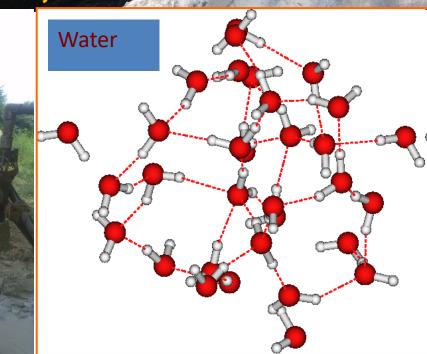
Environmental Tracers in salinity studies

ues and

NIH, Roork



Groundwater salinig management solutio



247667

Contents of Talk

Background – groundwater salinity and use of tracers
 Need for Environmental tracers
 Introduction of environmental tracers
 Use of tracer for Identification of sources, evolution of groundwater age

Some major issues 1. Increased Groundwater Abstraction Increase in demand Falling groundwater levels in agricultural areas





- 2. Groundwater salinity
- Salinity from flooding
- Agriculture sources
- Salinisation problems in irrigated soils

Background

•Groundwater salinization can derive from numerous sources/processes which may carry a distinct "fingerprint" that allows for identification of the source of salinization or

natural or anthropogenic sources:

the process which gave rise to the salinization -

Identification of naturally occurring surface-water contributions; Identification of mixing of different groundwater bodies

•Mixing of salts -e.g. migrating fluids drive (bio)geochemical processes rock-water interaction, reverse exchange, evaporation, ion exchange, silicate weathering etc. that result in the release of salts to the groundwater or naturally occurring species present in groundwater at concentrations that exceed threshold values.

Background

•Tracer techniques can identify the source of salinization and yield information on process such as redox or chemical evolution, mixing and migration.

•The chemical composition of relevant end members (groundwater and fracturing fluids) are needed to make best diagnostic use of isotope or other geochemical techniques.

Major causes of salinization

Poor groundwater management (often dictated by immediate social needs) and the lack of regulations and control over the use and disposal.

Agricultural practices, with the sometimes indiscriminate and frequently excessive use of fertilizers, are among the most relevant sources of groundwater salinity

Industrial and domestic contaminants are among the most dangerous. This is partly due to the fact that they are produced mainly in urbanized areas, where water demand is higher and groundwater exploitation more intense. Here, as the groundwater pressure is lowered, contaminated surface waters may be able to penetrate to depths where artesian pressure had previously prevented infiltration.

In coastal regions, over-development is frequently the cause of seawater encroachment and consequent groundwater salinization. In arid areas, overdevelopment usually invites a rapid decline of groundwater resources, which are insufficiently recharged by prevailing climatic conditions. In addition, poorly designed irrigation schemes may hasten the salinization of soil, which eventually becomes sterile.

Environmental Tracers

Tracer: a substance introduced into a biological organism or other system so that its subsequent distribution may be readily followed from its colour, radioactivity, or other distinctive property

Environmental tracers are ambient, natural or man-made compounds widely distributed in the Earth's near-surface.

May be injected naturally into the hydrological system from the atmosphere at recharge and/or are added/lost/exchanged inherently as waters flow over and through materials.

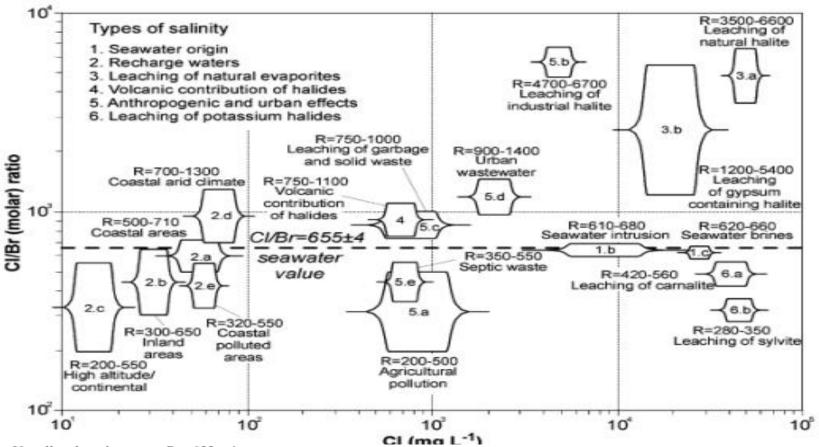
Important Tracers Stable Isotopes (Recharge sources)

Age Dating Techniques (Groundwater Residence time tracers) CFCs & SF6 Noble gases Environmental tritium

Inorganic chemistry: Mineralogy Cl, NO₃ and trace elements, ionic ratios/correlations, reaction path simulations, mineralogy

Others Loggers (water level and conductivity)

CI/Br ratio



- Unpolluted marine water, R = 655 ± 4
- Recharge water, R = 400-500
- Continental rainwater, R = 50 650. In area where atmospheric air is seriously affected by the burning of automotive fuels, R is sometimes < 50
- · Coastal rainwater, R is similar to or smaller than marine value
- Deposition derived from marine aerosol, R > 800
- Salinity from leachate or saline urban waste, R = 750 -1000
- Leachate from septic tank, R 450
- Volcanic gas contributing halides, mostly R > 650, sometimes up to 900, although widely variability is observed

Naily and Sudaryanto, 2018

Application of Tracers

tracers separately or in conjunction may suggest a unique solution in detailing the hydrogeochemical processes operating

for trace elements, environmental isotopic signatures of dissolved compounds, and the water molecule itself, can prove particularly sensitive tracers, as they occur generally at low levels of concentration and can be affected by chemical and physical fractionation effects shifting their signatures

groundwater chemical abundances and isotopic compositions can be used as natural tracers to determine sources (provenance),

pathways (of reaction or interaction), and also timescales (dating) of environmental processes

environmental tracers in groundwater systems can give information both on current and past flow conditions independently of hydraulic analyses and groundwater modelling

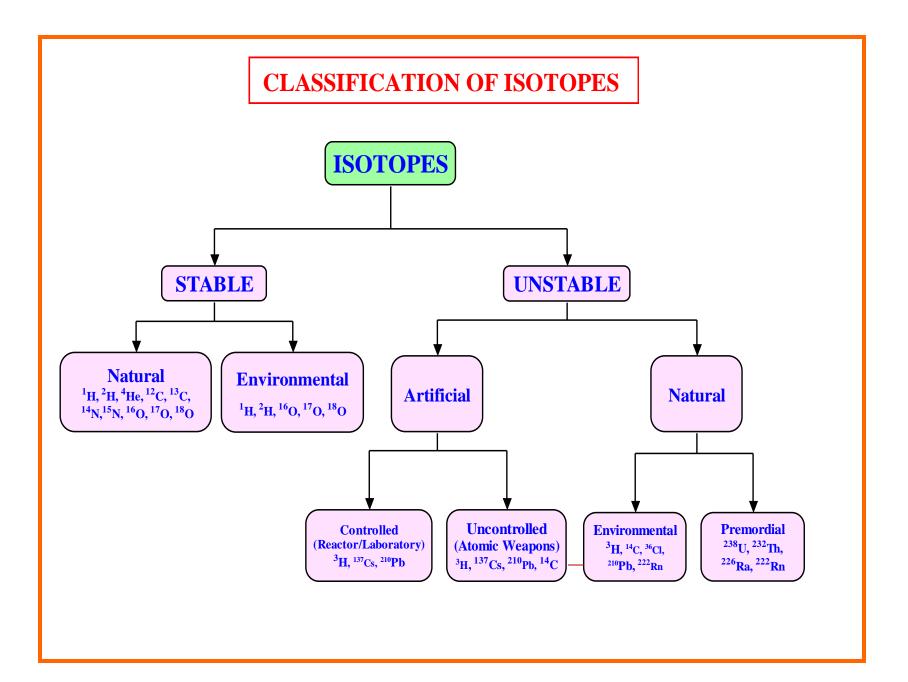
Why suite of tracers ?

