IAEA/GNIP precipitation sampling guide

This booklet on precipitation sampling for isotopic analysis serves as a guideline for the Global Network of Isotopes in Precipitation (GNIP), but also includes siting and equipment guidelines for projects that may not be contributing to GNIP.

Part A is for managers who are involved in the assessment of the sampling station and are responsible for adopting operational protocols. We promote an open formulation; however the responsible persons for GNIP stations are requested to clarify changes in protocols in advance with the GNIP team at IAEA.

Part B details the routine operations such as integrated accumulation and sample preparation.

Introduction: The Global Network of Isotopes in Precipitation (GNIP)

The IAEA-WMO Global Network for Isotopes in Precipitation (GNIP) has been in operation since the 1960's, and is comprised of hundreds of observation stations located around the world. The GNIP database houses high-quality, long-term, stable isotope ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) and radioactive tritium (^{3}H) data of monthly composite rainfall samples for an increasing number of locations worldwide.

Though GNIP has its roots in monitoring the fallout of thermonuclear testing, precipitation isotopic data nowadays facilitates research in a diverse range of scientific fields, including the disciplines of hydrology, hydrogeology, limnology, meteorology, climatology, ecology, food authentication and forensic studies.

This guidebook describes the main aspects of siting a GNIP station, gives a brief overview on sample integrity, evaporation and corresponding protection strategies, introduces the necessary materials and discusses sampling strategies. However, the following aspects will not be covered in detail:

- **Isotope analysis:** For many GNIP stations isotope assays are performed by the IAEA Isotope Hydrology Laboratory, usually by isotope-ratio mass spectrometry and by laser absorption spectrometry for stable isotopes, and by liquid scintillation counting after electrolytic enrichment for ^{3}H. Some GNIP collaborators are able to measure their own samples and contribute the isotopic data.

- **Data collection and dissemination:** Isotope and meteorological data are collated by the IAEA Isotope Hydrology Section. All GNIP data are QA/QC assessed beforehand, and then archived in an online database that is accessible to registered users via the WISER (*Water Isotope System for Data Analysis, Visualization and Electronic Retrieval*, e.g. via http://www.iaea.org/water) internet portal.

Get involved in GNIP: At the IAEA, we are happy to receive proposals for additional GNIP stations. To evaluate a new station proposal, please send the following information to the GNIP team (gnip@iaea.org):

The new station's geographical coordinates (decimal degrees or UTM, e.g. from a GPS), and altitude (meters above sea level) of the rain collector.

A short description of the rain collector and location (a digital photo is also very useful).

New GNIP stations are assigned a unique station code that is derived from the nearest WMO station code. The IAEA may provide support to stations by providing sample bottles, and by analysing water samples at the Isotope Hydrology Laboratory in Vienna. In some cases, IAEA may cover water sample shipment expenses to Vienna. If analysing GNIP samples in a local isotope laboratory, please consider participating in the IAEA-organized water isotope intercomparison exercises conducted every four years.

Part A: Station guidelines

This section addresses the main precautions around precipitation sampling for isotopic analysis in general, different siting and sampling strategies, as well as equipment specifications needed for running a successful precipitation isotope station.

Main considerations

Before establishing a precipitation isotope station, the IAEA recommends evaluating the location and operational procedures to ensure that it maintains appropriate standards and precautions to ensure reliable isotopic data. The main points to consider are:

- **Evaporation prevention.** Open exposure of a precipitation sample to the atmosphere can result in evaporation and alter the isotopic composition of the water sample, which renders the measured isotopic data unusable. Sample evaporation may occur during sample collection (improper sampler, stagnation), during accumulation and storage (improper or loosely capped accumulation bottles), or during shipment or awaiting isotopic analysis (evaporation via unsecured caps or cracked bottles).

- **Representativeness of the sample.** A rainwater sample should represent the integrated natural precipitation of the targeted sampling period. (The targeted GNIP integration period is one calendar month.) Rainwater overflowing out of a collector (from extreme rain events, e.g. monsoon, hurricanes, etc.) may result in loss of an important part of a month's precipitation, particularly at sites with monthly totalizing samplers. Improper placement of the rain collector (e.g. in the shadow of a structure or exposed to building exhaust fans) will render samples unrepresentative of precipitation at the location.

