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Introduction to isotope analysis of water samples

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ABSTRACT

Groundwater contains environmental isotopes in its natural state. Isotope used in groundwater hydrology indicates the movement and distribution processes within aquifers. It provides complementary information on the type, origin and age of groundwater. Usually radio-isotopes such as tritium (^{3}H) and carbon-14 are used for age dating whereas stables isotopes of hydrogen (^{2}H) and oxygen (^{18}O) are used to identify recharge sources of groundwater. Stable isotopes of hydrogen (^{2}H) and oxygen (^{18}O) can be analysed by using mass spectrometer (IRMS) in the lab.

Keywords: Isotope, Stable isotopes, Groundwater quality, Mass spectrometer

INTRODUCTION

Isotope is a kind of element having the same number of electron and protons but different numbers of neutrons. There are two types of isotopes: 1) Radio isotopes (about 1200– eg. Tritium ^{3}H, Carbon ^{14}C, Uranium ^{235}U) and 2) Stable isotopes (about 300– eg. hydrogen ^{2}H, Carbon ^{13}C, Nitrogen ^{15}N, Oxygen ^{18}O).

Generally, water consists of two atoms of hydrogen and one atom of oxygen. Most of the hydrogen atoms have atomic mass one (^{1}H), but a small number, referred to as isotopes, appear to have atomic mass two (^{2}H = D) known as deuterium, and three (^{3}H = T), tritium. In the same way the normal oxygen atoms (^{16}O) are accompanied by isotopes of mass 17 and 18.

Radio-isotopes

Isotopes with unstable nuclei are called radio-isotopes and in reaching a stable nuclear configuration, they undergo radioactive disintegration or decay. This process is spontaneous and cannot be changed by external influences. The rate of decay is unique for each radio-isotope and is described by the half-life ($T_{1/2}$) which is the time required for one half of the radioactive atoms to decay. The half-life of tritium (^{3}H) is 12.3 years and that of carbon-14 is 5730 years.

Tritium is the radioactive isotope of hydrogen which occurs in precipitation and originates from naturally and artificially. The manufacturing and testing of nuclear weapons increase the amount of tritium in the atmosphere.

Stable isotopes

The heavy stable isotopic components of water are HD^{16}O, and $H_2{}^{18}O$. The stable isotopes of hydrogen (D) and oxygen (^{18}O) can be analysed by using an isotope ratio mass spectrometer (IRMS) (Fig. 1). The isotopic composition of water sample is expressed as the per mill (parts per thousand) deviation of the isotopic ratio, R = D/H or ^{18}O/^{16}O from that of a standard. The standard of reference is an arbitrary point of reference called VSMOW (Vienna Standard Mean Ocean Water). And the data are expressed as delta (δ), defined by:

$$\delta = \frac{(R - RSMOW)}{RSMOW} + 1000 \quad ^0/_{00}$$

When water changes state, through condensation or evaporation, an isotopic fractionation occurs because the heavy isotopic components such as HD^{16}O and $H_2{}^{18}O$ have lower vapor pressure than $H_2{}^{16}O$. Analysis of precipitation and water not subjected to evaporation shows a good linear relationship between the deuterium and oxygen-18, which is also known as Global Meteoric Water Line (GMWL) and is given by

$$\delta D = 8\delta 180 + y$$

The excess of deuterium (y) is normally +10 but this may vary. Waters which have been subjected to evaporation are found to fall below the general line of slope 8 (Terwey, 1998). The linear relationship of δD and δ^{18}O of rainfall is different in different countries so local meteoric water line is developed using isotopic data of rain water for different countries. The local meteoric water line for Nepal is (Gajurel et al., 2006):

$$\delta D = 8.10\delta 180 + 12.3$$

A stable isotope has inverse relation with rainfall amount and altitude. δ^{18}O values decreased by 1.24‰ per 100 mm increase of monthly rainfall. Surface water δ^{18}O values show an altitude effect of -1.9 to -2.4 ‰ km-1 and a continental effect of 0.69‰ per 100 km once corrected for altitude effects .

Most of water samples show negative isotopic value as they have fewer values as compared to standard samples of VSMOW. Three different samples are included in VSMOW standard having low, medium and high isotopic value. In the case of IMRS in University of Yamanashi, Japan, distilled water of Japan sea water is used for low isotopic value; tap water for medium; and Antarctic ice/Canadian bottle water (crystal geyser) for high isotopic value.