There is a need to establish natural baseline conditions to assess deviations from the natural system.

•Major-ion chemistry alone may not yield definitive results as to the source(s) of any identified deviations.

•The application of multiple isotope systems allows for a more robust and comprehensive assessment of potential sources of contamination and allows for quantitative estimates of the contribution of these sources to be made.

•Sampling of potential end member fluids (surface water, groundwater and introduced fluids used during the fracturing process) may provide important compositional information that could prove useful when attempting to identify the existence and/or source of any perceived contamination.



Stable Isotopes



Isotope = atoms of the same element with a different number of neutrons (different mass)

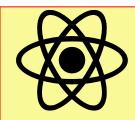
Example: Oxygen Isotopes

Name	Electrons	Protons	Neutrons	Abundance
16 ()	8	8	8	99.76%
¹⁸ O	8	8	10	0.20%

- Do not decay with time
- Most of the Elements have Stable Isotopes.
- Many Stable Isotopes are also available in the Earth's atmosphere: (Environmental Stable Isotopes)
- For most of the hydrological studies environmentally occurring stable isotopes are used

- 1. Heavier molecules have lower velocities → smaller collision frequency →slower rate of reaction.
- 2. Heavier molecules have greater binding energies and require more energy to break the bonds. Therefore, heavier isotopes form stronger bonds.
- 3. Heavier molecules prefers more condensed phase.

Measured using Isotope Ratio Mass Spectrometers

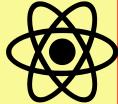




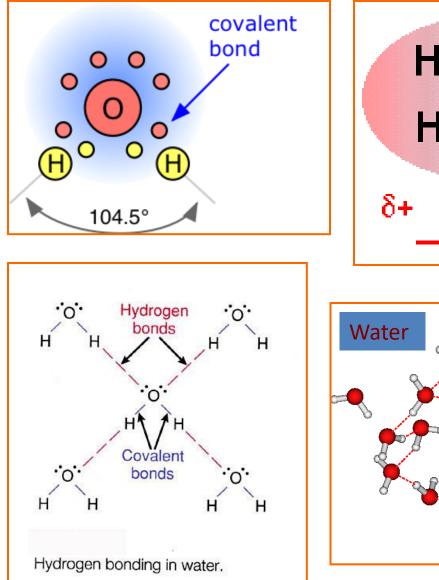
- Also known as Radioactive Isotopes or Radioisotopes
- Spontaneously emits radiations
- In the process of decay, transforms to atom of another element, which in turn could be radioactive
- The chain continues till a stable isotope is formed

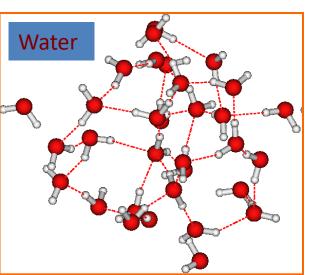
ENVIRONMENTAL ISOTOPES

- Available in the Earth's Atmosphere
- These may be Stable and Radioactive
- Neither to Buy nor to Inject
- Naturally introduced in the hydrological cycle
- Different Processes are Responsible (Evaporation, Condensation, Mixing)
- Very Sophisticated Instruments are Available
- Not Harmful

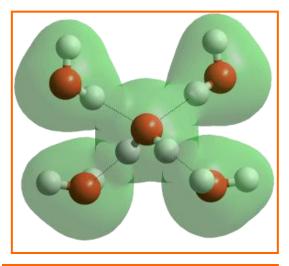


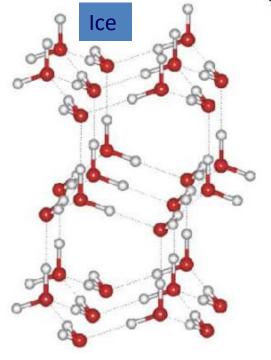
The Structure of Water Molecule



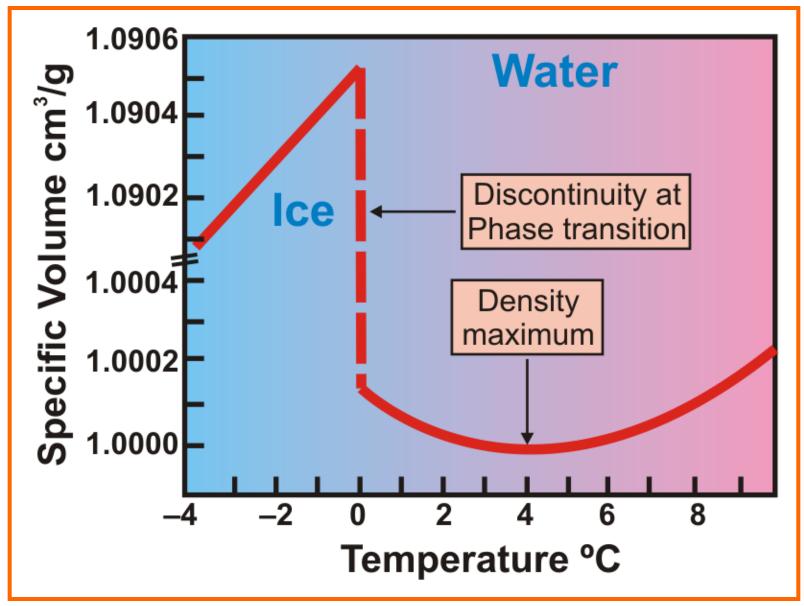


δ-



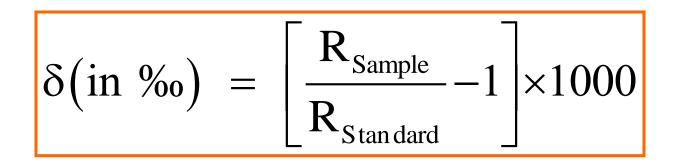


Specific heat capacity				
Water	4.187 kJ/kgK (Copper it is 0.386 kJ/kgK)			
Ice	2.108 kJ/kgK			
Vapor	1.996 kJ/kgK			
Latent heat				
Melting	334 kJ/kg (Consumed)			
Condensation	2,520 kJ//kg (Released)			
evaporation	2,270 kJ/kg (Consumed)			
Bond Strength				
Hydrogen	21 kJ/mol			
Covalent	458.9 kJ/mol			



NIH, Roorkee

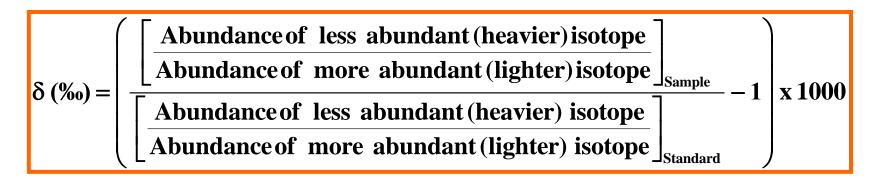
How Isotopic Composition is expressed and why it is done this way?