- **Logistical and safety aspects.** The choice of sampling equipment is often related to the accessibility and/or staffing of a sampling station. For remote or stations using automatic equipment, consider installing a low maintenance "rain totalizer", as long as at least one visit per month is possible. Finally, remember to monitor safety and security of all staff involved (e.g. natural and human hazards, etc.). Check for availability of snow sampling equipment at stations at higher latitudes and/or altitudes. Wind protection may be required to keep a sampler firmly in place. Finally, check that the sampler is protected against animals, vandalism, or external contamination by irrigation equipment.

Sampling site

Unless specified by other protocols (e.g. WMO or your National Meteorological Agency, which may be more restrictive), attempt to follow these rules for locating the sampler or rain gauge:

- 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 structures on the sampler. As a rule of the thumb, 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 (see Figure).

- In natural areas, the sampling device should be mounted so its funnel is about 30 centimetres above ground (to reduce wind turbulence). In developed areas, the funnel should be about 1-1.2 m above ground (to reduce the impact of nearby structures). Level the sampler or gauge and avoid splashing from the post into the rain gauge (i.e. bevel the funnel if necessary).

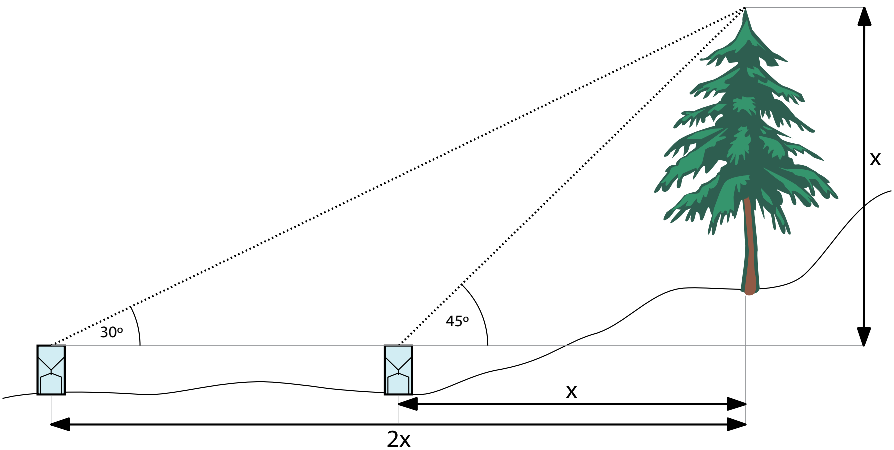


Figure 1: Placement of a rain collector to minimize the influence of nearby objects

	Cumulative integrated sampling	Event-based sampling
Advantages	• Sufficient temporal resolution for groundwater and watershed hydrology • Compliant with any other monthly averaged data • Lower analytical effort and cost (12 samples / year / station)	• Obtains isotopic data at high temporal resolution • Is the method of choice in hyper-arid areas with few rainfall events each year (risk of evaporation is high when accumulating).
Disadvantages	• Can blur significant rainfall events (which may have distinctive isotope values) • Risk of sample evaporation during totalized collection or longer storage	• Needs observer or highly sophisticated sampling equipment, high cost • Higher analytical effort and cost (up to hundreds of samples per year/station)

Table 1: Sampling strategies, advantages and disadvantages

Sampling strategy

Dependent on the needs of the project, you will typically have to decide between event-based (or daily) and cumulative integrated (e.g. monthly, as done for GNIP) sampling. Event-based sampling means a rainfall sample is collected after each rain event (or at least daily), whereas cumulative integrated sampling means a single sample pooled over the stated observation period, which is a calendar month for GNIP.

Equipment

Rain Collector: The choice of the rain collection equipment depends on the required/selected sampling strategy (e.g. event-based vs. monthly) and on the resources available (personnel, collection equipment etc.).

