THE INJECTION AND SAMPLING POINT

 SAMPLING SHOULD BE CARRIED OUT AFTER THE MIXING LENGTH.

TYPES OF WATER TRACERS

THREE TYPES OF TRACERS

CHEMICAL TRACERS

> FLUORESCENT DYES

> RADIOACTIVE TRACERS

RADIOACTIVE TRACERS

EXTRAORDINARY ACCURACY IN MEASUREMENTS

CONCENTRATION UP TO TENS OF CURIES PER LITRE ARE POSSIBLE FOR INJECTION

MOST ISOTOPES ARE ACCURATELY DETECTABLE DOWN TO TENS OF PICO CURIES PER LITRE.

TWO RADIOISOTOPES ARE RECOMMENDED FOR ACCURATE GAUGING AT ANY RATE OF FLOW

(a) **BROMINE-82** (b) **TRITIUM IN THE FORM OF TRITIATED WATER (HTO)**

ADVANTAGES OF USING RADIOACTIVE TRACERS

>BACKGROUND LEVELS OF BROMINE – 82 ARE USUALLY ZERO. IT IS SHORT LIVED, WITH A HALF-LIFE OF ONLY 35.4 H, -DISAPPEARS QUICKLY AND CANNOT CAUSE PROLONGED RADIOACTIVE POLLUTION OR CONTAMINATION

>RADIO-TRACERS EMITTING GAMMA-RAYS ARE DETECTABLE AT EXPERIMENTAL SITES BY REMOTE MEANS

> TRITIUM CAN BE CONSIDERED AS THE IDEAL WATER TRACER, SINCE IT IS IN THE FORM OF A WATER MOLECULE (HALF-LIFE IS 12.32 YEARS)

TRACERS GENERALLY USED

Sl. No.	Name of Radioisotope	Half life	Approx. Qty. of tracer reqd. for stream gauging mCi/cumec	MPC in drinking water μCi/cm ³
1	lodine, I-131	8.05 days	1.7 to 2.0	2 x 10 ⁻⁵
2	Bromine, Br-82	35.5 hours	1.7 to 2.0	4 x 10 ⁻⁵
3	Sodium, Na-24	15.0 hours	1.7 to 2.0	3 x 10 ⁻⁵
4	Phosphorus, P-32	14.3 days	-	2 x 10 ⁻⁵
5	Chromium, Cr-51	27.8 days	-	2 x 10 ⁻³
6	Tritium, H-3	12.34 years	30.0 to 80.0	3 x 10 ⁻³
7	Gold, Au-198	64.8 hours	3.0 to 3.5	5 x 10 ⁻⁵

SELECTION OF MEASURING REACH

A SUFFICIENT LENGTH BETWEEN THE INJECTION AND SAMPLING POINTS - LENGTH OF THE REACH REQUIRED FOR SATISFACTORY MIXING – MIXING LENGTH

THERE SHOULD BE SUFFICIENT TURBULENCE /MEANDERING FOR GOOD MIXING

THERE SHOULD BE NO INGRESS OR EGRESS OF WATER ALONG THE MEASURING REACH

Table 1: Empirical Formulae Developed by Various Research Workers/Institutions							
-	S.No.	Name of Research Worker	Empirical Formulae				
-			$0.12 p^2 C(0.7C + C)$				
	1.	Rimmar	$L = \frac{0.12B \ C(0.7C+6)}{gD}$				
	2.	D.E. Hull	$L = a_1 Q^{1/3}$				
	3.	B.Andre's	$L = a_2 B Q^{1/3}$				
	4.	N.Yatsukura	$L = \frac{0.032R1/6B}{a nD}$				
	5.	U.P. I.R.I. Roorkee	L = K B + C'				

- U.P. I.R.I. Roorkee 5.
- where L = Mixing Length Q = Estimated discharge R = Hydraulic radius (are a = Manning's coefficien a_1 = 50 for centre point in = 200 for bank side injo a_2 = 27 for small stream v a_3 = 0.3 to 0.8 B = Average water surfact D = Average depth of flow C = Chezy's coefficient (1) K = 77 for bank side injo Hydraulic radius (area divided by wetted perimeter) Manning's coefficient of rugosity 50 for centre point injection 200 for bank side injection 27 for small stream with centre point injection Average water surface width Average depth of flow downstream of injection point Chezy's coefficient (15-50) 77 for bank side injection **C**' \equiv 120