Why ratio of sample to standard ?

Why multiply by 1000?

Expressing the Isotopic Composition



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

$$\delta$$
 (%) = (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‰ → Sample has 2025.252 atoms of ¹⁸O /1000000 atoms of ¹⁶O

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

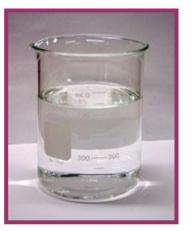
Expressing the Isotopic Composition-1

- Absolute abundance of heavier isotopic molecular species of water is very small in any natural water sample.
 ~2000 H₂¹⁸O and ~150 HD¹⁶O in 1000000 H₂¹⁶O
- 2. Variation in absolute abundance of heavier isotopic molecular species is even smaller

2025 atoms of ¹⁸O

per million atoms of ¹⁶O

2005 atoms of ¹⁸O per million atoms of ¹⁶O



 $^{18}O/^{16}O = 0.002005$

¹⁸O/¹⁶O = 0.002025

Instruments for Stable Isotope Analysis



NIH, Roorkee

Oxygen and hydrogen isotopes of water are widely used as tracers to understand hydrogeological processes such as precipitation, groundwater recharge, groundwater-surface water interactions, and basin hydrology

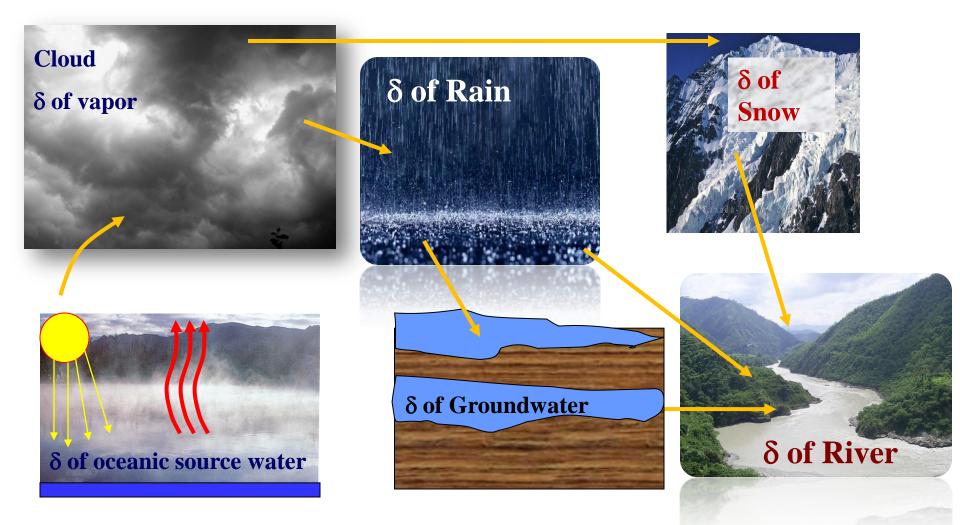
```
In hydrology, fractionation of \delta^{18}O and \deltaD is driven by kinetic processes during evaporation and
condensation
An Empirical equation was found by Craig, 1961:
\delta D = 8 \ \delta^{18}O + 10,
\delta D = 8.17 \ \delta^{18}O + 11.27 which was later modified by Rozanski, 1993
```

In the meteoric water line of oxygen and hydrogen isotopes, the slope represents the ratio of the temperature relationship between δD and $\delta^{18}O$ when condensation occurs; the value of the intercept is based on the evaporative conditions in the water source region.

North America:	δD = 7.95 δ ¹⁸ O + 6.03	Dansgard, 1964
Tropical Island area:	δD = 6.17 δ ¹⁸ O + 3.97	
Japan:	δD = 8.00 δ ¹⁸ O + 17.5	Sakai and Matsubaya, 1977
India (Punjab):	δD = 7.86 δ ¹⁸ O + 5.44	Rao and Krishan, 2014

$$C(V_A + V_B) = AV_A + BV_B$$
$$C = A \frac{V_A}{V_A + V_B} + B \frac{V_B}{V_A + V_B} = A(1 - X) + BX$$

Water molecules record the information about their origin and path in their isotopic composition



Isotope Fractionation

- Differential partitioning of isotopes between the two compounds or between the two phases of a compound in a physicochemical reaction. If conditions are equilibrium
 - a. Phase Change
 - b. Chemical Transformation
 - c. Isotope Exchange
 - d. Mineral Solution
 - e. Gas Solution

If conditions are non- equilibrium

- a. Sudden Temperature change
- b. Addition or removal of reactant or product
- Differential partitioning of one isotope over another on one side of the thermodynamic reaction.
- Differential partitioning of isotopes due to molecular diffusion.

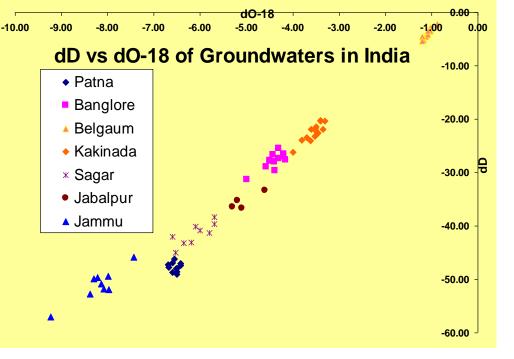
Isotope Effects

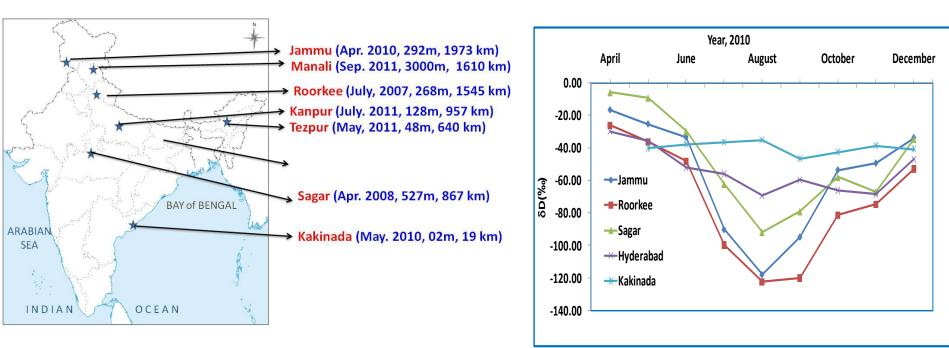
Latitude Effect

Continental Effect

Altitude or Elevation effect

Seasonal Effects





Chloroflourocarbons (CFCs)

