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MODIFICATION OF RAINWATER SAMPLE COLLECTOR FOR WATER STABLE ISOTOPE ANALYSIS

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Abstract

A rainwater sample collector for water stable isotope analyses was modified based on the rainwater collector at meteorological stations to ensure no separation of isotopes while sampling. The equipment is made using available materials in Vietnam in order to get reliable isotopic data with low costs. The modified collector was used to collect rainwater sample and was verified at the Water resources laboratory, Hanoi University of Natural Resources and Environment. The results showed that the modified rainwater sample collector meet technical requirements of the IAEA's standards for a water isotope sample collector.

Keywords: Isotope technique; Rainwater sample collector; Rainwater sample; Stable isotope; Modification.

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1. Introduction

Isotope analysis technique is a new tool for water investigation and integrated water management in the field of water resources. The technique uses water isotopes and other isotopes of solute minerals to evaluate average retention time (time of movement) of groundwater, as well as research on fundament of groundwater and groundwater movement in the water cycle.

Isotope techniques were successfully applied to plan for proper use of water resources, groundwater mapping, water supply protection and pollution control. It is partly replaced or used as an additional tool in research on water resources, hydro-geological with the supply of long-term monitored data of rainwater, hydro-logical regime of rivers, lakes or other water.

Application of environmental isotopes (stable isotopes and radio isotopes) is based on the concept of "tracing" is where the isotopes are part of the natural environment (atmosphere and hydrosphere) and they always move with the movement of the natural environment, so the changing of isotopic compositions will indicate a change in the natural environment. The application of isotope as tracer consists of (i) using radio isotopes in age estimation (average retention time) of groundwater, determining groundwater recharge resources, saltwater intrusion, water resource pollution and impact of climate change to water resources; (ii) stable isotope is applied in researches on the origin of groundwater, mixing ratio between rainwater, surface water and groundwater, or the origin of pollution sources such as Nitrogen in form of Nitrate or ammonium in water resources.

Stable isotope compositions in surface water, rainwater, ancient water, and buried seawater are different due to the isotope separation process. The separation process occurs in the water cycle brought about the change in heavy isotope of different water types all over the world. The linear relationship between ^{2}H and ^{18}O isotope ratios of the water samples will be presented in the form of first order graph. The graph will show a water line that present the relationship between ^{2}H and ^{18}O isotope ratios of the collected water samples; and Local Meteoric Water Line (LMWL) that present the linear correlation between ^{2}H and ^{18}O isotope ratios of the rainwater at the study area. By completing regression on the ^{2}H and ^{18}O isotope values of the sample, the relative position of the regression line related to the LMWL would be understood as the origin or nature of the aquifers and the Mixing ratio between different types of water.

The stable isotopes of ^{2}H and ^{18}O in rainwater and related global meteorological parameters were monitored by the Global Network of Isotope in Precipitation (GNIP) of the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) since 1960 were used to construct the Global Meteoric Water Line (GMWL). Until now, some stations have stopped operating but most of them are still monitoring and reporting results to the IAEA. The GNIP network consists of more than 100 stations that are relatively equally distributed on the Earth's surface, offshore, near shore, in the entire continent [1].

However, according to the official website of the International Atomic Energy Agency (http://www-naweb.iaea.org), Vietnam does not have a monitoring station for measuring the stable isotope composition of rainwater based upon the GNIP standard, so the Meteoric Water Line of Vietnam was constructed based on data taken from Bangkok, Thailand monitoring station. The reasons are (1) Lacking national technical standards for the design of rainwater collector equipment to analyze isotopes (2) the IAEA does not provide rainwater collector equipment, so the equipment has to be ordered from Palmex Ltd, Croatia, (3) so far no laboratory in Vietnam (except for Water Resources Laboratory, Hanoi University of Natural Resources and Environment) has the L2130 - I stable isotope analyzer that has been using for the analysis of stable isotope of water. This spectrometer is rapid (9 min. sample injection and output) and easy to use.