TRACER INJECTION TECHNIQUES -TWO BASIC TECHNIQUES OF TRACER INJECTION (a) INSTANTANEOUS (GULP) INJECTION (b) CONSTANT RATE INJECTION

(a) INSTANTANEOUS (GULP) INJECTION





$$Q_1 C_1 = Q_0 C_0 + Q_i C_i$$
(i

Equation (i) can solved for Q_0 and substituted into equation (ii) yielding

If the upstream concentration of the tracer $C_0=0$

(b) CONSTANT RATE INJECTION

 $Q = q.(C_1 - C_2)/(C_2 - C_0)$

Q - DISCHARGE OF RIVER TO BE DETERMINED

C₀ - **BACKGROUND TRACER ACTIVITY IN RIVER WATER**

q - DISCHARGE OF THE INJECTED TRACER

C₁ – ACTIVITY OF TRACER INJECTED AT CONSTANT RATE

C₂ - ACTIVITY OF TRACER AFTER DILUTION WITH RIVER WATER



Dilution Gauging (Gulp Injection) Worksheet						
Date:	Time:	Operater:				
Site: Mixing Reach 40 r	n	Meter Units: µScm ⁻¹				
Background conductivi	ty: 125 µScm ⁻¹	C0: 88 mgl ⁻¹				
Tracer volume (V): 20 l	(20 or 40 litres)	Tracer conc (C1): 45,000 mg l ⁻¹				
		Note: 900 g in 20 l is 45,000 mg l ⁻¹				
Time	Reading	Concentration	C2 - C0			
(mins)	(µScm ⁻¹)	C2 (mgl ⁻¹)	(mgl ⁻¹)			
0	125	88	0			
0.5	125	88	0			
1	125	88	0			
1.5	125	88	0			
2	250	175	87			
2.5	417	292	204			
3	369	258	170			
3.5	274	192	104			
4	202	141	53			
4.5	163	114	26			
5	145	102	14			
5.5	135	95	7			
6	130	91	3			
6.5	128	90	2			
7	127	89	1			
7.5	126	88	0			
8	126	88	0			

Graph Between Time & Concentration of Tracer


The integral of (C2-C0) is:

 $\frac{1/2(0.5\min s)(0+2*(87+204+170+104+53+26+14+7+3+2+1)+0)}{=1/2(0.5\min s)(0+2(671)+0)} = 336 \text{ mgl}^{-1} \text{ min}$

The discharge is:

 $(201 * 45000 \text{ mg } l^{-1}) / (336 \text{ mg } l^{-1} \text{ min}) = 2679 \text{ l min}^{-1} = 0.045 \text{ m}^3 \text{ s}^{-1}$

Note: This example and your field test is an illustration only. An accurate dilution gauging would require: (i) a more precise and accurate conductivity-salt calibration, (ii) a time increment of at least 0.25 mins, rather than the 0.5 mins presented here, and (iii) more precise conversions above.



TRACER INJECTION DEVICE

Isotope Stratification in High Mountain Glaciers; Examples from the Peruvian Andes and Himalaya, Autours: Jerzy Grabczak et al., 1993, Jour. of Glacio., 29, 103

Isotopic measurement of Snow ice samples collected from temperate glaciers high in Andes and in Himalaya.

Significant part of annual accumulation is removed by melting and sublimation the later being predominant.



Fig. 1. ¹⁸O and deuterium content vs depth for a glacier crevasse situated on Broggi glacier, Peruvian Andes (4 766 m a.s.l.).

Isotope Stratification in High Mountain Glaciers; Examples from the Peruvian Andes and Himalaya, Autours: Jerzy Grabczak et al., 1993, Jour. of Glacio., 29, 103



Fig. 2. ¹⁸O and deuterium content vs depth for a glacier crevasse situated on Gannakhui Glacier, Garhwal Himalaya, India (5 650 m a.s.l.).

DOKRIANI BAMAK GLACIER

- Using ¹³⁷Cs activity in surface ice sample collected at an altitude of 4380m, the average flow rate of 32 m/yr is estimated near the equilibrium line which is higher than the average flow rate as expected.
- Based on ¹³⁷Cs concentrations in a 6 m shallow ice core, the average snow accumulation on Dokriani Bamak glacier for the last few years, has been calculated to be 0.43 m/yr.
- > The extreme low value of δ^{18} O at a depth of 0.25m in a 6 m shallow ice core indicates the very cold winter during 1992.
- The depletion of δ¹⁸O value in snout ice (-13.41 ‰) compared to that of average value of snow samples on the glacier indicates that the climatic conditions three centuries ago during Little Ice Age period were much cooler than present.