- If a standard rain gauge is available, and if there are staff that can transfer rainwater into the accumulation bottle after each event (at least once per day), a standard rain gauge as recommended by the local meteorological service can be used. This approach is used at many of the WMO stations participating in the GNIP network. (Option 1 in Table 3)

If the rain sampling device cannot be emptied on at least a daily basis, a low maintenance "rain totalizer" is needed. A totalizer accumulates, integrates and preserves all rain fallen within the sampling period (one month for all GNIP stations). A rain totalizer can be hand-crafted but there are devices available commercially. It is absolutely necessary that totalizer devices protect against sample evaporation. Means to prevent evaporation include:

Part A: Station guidelines

- *Highly Recommended:* **Dip-in samplers** (Option 2) consist 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. Devices of this kind are available commercially at low cost (~180 €), allowing 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.[1]

- Placing a plastic **table tennis ball** (Option 3) 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. After the rain event the ball returns to its original position.

- A layer of light pure **paraffin oil** (Option 4, available at all pharmacies or chemists) floats on the water sample 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.

- **Buried samplers** (Option 5) are common in some parts of the world. This model connects a funnel on a vertical post via a tube to a recipient hosted in a ground cavity, relying on 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.

1 Note that IAEA does not sell these devices, but may not endorse any commercially available product either. Contact the GNIP team at gnip@iaea.org for their experience.

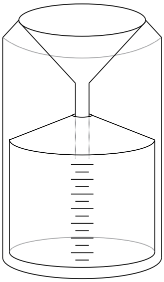
At many higher latitude locations, wintertime samples are comprised of the accumulation of daily, bi-weekly, or monthly snow samples in box or bucket collectors. Traditional rain and funnel samplers and totalizers do not work well in freezing conditions due to frozen tubing. Proper wind shielding is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

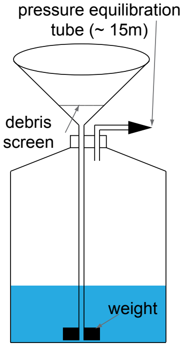
Amount (mm)	**Funnel diameter in cm (orifice area in cm²)**				
	12.72 (127)[A]	**15.96 (200)[B]**	**20.32 (324)[C]**	**25.24 (500)**	**30.48 (730)[D]**
0.1	1.3	2.0	3.2	5.0	7.3
0.5	6.4	10.0	16.2	25.0	36.5
1	12.7	20.0	32.4	50.0	73.0
5	63.5	100.0	162.1	250.0	364.8
10	127.0	200.0	324.3	500.0	729.7
50	635.0	1000.0	1621.5	2500.0	3648.3
100	1270.0	2000.0	3242.9	5000.0	7296.6
500	6350.0	10000.0	16214.6	25000.0	36482.9

Table 2: water volumes collected (mL) in relationship to gauge size and precipitation amount (exemplified by widely used rain gauges: A – 5″ gauges, e.g. UK Mk2/Mk3 or Nipher; B – WMO Standard, e.g. Hellmann or Tretyakov; C – NOAA 8″; D – NOAA 12″)

Sample Accumulation Bottle: The sample accumulation 'bottle' used to store the precipitation during the collection period (for GNIP typically one calendar month) should be of high quality high-density polyethylene (HDPE) or glass with a cap that can be tightly sealed after each precipitation event is poured in. Please choose a size appropriate to the climatic conditions and the diameter of the funnel of your collector (see also Table 2 and the rainfall averages/extremes for your place). The bottle size could range from < 1 L in arid regions to > 10 L in very rainy regions. Also take into account the possibility of extreme events (monsoons, hurricanes, typhoons, etc.), to ensure that the accumulation bottle is capable of accep-

Part A: Station guidelines

Option 1: Rain gauge (for event sampling or daily water transfer)		
	Pro	Usually well-calibrated by national weather services
	Pro	Precipitation amount recorded without additional equipment
	Con	Operatory needed on daily basis, higher operational cost
	Con	Risk of evaporation of small events during the day if the collection is carried out once per day.
	Requires also	Accumulation bottle (when collecting monthly samples)