•contains only carbon, chlorine, and fluorine (CCI3F (CFC-11), CCI2F2 (CFC-12), C2CI3F3 (CFC-113), produced as a volatile derivative of methane, ethane, and propane – Dupont brand name Freon

•CFC-11, 12 - refrigeration & air conditioning •CFC-13-solvent

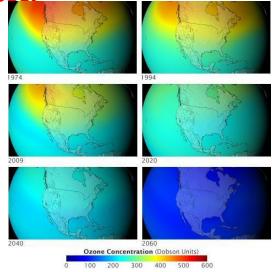
•Have been used since 1940s and inevitably they leaked into the environment, with atmospheric

concentrations rising until the 1990s, when production was cut

back to protect the ozone layer as a result of the Montreal Protocol

•Due to the role in ozone depletion in upper atmosphere have been phased out in Montreal protocol and are replaced by Hydrofluorocarbons (HFCs)

Contamination may be atmospheric or in-ground and I s not too surprising: for example it has been calculated that less than one-tenth of the amount of CFC-12 present in a single domestic refrigerator (of older design) could theoretically contaminate a moderately sized aquifer to more than ten times current atmospheric equilibrium Levels i.e. giving the water a modern fraction value of 10.



Measured by gas chromatography (electron capture detector)

Noble gases

The noble gases make a group of chemical elements with similar properties. Under standard conditions, they are all odorless, colorless, monatomic gases with very low chemical reactivity. The six noble gases that occur naturally are helium (<u>He</u>), neon (<u>Ne</u>), argon, (<u>Ar</u>), krypton (<u>Kr</u>), xenon (Xe), and the radioactive <u>radon</u> (<u>Rn</u>).

Noble gases are biologically and chemically inert and have a wide range of solubilities and diffusivities, making them useful environmental tracers.

Noble gases have been measured in seawater, groundwater, ice cores, and rocks in order to address a variety of important problems in environmental science such as air-sea gas exchange, marine biological production, groundwater temperatures, firn temperature and thickness, surface exposure ages, etc.

Measured by helium isotope mass spectrometer (**HIMS**)

Quadrupole mass spectrometry (QMS)

Tritium 1 TU is defined as the presence of one tritium in 10¹⁸ atoms of hydrogen (H)

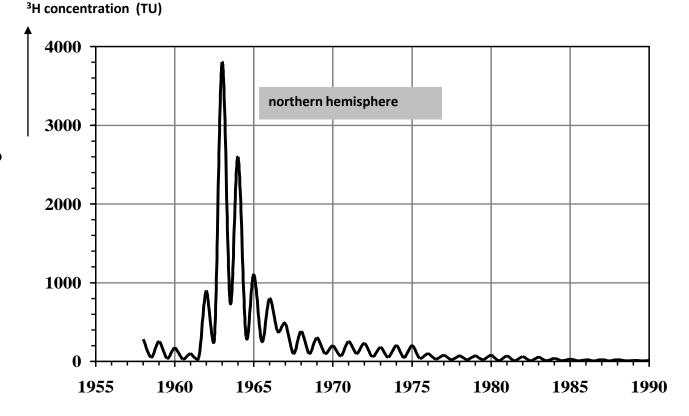
 $^{14}N \rightarrow ^{12}C + {}^{3}H$

 ${}^{3}H \rightarrow {}^{3}He + B^{-}$

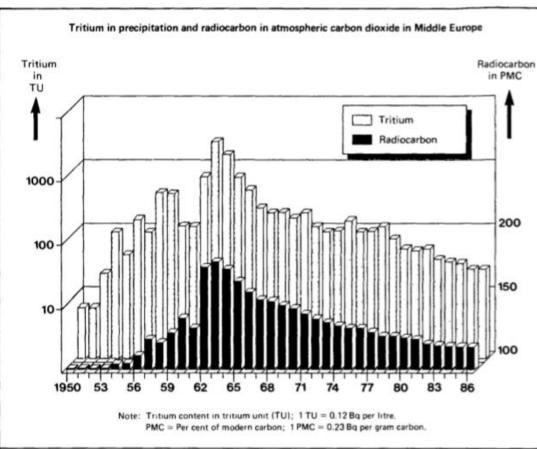
³H enters the hydrologic cycle after oxidation to ¹H³HO and finally decays according to:

Initial concentration = 2-8 TU Added 1.13 x 10⁹ TU in 1963 Presently = 12 - 15 TU <0.8 TU = submodern <0.8 TU - 4TU = submodern to

modern 5-15 TU=modern 15-30 TU= bombed tritium >30 TU = 1960's



Smoothed curve representing the average ³H content of precipitation over the continental surface of the Northern hemisphere.



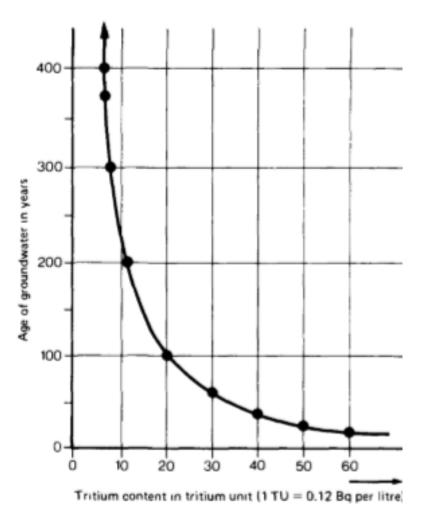
Tritium and carbon-14 are naturally produced by secondary cosmic radiation and have been injected into the atmosphere in **quantities** large bv the atmospheric thermonuclear tests conducted until 1963 by the **United Kingdom, United States,** and USSR. Only minor amounts have been produced later by **Chinese and French tests. The** decrease tritium of and carbon-14 concentrations in precipitation and in atmospheric carbon dioxide after the Partial Test Ban Treaty of 1963 has provided and invaluable new insight into atmospheric processes

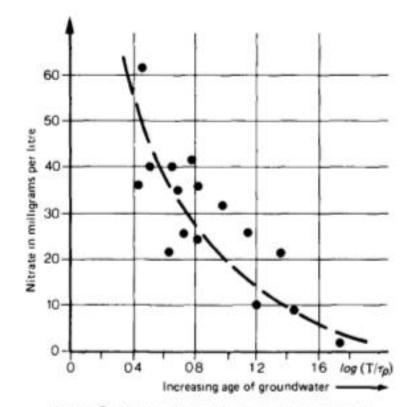
IAEA Bulletin, 1989

Tritium, with a half-life of only 12.43 years, can be used to reveal the occurrence of modern groundwater recharge

If tritium is present, the transit time of water from the recharge area to the aquifer is short, as is the residence time of groundwater in the aquifer. This lowers the chance of any contaminant dissolved in the recharge water to become adsorbed by the aquifer matrix. Consequently, the contamination risk is potentially high. NIH. Roorkee







Notes: T is the age of groundwater, τ_p is the time period between the occurrence of tritium from atmospheric weapons tests and the implementation of the field study.

These figures show the correlation between nitrate and tritium concentration observed In an unconfined Permian aquifer In the German Democratic Republic. The correlation Indicates that the **Hnitrate** has been transported into the groundwater by the infiltration of rain water.