CHANGME-KHANGPU GLACIER

- The radiometric model age using ³²Si and ²¹⁰Pb activities of the snout ice has been calculated to be 100 yrs based on which the past average flow rate of ice along the glacier has been estimated to ~40 m/yr.
- The ²¹⁰Pb activity in samples collected from different altitudes during a single precipitation event on 28th Aug. 1978 showed a gradual increase with altitude from 1.8 dpm/l at 4650 m to 8 dpm/l at 5450 m.
- The ²¹⁰Pb activity in a shallow ice core (10m depth) in the accumulation zone showed a peak value of 7.5 dpm/l between 2-4m depth.
- Artificial nuclear debris consisting ⁹⁵Zr, ¹³⁷Cs, ¹⁴⁴Ce etc. was observed in a fresh snow fall samples collected in the year 1981 from the accumulation zone of the glacier. This confirms the presence of nuclear debris produced during the China atmospheric nuclear tests conducted in the year 1980.
- In a 10m shallow ice core collected form the accumulation zone, the concentration of artificial radionuclide ¹³⁷Cs varied from 4 to 22 dpm/l. Several peak values appear to coincide with the Chinese atmospheric nuclear explosion during the period 1970-80 based on which the net accumulation rate of ice has been estimated to be ~0.7 m/yr.

- The basal flow rate of the deeper ice near the bedrock is much lower than the surface ice. Based on the the radiometric ages of surface and deeper ice, the net accumulation rate of ice (0.7 m/yr) and applying a simple flow model assuming the melting of ice of 1 cm/yr at the base of the glacier, it has been estmated that the average basal flow rate of ice is much smaller (at least by factor of three) than that of 40 m/yr estimated for the surface ice.
- The δ¹⁸O values in the core correlated well with the dust dontent a) These values range from -14 to -21‰ and 18O values were lower in the upper strate above 4m than between 4 to 12m in the CK core. b) Surface ice samples collected between 4900 and 5450m a.s.l. showed δ¹⁸O values ranging from -19 to -13 ‰, whereas samples of recent snow from the same altitude range gave values between -21 and -17 ‰
- From 1971 to 1981, the δD of the annual ice layers has remained more or less at the constant value of -98 ‰ but from 1968 to 1971, δD values are higher by ~10 ‰. This indicates tah the period was relatively warmer by about 2°C

NEHNAR GLACIER

- The ³²Si activity decreased from the equilibrium line to the snout, first gradually and then abruptly, from 0.37 to 0.18 dpm t⁻¹ indicating an increase in the age of the ice towards the terminus.
- The ²¹⁰Pb in surface ice showed complex behavior with five zones having alternatley high and low values of ²¹⁰Pb.
- The model age of the snout ice, based on ³²Si and ²¹⁰Pb radioactivities, has been calculated to be ~500 yrs.
- ➤ The surface ice flow rates near the equilibrium lines are highest compared to that in the accumulation zone as well as the snout (2 m/yr). The past average flow rate of ice along the glacier during past few centuries has been estimated to be ~6 m/yr.
- A well defined peak of ²¹⁰Pb, ¹³⁷Cs total beta activity and dust content at 2 to 3 m depth in the 1977 core taken at 4150m altitude. A similar horizon also occurred at 4180 m altitude. The ²¹⁰Pb activity of 30 dpm l⁻¹in this horizon was four times higher than the expected fresh fallout value.
- The ¹⁸O values in the upper strate (0-46) of 102 m ice core from the ablation zone at 4150 m.a.s.l, fluctuate in the narrow range of -9 to 10.2‰ where as the amplitude increased between 66 m depth (-9 to -12 ‰)