Application

The isotopes commonly used in groundwater investigations are stable isotopes of hydrogen (^{2}H), oxygen (^{18}O) and radio isotopes, tritium (^{3}H) and carbon-14. The stable isotope of hydrogen (δD) and oxygen (δ^{18}O) are specially used to identify recharge sources of groundwater; connection condition of groundwater and surface water (Awad et al., 1997; Hunt et al., 2005; Yang et al., 2012; and Ali and Ajeena, 2016) and to find out contribution ratios of different groundwater recharge sources (Malla et al., 2015 and Nakamura et al., 2017).

The radioactive isotopes are used to find out residence time of groundwater. The short half-life of tritium provides valuable information on recent recharge whereas long half-life of carbon-14 dates slow-moving groundwater (Terwey, 1998).

Sample collection and preparation for analysis of δD and δ^{18}O

Samples from precipitation, groundwater and surface water can be collected in plastic bottles with airtight cover. The amount of water sample is dependent on the type of isotope analysis such as only 1ml of water sample is needed for ^{2}H and ^{18}O, so for this analysis about 30 ml water sample is sufficient. But in the case of radio-isotope ^{3}H, it needs to collect 1 liter water sample. The amount of water sample is also dependent on the type of instrument. Thus before collecting water samples, it should be clear that which type of isotope analysis and instrument are being used for the groundwater investigation.

Before filling sample in bottles, it needs to ringe sample bottle with same water samples 2 or 3 times to reduce contamination. It needs to check that there is no any air bubbles present in sample bottles. Sample number is very necessary to write down in each sample bottle clearly to minimize analytical problems. These samples need to store in deep freezer that's why it can be used after long time from the sample collection.

The amount of water sample for analysis of δD and δ^{18}O by using mass spectrometer (IRMS) is very low (only 1ml) and the instrument can analyze 20 water samples per day. Before water sample used for isotope analysis, it need to filter these samples using 0.2 µm filter paper (Fig. 2).