The authors realized that the above mentioned issues can be solved as the fact of (1) The IAEA has published detailed technical guidelines for the design and construction of the rainwater collector equipment; (2) The IAEA standard sampling equipment only requires the "two zero" principle: there is no isotropic separation of water in the equipment and no exchange of the isotopic composition with the surrounding environment. Therefore, in the process of equipment modification, the authors have fully complied with the above principles in order to ensure quality, simple procedure and reasonable cost; (3) Our group is assigned to manage and operate the Picarro L2130 - i spectrometer from 2016 at the Water Resources Laboratory, Hanoi University of Natural Resources and Environment, so we have experience in analyzing stable isotope components of the water samples to check the quality of the water sample as well. Consequently, the research to construct modified rainwater collector equipment for stable isotope analysis not only solves technical problems in the academic work on water resources management using stable isotope technique in general but it also addresses the urgent need at our lab.

2. Methodology

2.1. Documentary analysis method

To conduct the research, we first analyzed available documents from IAEA on design principles and design options of rainwater sample collector and found out advantages and limitations of each option as described as follows:

2.2.1. Design principles of IAEA

Principle 1: Sampling strategy

There are two types of sample strategy: (1) event-based or daily sampling (2) cumulative integrated sampling

Principle 2: Design of rainwater collector equipment

The rainwater collector equipment is designed based on sampling strategy

2.2.2. Type of rainwater collector equipment for stable isotope analysis of water (see Tab. 1)

Option 1: Rain gauge at meteorological station

This option is only selected if the sampling strategy is applied at least once per day at meteorological stations.

Option 2: Tube-dip-in-water collector with pressure equilibration - cost effective (~180 €) used for cumulative integrated sampling strategy.

The sampler consists of a tube leading from the funnel to the bottom of the recipient with the tube dipping into the water already collected. A pressure equilibration system ensures flow. The device allows precipitation accumulation for up to one calendar month depending on the rain amount. This device facilitates low - cost unattended monthly sampling and eliminates the need for paraffin oil.

Option 3: Totalizer - a table tennis ball is used for the cumulative integrated sampling strategy to protect against evaporation and debris

Placing a plastic table tennis ball in the collection funnel may help to seal the collector bottle against evaporation and debris. When rainfall accumulates, the ball floats and opens the funnel.

Option 4: Totalizer, paraffin - based used for cumulative integrated sampling strategy, prevent-sample evaporation.

A layer of light pure paraffin oil (Option 4) available at all pharmacies or chemists floats on the sample water in the rain collector and prevents sample evaporation. The thickness of the paraffin oil layer floating on the water should be at ~0.5 cm. Never use flavoured oils (e.g. baby oil) or heavy oil which does not float on water. Important: paraffin oil can severely compromise stable isotopic analyses made by laser spectroscopy technology. Please inform the laboratory if paraffin oil is used; also consider that laboratories may reject samples treated this way.

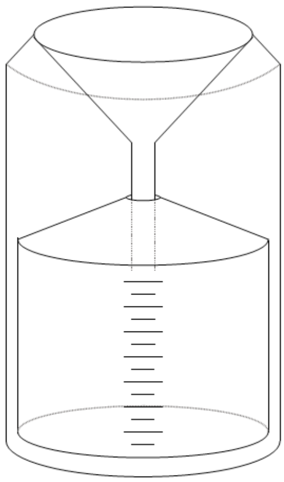
Option 5: Buried totalizers are used for cumulative integrated sampling strategy to minimize sample evaporation.

This model connects a funnel on a vertical post via a tube to a recipient hosted in a ground cavity provided that the lower temperatures beneath the surface prevent evaporation. IAEA considers these samplers being vulnerable to evaporation and recommends combining them with the evaporation prevention mechanisms of options 2 or 3.

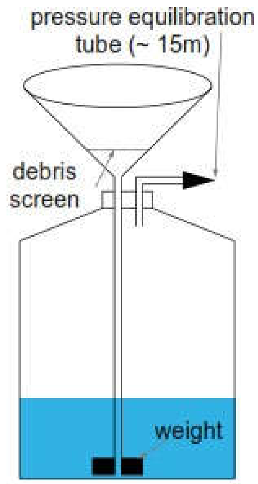
They are common in some parts of the world. At many higher latitude locations, wintertime samples are comprised of the accumulation of daily, weekly or monthly snow samples in box or bucket collectors. Traditional rain and funnel samplers and totalizers do not work well in freezing conditions due to frozen tubing. Proper wind shielding is important in these cases.