CHHOTA SHIGRI GLACIER

- Based on ³²Si concentrations, the radiometric age of snout ice of C.S. glacier has been estimated to be ~250 yrs.
- The past average surface ice flow rate of C.S. glacier over a period of few centuries has been estimated to be ~28 m/yr.
- ³²Si studies on englacial meltwaters indicate that at least 55% of the snow meltwater is mixed with 45% of the old ice meltwater that emergs out from the englacial lake in summer month.
- The identification of Fission product (¹³⁷Cs and total β activities) in snow samples confirm the evidence of Chernobyl fallout deposition on Chhota Shigri glacier, Indian Himalaya.
- The δ¹⁸O value in snout ice is depleted by 4% as compared to average fresh snow values. This indicates that the climatic conditions few centuries ago may be cooler than that at present.
- The rough estimate of accumulation rate of ice based on δ¹⁸O variations in a shallow pit has been estimated to be ~50 cm of water equivalen/yr. The scanty data on shallow ice cores suggests that it is necessary to raise long ice cores (upto 200 m) to get meaningful data on past climatic variations for a period of ~1000 years.

GARA GLACIER

- The ³²Si activity decreased from the equilibrium line to the snout from 0.55 to 0.175 dpm t⁻¹
- The radiometric age of snout ice has been calculated to be 200 yrs based on which the average past ice flow rate along the glacier has been estimated to ~20 m/yr.

ISOTOPES IN CLIMATE CHANGE

Environmental isotopes are one of the most powerful tools to investigate climatic changes and the environmental response to those changes. This is because the isotopes, both stable and radioactive, are preserved in various natural archives such as sediments in lakes and oceans, ice in glaciers or polar ice caps, water in precipitation and oceans, and even trees.

Among the various isotopes Carbon and Oxygen isotopes are used to understand the present and past climatic conditions.

Oxygen isotope records have been used to estimate past water temperatures, ice sheet sizes, and local salinity variations, while Carbon stable isotope records have been used to provide constraints on water mass circulation patterns, oceanic nutrient levels, and source of atmospheric CO_2 concentrations. Carbon isotope has been also used for dating.

Isotopes help us

- (i) reconstruction of the range of natural climatic variability observed over the history of the earth. Among this, special interest are abrupt changes.
- (ii) to test climate models using past environmental conditions in order to understand better how the present climate system works
- (iii) by improved model calibrations, to enable predictions of future climate to be made with more confidence.

CAUSES OF CLIMATE CHANGE



CHANGES IN ATMOSPHERIC COMPOSITION



Uplift of large Mountain ranges (Himalayas, Tibetan Plateau) increased chemical weathering of exposed rocks lowers atmospheric CO₂

CAUSES OF INCREASING GHGs

Compared to natural changes over the past 9750 years, there is extraordinary increase in concentrations of CO_2 & CH_4 in the past 250 years.

Reason I

Ocean warming is resulting in increased CO_2 . Since, the solubility of gases is inversely proportional to temperature.

Reason II

The increase in greenhouse-gases is caused by anthropogenic activities.

It has becomes important to determine the source of the increase in CO₂ from 280 to 380 parts per million by volume between 1800 and 2005



IPCC AR4, WG1 SPM, 2007

TEMPERATURE VARIATION

The Earth is getting hotter



Climate change over short time scales (<1,000 years) Related to complex, poorly understand interactions between atmosphere, hydrosphere, and lithosphere

USE OF CARBON ISOTOPES IN CLIMATE CHANGE

Carbon has three isotopes: <u>C-12</u>, <u>C-13</u> and <u>C-14</u>.

C-12 and C-13 are Stable isotopes and C-14 is radioactive, which is used in dating of ancient material.

Isotopic ratio of the C-13 and C-12 are useful to study the climatic conditions of present and past.

IDENTIFICATION OF CO₂

Carbon isotopes are useful in separation of Carbon cycle CO_2 , deforestation CO_2 , oceanic CO_2 and fossil fuel CO_2 .

C-12 is most prevalent carbon isotope and plants prefer Carbon-12.

Therefore, photosynthetic CO_2 (fossil fuel or wood fuels) is much lower in C-13 than CO_2 that comes from other sources (e.g.: animal respiration, oceanic sources).

Carbon-14 is radioactive. Fossils do not contain ¹⁴C because they are much older than 10 half lives of ¹⁴C.

There has been observed decline in the ${}^{14}C/{}^{12}C$ ratio in CO₂ that parallels the increase in CO₂. There has been a parallel decline in ${}^{13}C/{}^{12}C$ ratio of atmospheric CO₂. This has been linked to the fact that fossil fuels, forests and soil carbon come from photosynthetic carbon which is low in ${}^{13}C$.