Sampling for CFCs, SF6 and stable isotopes

- CFCs and SF6 modern groundwater dating tools
- Sample collection by the bottle-in-can method
- atmospheric air is excluded during sampling to obtain a representative sample
- air displacement method for CFCs and SF6
- specialist techniques and are not routinely sampled or analysed

Analysis (rapid and cost-effective)

CFCs and SF6 are measured by gas chromatography using an electron capture detector (GC- ECD) following cryogenic pre-concentration

The detection limit for CFC concentrations in water is 0.01 pmol/L, while for SF6 it is 0.1 fmol/L

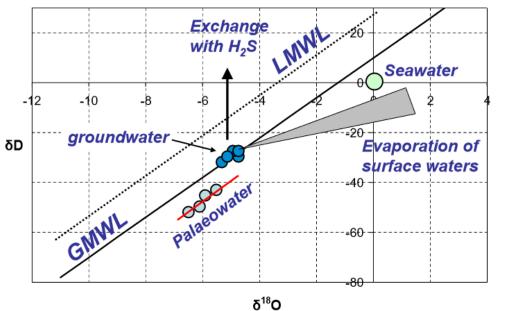


CFC sampling

Sampling for noble gases

- Noble gases thermometry, i.e. recharge temperature, and excess air assessment
- atmospheric air is excluded during sampling to obtain a representative sample
- sealed copper tubes for noble gases
- are specialist techniques and are not routinely sampled or analysed

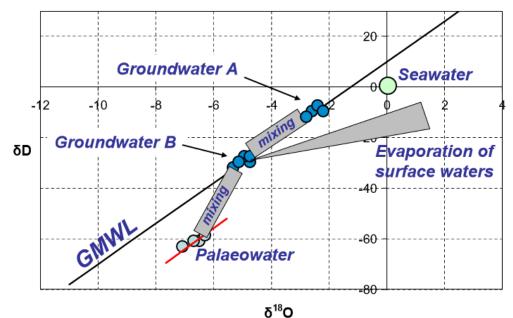




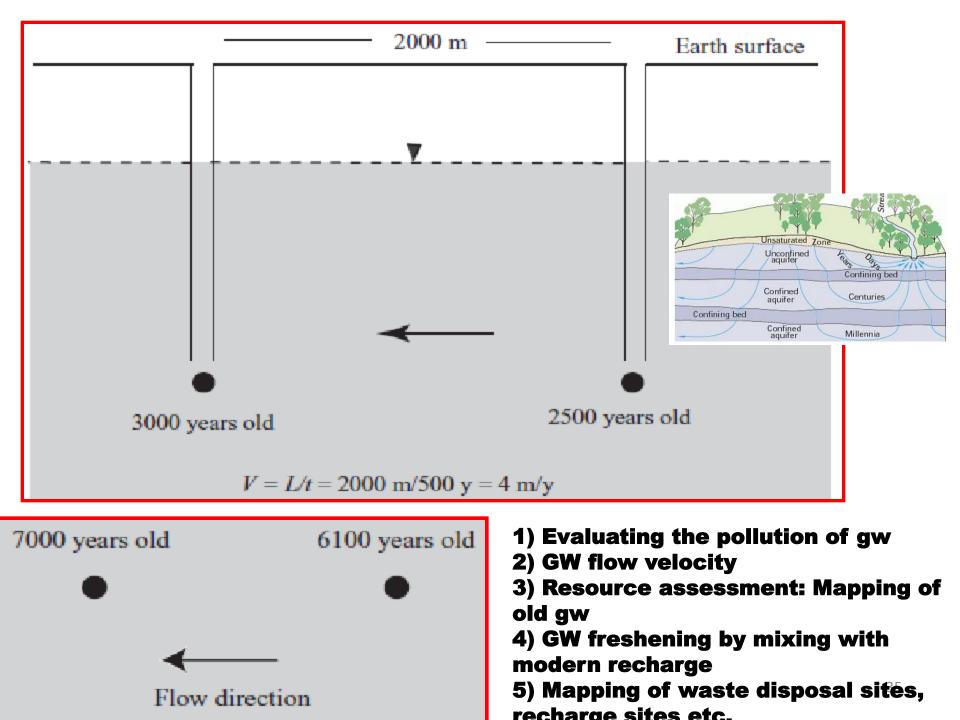
Natural conditions



Mixing processes



After Geyh (2000)



Surface Water

- Hydrographs separation
- River discharge measurements
- Dynamics of lakes and reservoirs
- Water balance
- Interconnections of water bodies
- Leakage through dams,
- Seepage to subways
- Suspended and bed load sediment transport
- Sedimentation rate
- Evaporation/Evapotranspiration
- Surface water and groundwater interaction
- Sources and tracing of pollutants
- Snow and glacial melt runoff

Ground Water

- **. Soil moisture variation, movement and recharge**
- . Origin
- . Mixing and distribution
- . Occurrence and recharge mechanism
- . Groundwater flow velocity and direction Interconnections between groundwater bodies
- Identification of recharge sources and areas of deeper aquifers and springs
- Effectiveness of artificial recharge measures Groundwater and surface water interaction Data on lithology, porosity and permeability of aquifers
 - **Pollution source and mechanism**

Meteorological

- . Variability of environmental conditions/ climate change
- . Movement of clouds and variability in precipitation
- **Environmental pollution and mechanism**
 - **Prediction of Arrival and retreat of Monsoon**

Radon decay

Natural radioactivity (half-life)

in the ground uranium-238 ⇒ ⇒ radium-226 ⇒ 4.5 billion years

1600 years

radon-222 *gas* has time to leak into the air $\Rightarrow \Rightarrow$

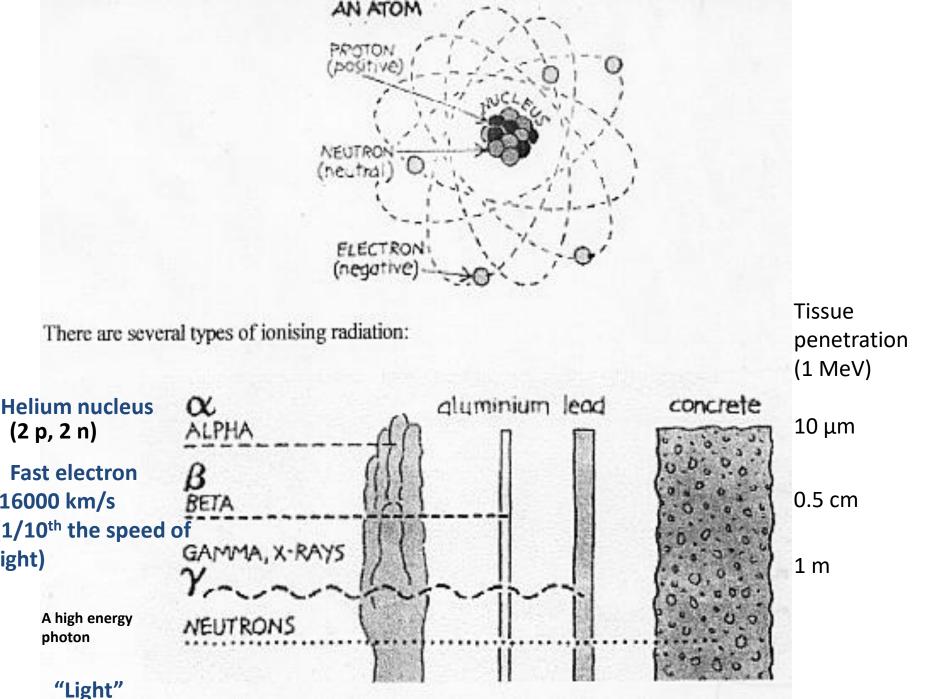
3.8 days

lead-210 $\Rightarrow\Rightarrow$ **lead-206**

22 years stable

radon progeny (daughters)