Table 1. Rainwater sample collector design option [4]

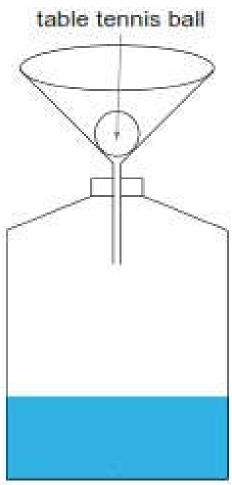
Option 1: Rain gauge (for event sampling or daily water transfer)



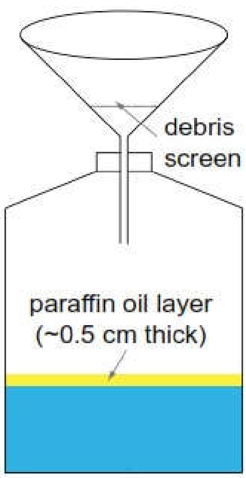
Option 2: Tube-dip-in-water collector with pressure equilibration



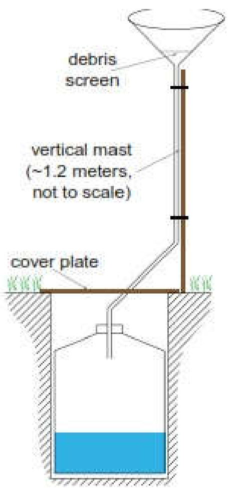
Option 3: Totalizer, table tennis ball



Option 4: Totalizer, paraffin-based



Option 5: Buried totalizers



2.2. Practical method

Based on design principles and design recommendations option by IAEA, our rainwater collector for stable isotope analysis was modified according to the principle as follows:

1. Sampling frequency: twice per month at 01 and 15 of the month.

2. The equipment is located on the roof of 10th floor, A building, Hanoi University of Natural Resources and Environment.

3. The sample will be filled by Whatman, an English paper with the diameter of 0.45µm to remove debris or dissolved solids (if any) before analyzing.

Consequently, the sampling equipment is the combination of IAEA design option 02 and 03 (cumulative integrated sampling) and the volume of the equipment is calculated based on average monthly rainfall.

2.2.1. Equipment structure

The equipment consists of 5 main parts: main container, funnel, drainage pipe, outer shell and holder.

Main container: It should be made by a strong material to avoid cracking. Based on the rainfall of Hanoi, the main container volume would be selected as 20 liters. The main container cap has a small hole to drain water from a funnel to the main container. There is a discharge valve located at the bottom of the container to drain water after each sampling to avoid mixing water between sampling.

Funnel: Funnel should be made by a strong and high-stand temperatures material as Hanoi has a very high temperature in the summer. There are needs of a diaphragm and a tennis ball to seal the main container against evaporation and debris.

The diameter of the funnel is calculated based on average monthly rainfall of Hanoi (see Tab. 2) and volume of the main container [4] described as follows:

$$ppt = \frac{10V}{pr^2} \quad (1)$$

Where: ppt is rainfall l (mm)

V is volume of collected water (mL)

r is radius of the funnel (cm)

Table 2. Average rainfall of the rainy and dry season in Hanoi from 2002 to 2015 [3]

Year	Rainy season (mm)	Dry season (mm)	Year	Rainy season (mm)	Dry season (mm)
2015	222.3	48.3	2008	249.2	52.7
2014	254.6	47.5	2007	266.6	39.2
2013	359.6	46.4	2006	204.2	37.7
2012	314.5	47.3	2005	304.0	37.9
2011	271.9	48.9	2004	256.8	39.0
2010	210.3	47.4	2003	285.0	36.9
2009	278.4	50.0	2002	219.4	48.9

Consequently, the average rainfall of Hanoi in dry season is around 44.85 mm and in rainy season is around 264.07 mm.