Option 2: Tube-dip-in-water collector with pressure equilibration		
	Pro	Unattended, low cost
	Pro	Excellent evaporation protection
	Pro	Inexpensive commercial version available (~180 €)
	Pro	Recipient serves as accumulation bottle (depends on rain amount)
	Pro	Fully adjustable (in terms of funnel and recipient size) when custom-built – see Table 2
	Con	Amount to be determined volumetrically or gravimetrically when no rain amount recorder on site
	Requires also	Balance or graduated measuring jug, and accumulation bottle depending on rain amounts

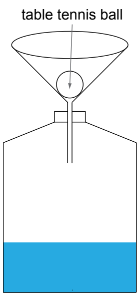
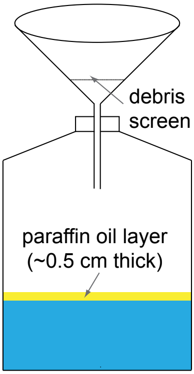
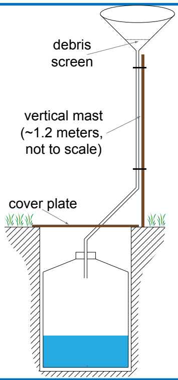
Option 3: Totalizer, table tennis ball		
	Pro	Unattended, low cost
	Pro	Evaporation protection (though not of proven quality)
	Pro	Fully adjustable (in terms of funnel and recipient size) – see Table 2
	Pro	Recipient may also serve as accumulation bottle
	Con	Amount to be determined volumetrically or gravimetrically when no rain amount recorder on site
	Requires also	Balance and graduated measuring jug

Table 3: Rainwater sampling methods

		Option 4: Totalizer, paraffin-based
	Pro	Unattended, low cost
	Pro	Evaporation protection
	Pro	Adjustable (in terms of funnel and recipient size) – see Table 2
	Pro	Collector also serves as accumulation bottle
	Con	Need separation funnel for removal of paraffin oil
	Con	Possible spectral contamination from oil using isotope laser spectroscopy
	Con	Amount to be determined volumetrically or gravimetrically when no rain amount recorder on site
	Requires also	Separation funnel, balance, graduated measuring jug

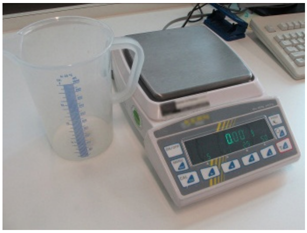
		Option 5: Buried totalizers
	Pro	Unattended
	Pro	Fully adjustable (in terms of funnel and recipient size) – see Table 2
	Pro	Recipient may also serve for accumulation
	Con	Protected ground cavity needed, drained to protect from surface runoff
	Con	No proven record of evaporation protection (but may be combined with elements of options 2 or 3).
	Con	Amount to be determined volumetrically or gravimetrically when no rain amount recorder on site
	Requires also	Balance or graduated measuring jug

ting all of the rainwater collected during the sampling period. Do not use sports drink containers as an accumulation bottle. Store the accumulation bottle, tightly sealed, at room temperature in the dark, or in a refrigerator (~4°C) . It is prudent to replace accumulation bottles if they show signs of wear or deterioration (discoloration, cracking).

Part A: Station guidelines

Basic laboratory equipment: depending on the sampling device and strategy, a plastic funnel, a graduated measuring cylinder or a paraffin separation funnel may be needed in addition to the equipment listed above. An electronic balance with 0.1 gram level accuracy may also be helpful for determining sample volumes.

Accumulation bottle / can (for options 1 and 2)



Measuring jug or balance (for options 2, 3, 4 and 5)

Paraffin separation funnel (for option 4) [2)]

Sample bottles: It is essential that high quality, tightly-capped, HDPE or glass bottles are used for both the storage and shipment of rainfall samples to the laboratory. The typical minimum requirement for isotopic analysis is ~20 mL for stable isotopes and ~300 mL for tritium.

For GNIP stations, we recommend using bottles provided by IAEA, which have been checked for their integrity. For stable isotope sampling, QA/QC tested 30 or 50 mL amber glass or HDPE bottles are used; for Tritium sampling 500 mL HDPE bottles. Please make sure that the correct combination of caps and inlays is used.

2) Photo taken from www.wikipedia.org. Colouring of the water is for illustrative purposes only.