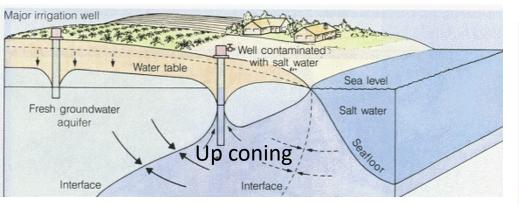
radioactive isotopes of lead, bismuth, and polonium can be *inhaled and deposited in the lungs*



- Radon in groundwater originates due to decay of parent radioactive member radon-226 which is derived from the decay of the ultimate parent source uranium-238.
 - Radon-222 concentration in groundwater is a function of radioactivity concentration of radium.
 - Radon concentration in groundwater at a given location depends on the
 - * local hydrogeology
 - soundwater fluctuation
 - soil moisture conditions.

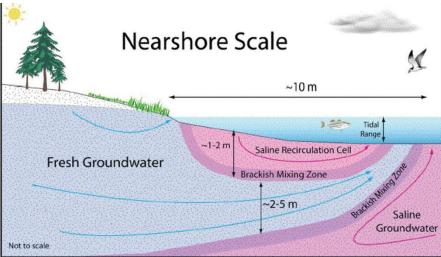
In the coastal aquifer, the difference in hydrostatic pressure between groundwater and sea water results into:

>Inflow of seawater into groundwater system: Seawater Intrusion (SI) or
>Fresh GW discharge into the sea: Submarine Groundwater Discharge (SGD)



SI: Reduces available freshwater volume

When SGD \rightarrow 0 \Rightarrow SI begins (Freshwater) (saline water)



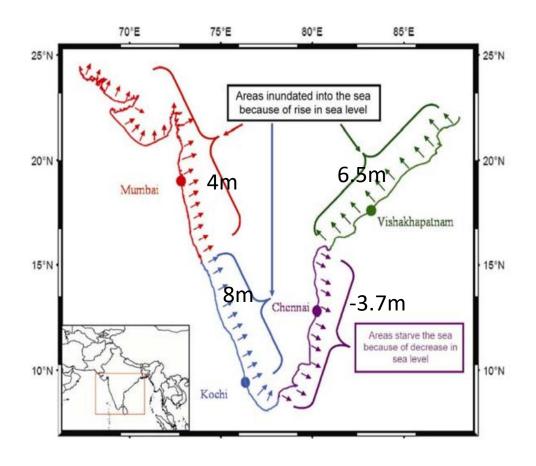
SGD: Loss of fresh-groundwater to sea Discharge of fresh groundwater and/or recirculated seawater

Use and development of SGD based groundwater resource is environmental friendly and cost effective compared to seawater desalination technique in the

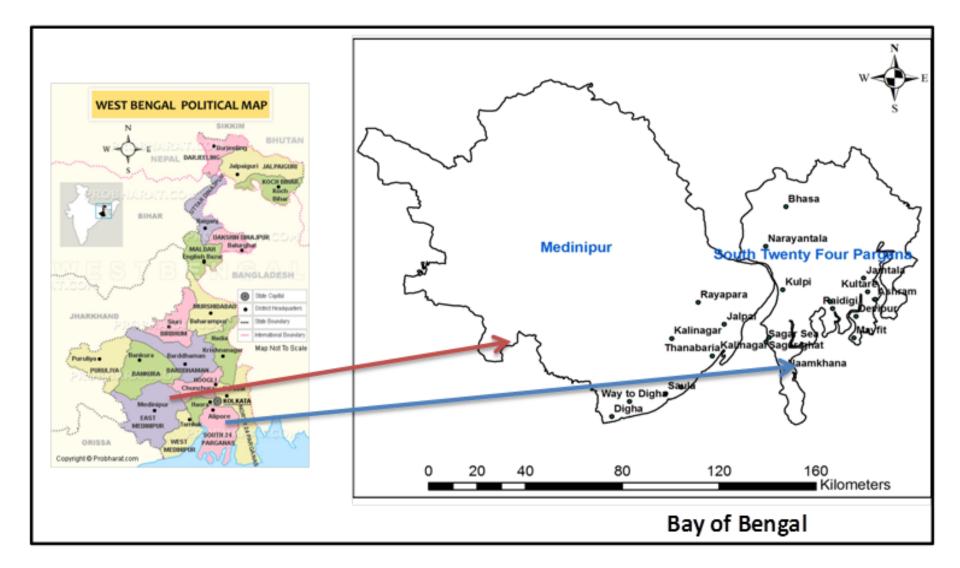
IMPORATANCE OF MAPPING of SI/SGD ZONES IN INDIAN CONTEXT

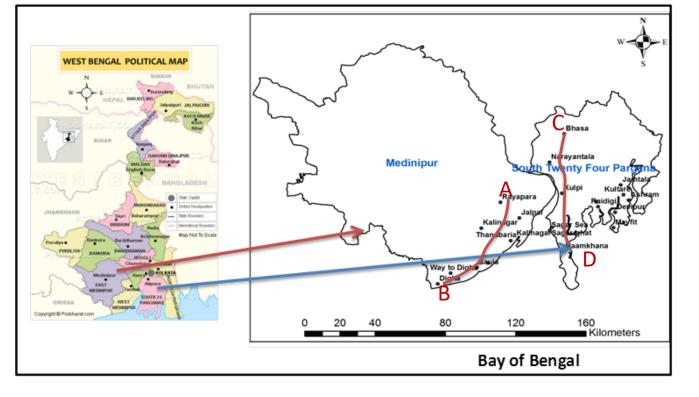
India has over 8000 km length of shore line with people living over 250 million within 50 km of the coast.