Drainage pipe: It should be made by abrasion resistance, lightweight, good mechanical strength material, of sufficient length (around 5 m), wrapped in rings and placed inside to balance the pressure in the main container, and to ensure a constant flow inside the bottle to minimize the evaporation and isotope exchange with the outside air while sampling.

Outside shell: It should be made by material which is durable, ductile, not deformed, and has no rust, especially to avoid absorbing heat from sunlight (regular sunshine and high heat amplitude in Hanoi summer) to minimize the evaporation of the water inside the container. The size of the outer shell is larger than the main container. There is a gap between the outside shell and the main container of 25 cm containing the insulated foam.

Holder: It should be made by stable and strong material and should be mounted to the floors where place the equipment to avoid falling due to rainstorms, cyclones or other adverse weather.

2.2.2. Sampling location

The location of stable isotope sampling has some requirements as follows:

- The sampling device is preferably installed upon undisturbed, naturally vegetated land. Grassed areas and slopes up to ± 15 % are acceptable, but there should not be a sudden change of slope within 30 metres. The height of surrounding vegetation should be less than 0.5 metres.

- Try to minimize the influence of surrounding structures on the sampler. In developed areas, buildings, poles, trees, etc. should be at least as far away as they are high (i.e. project onto the sampling device at an angle of no more than 45°). In undeveloped areas, place the sampling device twice as far from trees as they are high as seen in Fig. 1.

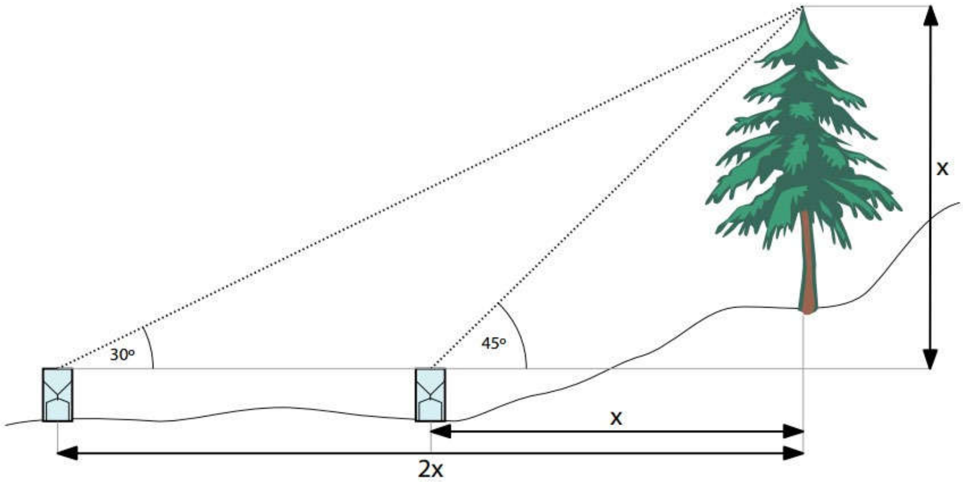


Figure 1: Placement of a rain collector to minimize the influence of nearby objects [4]

3. Result and discussion

3.1. Rainwater collector (Test version)

The test version of the rainwater collector consists of 3 part as shown in Fig. 2a and 2b. The structure of this version is described as follows:

Main container: It is made of PET with a volume of 20 L. A discharge valve located on the container body with a distance of 10 cm above the bottom of the container. A 12 mm hole in the container cap is drilled to hold the drainage pipe.

Funnel: It has a diameter of 15 cm made of steel. A tennis ball is placed inside the funnel; the funnel mouth is covered by an iron diagram to trap debris and prevent the tennis ball from falling out of the funnel when water rises. A steel pipe is mounted at the bottom of the funnel to connect the funnel with the drainage pipe.

Drainage pipe: It is made by Polyvinylclorua (PVC) with a length of 3 m and a diameter of 12 mm.

There are some limitations of the test version as follows:

1. It isn't outside shell and the holder.

2. The drainage pipe is too hard as it is made of PVC. With the length of 5 m, the pipe may occupy most of the container volume, then the length of the pipe is reduced to 3m, thus it affects the balance of the pressure in the main container.