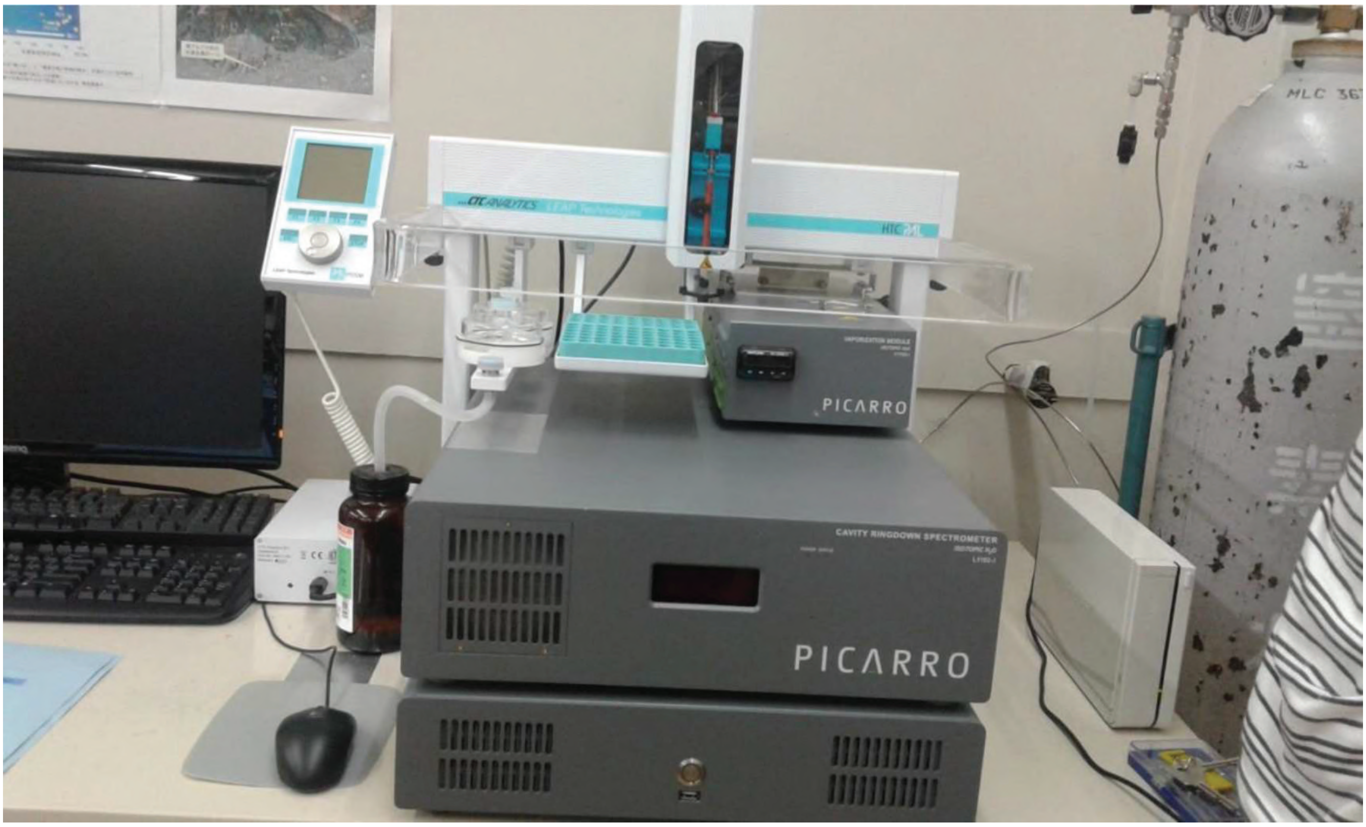

Fig. 1: Instrument of isotope analysis, mass spectrometer (IRMS)

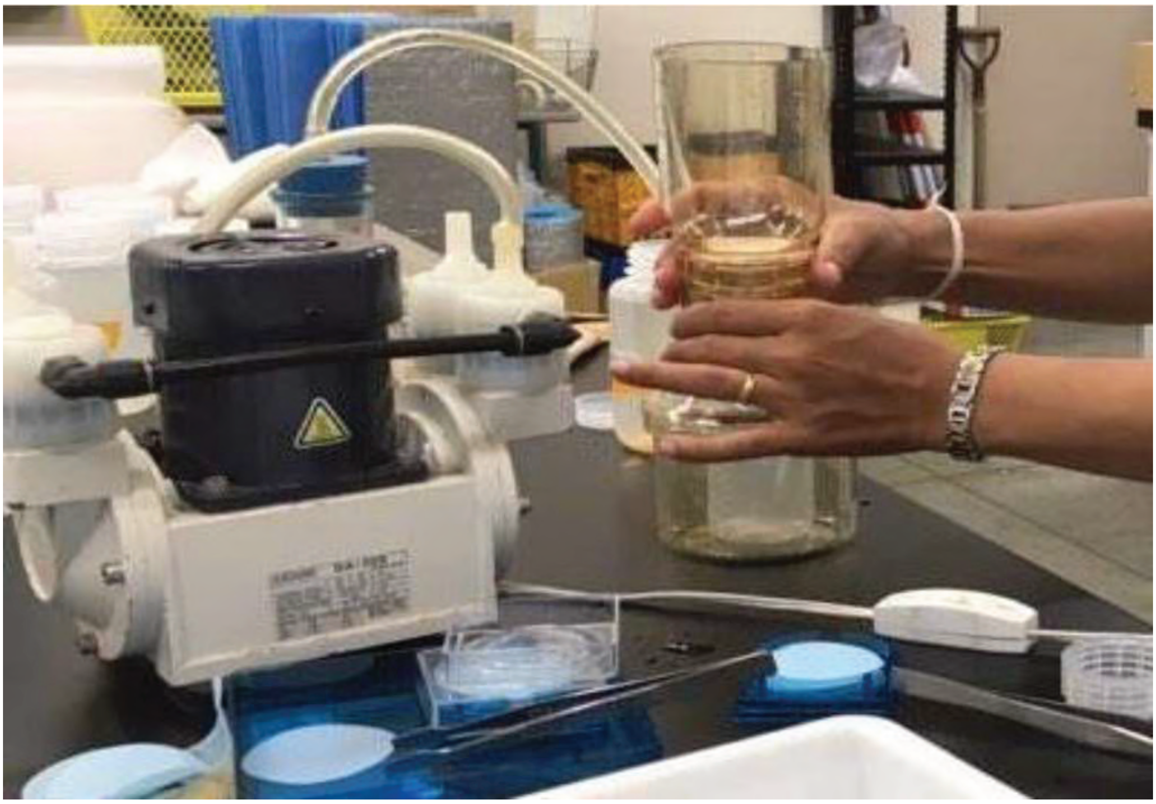

Fig. 2: Filtration of water sample

Materials used for sample preparation:

1.1 ml of glass bottles (Fig. 3)

2.1 ml of pipette

3. Label tape and marker

Sample preparation procedure:

1.Before sample filling in the bottles, it needs to write sample number in all carefully.

2.Sample bottles has to ringed with samples 2 or 3 times which has to be filled in the bottles

3.Then sample is filled using 1 ml of pipette but it need to be free of gas bubbles in pipette and then tight with bottle cover (Fig 4).

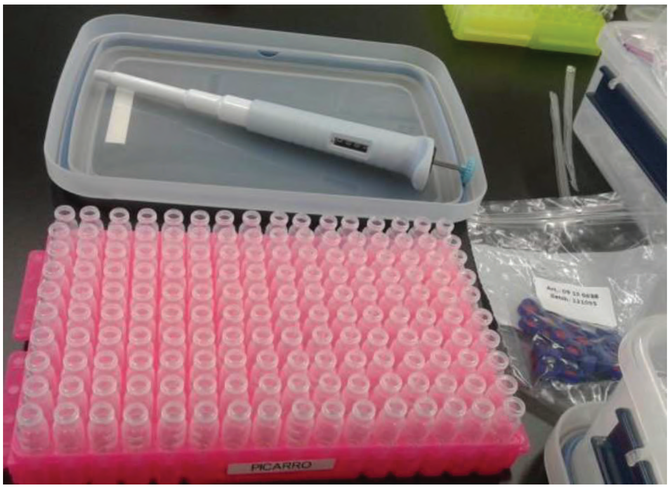

Fig. 3: sample bottles and pipette

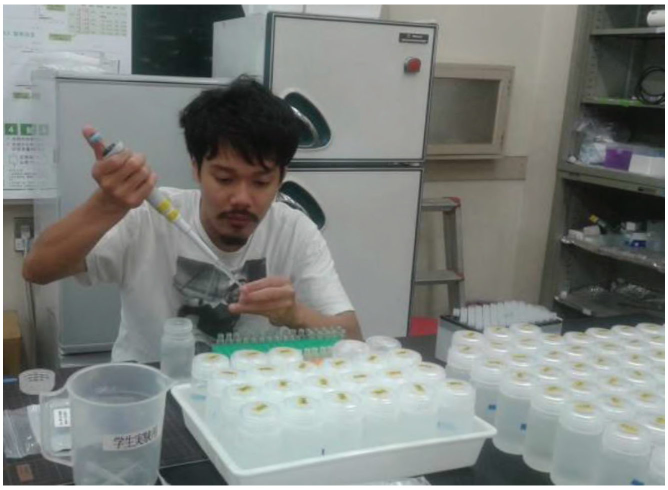

Fig. 4: Sample filling in the bottles using pipette

CONCLUSIVE REMARKS

Stable or radio-isotopes of water molecules (^2H, ^{18}O and ^3H) are commonly employed in groundwater investigations. These isotopes are very useful to identify residence time, recharge sources of groundwater and connecting condition of surface water and groundwater. But in the context of Nepal, isotope analysis is not much utilized for groundwater investigation may be due to lack of instrument presence in Nepal. Most groundwater analysis was conducted based on physio-chemical and biological parameters. These parameters are very helpful for water quality analysis of groundwater as well as surface water but only using these parameters, it will be very difficult to identify recharge sources.

Analyzing stable isotopes of precipitation, groundwater and surface water, recharge source for groundwater can be identified. Similarly, analysis of 3H of deep aquifer (fossil water) can find out residence time and can also be investigate possibility of recharge of deep aquifer. This source identification of groundwater and residence time of deep aquifer analysis may help to manage groundwater.

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