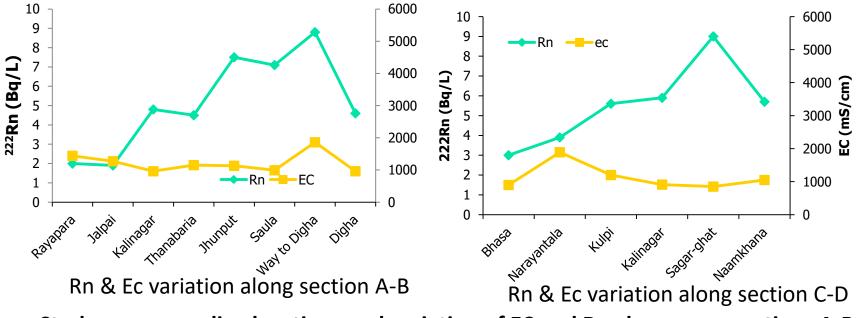
Length of Indian coast line	
State	Length
	(km)
Gujarat	1600
Daman, Diu	21
Maharashtra	720
Goa	104
Karnataka	300
Kerala	590
Tamil Nadu	1076
Puducherry	41
Andhra Pradesh	974
Orissa	480
West Bengal	158
Andaman and Nicobar	1962
Islands	
Lakshadweep Islands	132
Total length:	8158 km



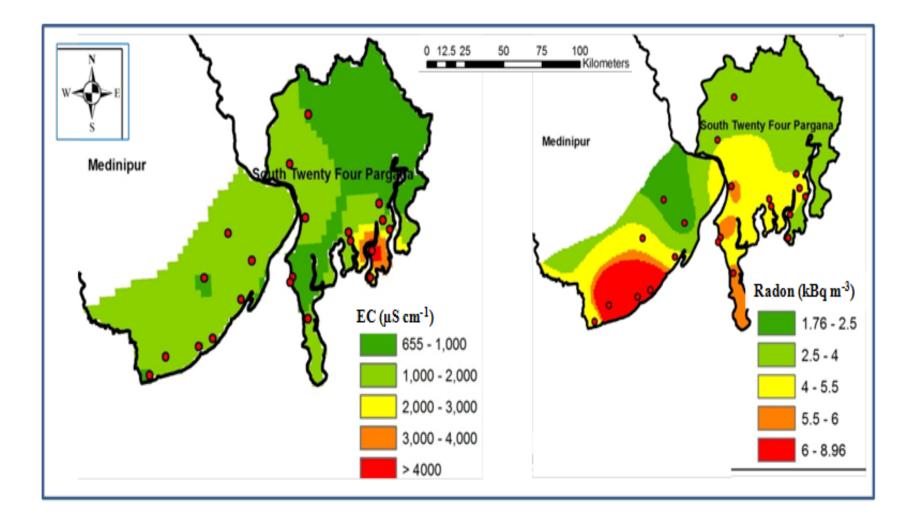
The increasing water withdrawal may pose problems like salinity hazard, seawater intrusion, salt water upconing, land subsidence etc.,







Study area compliand locations and variation of EC and Dn along cross sections A D and C D





Available online at www.sciencedirect.com

ScienceDirect

Aquatic Procedia 4 (2015) 3 - 10

Aquatic



www.elsevier.com/locate/procedia

INTERNATIONAL CONFERENCE ON WATER RESOURCES, COASTAL AND OCEAN ENGINEERING (ICWRCOE 2015)

A study on identification of submarine groundwater discharge in northern east coast of India

Gopal Krishan^a*, M. Someshwar Rao^a, C.P. Kumar^a, Sudhir Kumar^a, M. Ravi Anand Rao^b

*National Institute of Hydrology, Roorkee-247667, Uttarakhand, India *K.G.C.E.,Karjat-410201, Raigad, Maharastra, India

Radon concentration in groundwater of east coast of West Bengal, India

Gopal Krishan, M. S. Rao, C. P. Kumar

Case Study

Estimation of radon concentration in groundwater of coastal area in Baleshwar district of Odisha, India

Gopal Krishan, M. S. Rao and C. P. Kumar

Indoor and Built Environment

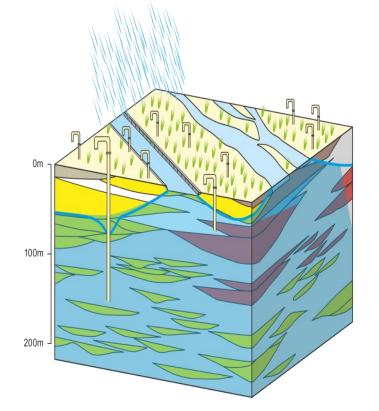
Indoor and Built Environment 2015, Vol. 24(8) 1147–1152 © The Author(s) 2014 Reprints and permissions: sagepub.co.uk/ journalsPermissions.nav DOI: 10.1177/1420326X14549979 ibe.sagepub.com \$SAGE

Journal of Radioanalytical and Nuclear Chemistry An International Journal Dealing with All Aspects and Applications of Nuclear Chemistry

Prabhat Semwal

ISSN 0236-5731 Volume 303 Number 3





Groundwater recharge:

Evidence from stable isotopes show that groundwater recharge is dominated by meteoric sources rather than canal leakage.

Groundwater residence times:

The shallow part of the aquifer system (0-50mbgl) has mean residence times between 1-50 years. The deeper part of the aquifer system (70-160mbgl) has mean residence times between 40-170 years.

Pumping enduced vertial leakage:

Widespread occurrence of modern tracers in deep groundwater, >60% of sites had modern fractions >0.1.

<mark>_</mark>

Q2

@AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER

10.1002/2015GL065798

Key Points:

- Tracers reveal low regional anisotropy in the sedimentary aquifer system of NW India
- Local meteoric recharge sources dominate in both shallow and deep aquifers
- Evidence of enhanced modern recharge at depth due to intensive abstraction

Supporting Information:

 Texts S1–S6, Figures S1–S8, and Tables S1–S4 Groundwater recharge and age-depth profiles of intensively exploited groundwater resources in northwest India

D. J. Lapworth¹, A. M. MacDonald², G. Krishan³, M. S. Rao³, D. C. Gooddy¹, and W. G. Darling¹

¹British Geological Survey, Wallingford, UK, ²British Geological Survey, Edinburgh, UK, ³National Institute of Hydrology, Roorkee, India

Abstract Intensive irrigation in northwest India has led to growing concerns over the sustainability of current and future groundwater abstraction. Environmental tracers and measurements of groundwater residence times can help quantify the renewal processes. Results from 16 paired locations show that the interquartile ranges for residence times in shallow alluvial groundwater (8–50 m deep) to be 1–50 years and significantly less than those from deeper groundwater (76–160 m deep) at 40–170 years. The widespread occurrence of modern tracers in deep groundwater (>60% of sites had >10% modern recharge) suggests

• Q1: Long term GWL data shows evidence of enhanced recharge potential

• But there are significant parts of the catchment where abstraction is outstripping recharge potential leading to long term loss of shallow groundwater security – cost implications for access to shallow GW

• Q2: Clear evidence, from a range of independent groundwater tracers, that there is significant vertical leakage and recharge from shallow sources to depth (>150) mbgl induced by pumping

• The natural regional groundwater flow regime is highly perturbed due to pumping and the system can be considered highly isotropic under pumped conditions

• This has implication for long term groundwater quality protection of deep aquifers and water resource management • Reduced shallow groundwater levels in some regions is good news: lower salinity build up, soil waterlogging and of course flooding