If the increased CO₂ was due to warming of the oceans, there should not be a reduction in the ratios of C-13 and C-14 to C-12.

¹³C/¹²C RATIO OF TREE RINGS

Sequences of annual tree rings going back thousands of years have now been analyzed for their ¹³C/¹²C ratios. Because the age of each ring is precisely known. Plots of the atmospheric ¹³C/¹²C ratio vs. time has been prepared for the last 10,000 years.

The ¹³C/¹²C ratios in the atmosphere as low as they are today. Furthermore, the ¹³C/¹²C ratios begin to decline dramatically just as the CO₂ starts to increase — around 1850 AD. This indicates that increased CO₂ is in fact due to fossil fuel burning



¹³C/¹²C RATIO IN CORALS AND SPONGES

Measurements of ${}^{13}C/{}^{12}C$ on corals and sponges — whose carbonate shells reflect the ocean chemistry just as tree rings record the atmospheric chemistry — show that ${}^{13}C/{}^{12}C$ is decreasing about the same time as in the atmosphere; that is, when human CO₂ production began to accelerate in earnest.

There are also of measurements of the ${}^{13}C/{}^{12}C$ ratio in the CO₂ trapped in ice cores. The tree ring and ice core data both show that the total change in the ${}^{13}C/{}^{12}C$ ratio of the atmosphere since 1850 is about 0.15%.

This sounds very small but is actually very large relative to natural variability. The results show that the full glacial-to-interglacial change in ${}^{13}C/{}^{12}C$ of the atmosphere — which took many thousand years — was about 0.03%, or about 5 times less than that observed in the last 150 years

OXYGEN ISOTOPES AND PALEOCLIMATE

- As climate cools, marine carbonates record an increase in $\delta^{18}O$.
- Warming yeilds a decrease in $\delta^{18}O$ of marine carbonates.





JOIDES Resolution

Scientists examining core from the ocean floor.

MARINE OXYGEN ISOTOPE





Microfossils made of CaCO₃ ¹⁸O/¹⁶O is a function of ice volume and hence global temperatures



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ANTARCTIC ICE CORE DATA

gases trapped in bubbles in the ice

oxygen isotope composition of the ice



Based in part on C. Lorius et al. (1900), The ice-core record: Climate sensitivity and future greenhouse warming. *Nature*, Vol 347, pp. 139-145; J. T. Houghton, G. J. Jenkins, and J. J. Ephraums (1990), *Climate Change: The IPCC Scientific Assessment* (Cambridge University Press), Fig. 2. Copyright 2000 John Wiley & Sons, Inc. All rights reserved.

OXYGEN ISOTOPE PALEOTHERMOMETRY

Development of a paleotemperature equation, from which the temperature of precipitation could be estimated by measuring the ¹⁸O/¹⁶O ratio in calcite secreting organisms (foraminifera, corals, mollusks) and the ratio in the water the organisms lived in.

$$T = 16.5 - 4.3 \times (\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.14 \times (\delta^{18}O_{calcite} - \delta^{18}O_{water})^2$$

where T and d18Owater are the temperature (°C) and oxygen isotope value of the water in which the organism lived, and $\delta^{18}O_{calcite}$ is the oxygen isotope value measured in the calcite.

Masured values revals that if 1°C temperature increase there is a 0.23‰ decrease in the measured ¹⁸O_{calcite} value. These relationships are routinely applied to interpret changes in $\delta^{18}O_{calcite}$ records generated from foraminifera, corals, and mollusks.

OXYGEN ISOTOPE STRATIGRAPHIES

Long-term oxygen isotope record

Ice cap begins to form on Antarctica around 35 Ma

> This may be related to the opening of the Drake passage between Antarctica and S. America



From K. K. Turekian, *Global Environmental Change*, 1996

APPLICATION OF ISOTOPES IN PRESENT CLIMATE

For the last 50 years WMO and IAEA are collecting precipitation sample all over the world isotopic analysis. The isotopic signatures are available for study the variation of present day climate.

ORIGIN OF OXYGEN ISOTOPIC VARIATIONS IN THE NATURAL ENVIRONMENT



Contour map of amount-weighted mean annual δ 18O in precipitation derived from the GNIP database, for stations reporting as of 1997. The pattern in δ^{18} O values reflect larger the surface air temperature gradients (i.e., changes with latitude and elevation).