3. The main container is made of

PET which is light, brittle, and easy to absorb heat, so it is not suitable for high temperature, dry weather and other unfavorable climatic conditions in Hanoi.

4. The steel diagram on the funnel mouth may be corroded in frequent contact with water.

5. The discharge valve is placed above the bottle bottom, so it is difficult to drain water after sampling.

Figure 2a: Rainwater collector (Test version)

Figure 2b: The funnel structure (Test version)

3.2. The modified rainwater collector (completed version)

The completed version of rainwater collector for stable isotope analysis is designed and constructed to reduce limitations of the test version. The structure of the completed version is described as follows:

Figure 3: Main container

Main container: It is made of HDPE with a volume of 18 liters. The diameter of the container mouth is 30 cm. The discharge valve is located at the middle of the container bottom (see Fig. 3). The main container is produced at a paint factory in Phu Dien, Tu Liem, Hanoi.

Funnel: It is made of HDPE with a diameter of 19.5 cm and a height of 6.3 cm. A vented floor drain with the diameter of 7.5 cm is placed at the bottom of the funnel that prevents the amount of evaporation in the main container. Besides, the funnel consists of funnel tail made of PVC that uses to connect funnel and main container (See Fig. 4a, 4b, and 4c).

Drainage and discharge pipe: The pipes are made of PE with a diameter of 2.0 cm and a length of 5 m. A 9.0 cm long pipe is used to connect the container cap and drainage pipe. The discharge pipe is placed at the bottom of the main container that has a diameter of 2.0 cm and a length of 21.3 cm. It is used for sampling and drain water after each sampling (See Fig. 5a and 5b).

Outside shell: Outside shell is made of galvanized aluminum. Its diameter is 40.4 cm and its height is 44.5 cm. The gap between the sample container and the outside shell is about 5.2 cm to place insulated foam (See Fig. 6a and 6b).

Figure 4a: Funnel mouth and preventer diagram

Figure 4b: Funnel tail

Figure 4c: Connection of the funnel on the main container

Figure 5a: The connection between container cap and drainage pipe

Figure 5b: Discharge pipe at bottom of the container

Figure 6a: Main container and outside shell

Figure 6b: Insulated foam between main container and outside shell

Holder: It is made of iron with anti-corrosive paint. It is 59 cm high to ensure the height from the ground surface to the funnel mount is 1.2 m as required by Vietnamese standard (TCVN 5997 - 1995) and recommendations by IAEA (2014) as seen in Fig. 7.

Two rainwater collectors are produced and one is placed on the roof of the A building of Hanoi University of Natural Resources and Environment at 41A Phu Dien, Tu Liem, Hanoi (see Fig. 8), and the other is placed on the roof of Cua Viet hydro - graphic station at Gio Viet ward, Gio Linh district, Quang Tri province. The equipment is placed as far away as around 2 m from high - rise building and big trees. The first water samples are taken on 15/7, 30/7 and 15/8/2017 for Hanoi area.

Figure 7: Completed set of rainwater collector for stable isotope analysis

Figure 8: Locating rainwater collect on the roof of the A building, Hanoi University of Natural Resources and Environment

4. Conclusions and recommendations

The completed version of the modified rainwater collector for stable isotope analysis has been used for sampling academic purpose at Hanoi University of Natural Resources and Environment. It is still in the testing stage and verifying the amount of evaporation. The design of the completed version has a number of advantages over the test version: (1) it can improve funnel structure against evaporation; (2) the outer shell is made by galvanized aluminum that can reduce heat absorption; (3) the discharge pipe located on the bottom of the container ensures that all of the water inside the container is removed after each sampling; (4) the material of the funnel is improved from a filament lamp that has high temperature resistance in several hours continuously; (5) the joints are made by heat-resistant PVC pipes suitable for outdoor use; (6) the height of the equipment and its location is in accordance with IAEA regulations.

To maximize the efficiency of the equipment, it is necessary to attach thermal hygrometer to the equipment to check the humidity inside the sample container and ensure that there is no evaporation. However, the adjusting requires additional investment in terms of fund and time allocation.

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