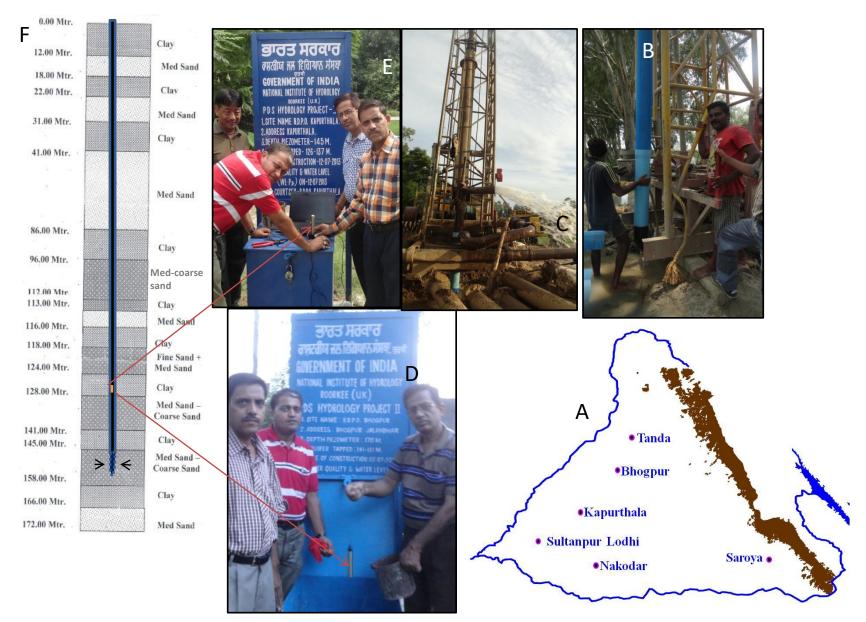


Fig : Piezometer (Pz) development in Bist-Doab: (A) Location points of Pz's (B) Lowering of Pz pipes (C) cleaning of Pz (D) Lowering the data logger (E) Measurement of recorded water level after 3 months (F) Pz strata chart (of Tanda)



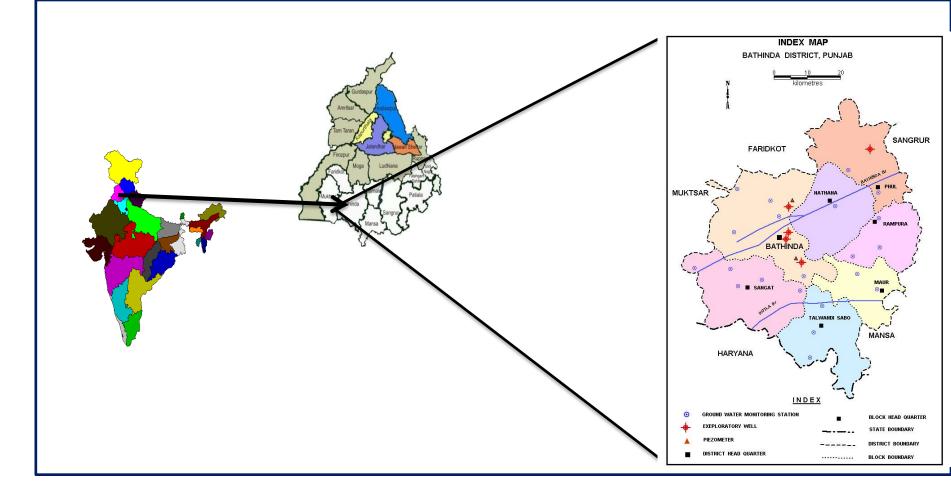


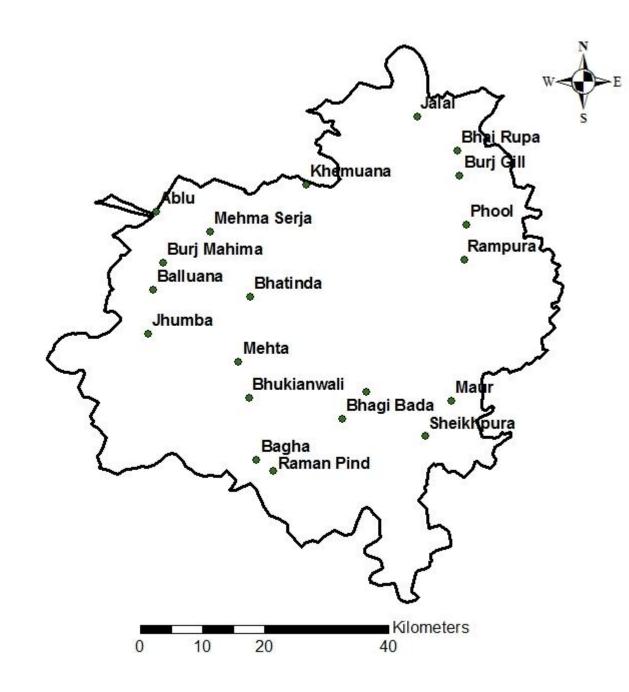
Downloading data (04-04-2016 to 06-04-2016) at Saroya, Bhogpur, Kapurthala and Sultanpur Lodhi





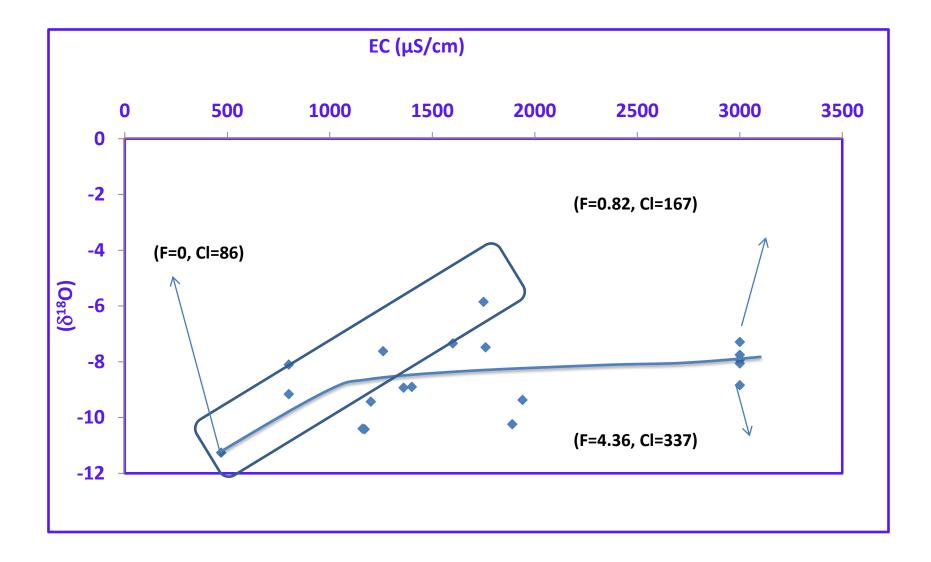






SAMPLING SITES = 20 (Sampled for groundwater Isotopes= (20) Water quality (20)

RELATIONSHIP BETWEEN EC & $\delta^{18}O$



ACKNOWLEDGEMENTS

Funding World Bank (HP-II)-Punjab Study; NHP- Haryana study BGS-DFID, UK- Indo-gangetic study, BGS UK study IAEA-Vienna (CRP)- Punjab study

NIH Director, NIH Dr. Bhishm Kumar (Consultant, IAEA) Dr. M.S. Rao, Scientist-D, HID Dr. R.D. Deshpande, PRL

Thank you

NIH, Roorkee

Questions ?

NIH, Roorkee