- **Borosilicate glass bottles:** The 30 (or 50 mL) borosilicate glass bottle is used for GNIP stable isotope sampling. Please assure that you always use a double-layer cap WITHOUT an inlay (the inlay would destroy the inner seal). Also, please wrap it into the protective sleeves supplied to prevent the glass from breaking during shipment.

- **High-density polyethylene bottles (HDPE)** are used for GNIP stable isotope (50 mL) and Tritium (500 mL) sampling. They are lighter in weight and less prone to breaking. Please always use the white cap inlay (even though sometimes difficult to place). Consider discarding HDPE bottles which have been in store for more than 5 years, or in case they came in contact with artificial tritium used for tracing.

Part B: Rainwater Accumulation and Sample Preparation

Below are the procedures for collecting and storing precipitation water. Note that this part mainly refers to the GNIP sampling procedures which are by default based on a monthly accumulation regime.

Accumulation by daily rainwater collection

- **Every day:** The rain gauge must be read and emptied as soon as possible following each rain event, or each morning. After reading and recording the gauge, the collected water is poured into the accumulation bottle. It is essential that water is transferred daily, and that the rain gauge collector is dried before returning it.

- **At the 1st of the month:** See 'sample preparation from accumulated water'.

Accumulation by precipitation totalizers

- **At the 1st of the month (more often if needed):** The rain sample (along with any paraffin oil) can be transferred to the accumulation bottle. Ensure the totalizer bottle is wiped free of water (and excess paraffin oil), and dried before redeploying for the next collection period.

- **At the 1st of the month:**
  - Remove paraffin oil if applied – see 'removing paraffin oil'
  - Prepare the monthly sample – see 'sample preparation from accumulated water'

Accumulation by snow samplers

- **Frequently** (the more often the better, especially in autumn/spring):
  - Take the snow bucket sample collector indoors and cover it with a lid.
  - Allow the snow to melt at room temperature (do not apply heat). It is prudent to have two collection buckets alternating; melting can take time.
  - Immediately after melting, pour the water into the accumulation bottle. Clean and dry the snow sampler before redeploying.
  - Note: there must not be any change of the funnel diameter during the accumulation period (i.e. in case of GNIP stations, only switch from bucket collection to funnel/bucket collectors at the 1st of a month)
- **At the 1st of the month:**
  - Please see 'sample preparation from accumulated water'.

Part B: Rainwater Accumulation and Sample Preparation

Sample preparation from accumulated water

- If there is no precipitation amount recorded at your site, record the volume of water collected (V, in mL) by weighing and subtracting the weight of the empty collection bottle, or by using a graduated measuring cylinder. In this case, it is indispensable to record the funnel radius (r_F, in cm). The rain amount can be estimated as: ppt [mm] = $10V/(\pi r_F^2)$

- From the monthly accumulation bottle, fill the isotope sample bottles. Dispense into a 30/50 mL stable isotope sample bottle first, and if relevant, repeat the procedure for the 500 mL tritium sample bottle. Leave ~5 % head space in glass bottles to allow for sample expansion due to accidental freezing during transport.

- Excess water in the monthly accumulation bottle can be discarded. If less than optimal water amounts are available (minimum 20 mL for stable isotope and ~300 mL if both stable isotope and tritium analysis are scheduled), prepare the samples nevertheless and advise the GNIP team by including a note with the sample submission form. It is however not necessary to prepare a sample bottle if there was no rain during the collection period.

- The Station Name and ID, Collection Month, and the Amount of Precipitation collected must be clearly printed on each sample bottle. For GNIP stations, labels may be provided by IAEA. To avoid confusion, sample bottle s should be filled and labelled immediately.

- The accumulation bottle should be exchanged with a clean spare, or immediately cleaned and dried before redeploying for the next month's sample. Always inspect the accumulation bottle for signs of deterioration.

- Established GNIP stations record meteorological data (monthly precipitation type and amount, mean air temperature and mean vapour pressure or relative humidity, if available) on the form supplied by IAEA, including months without precipitation. IAEA encourages electronic submissions to the GNIP contact point gnip@iaea.org

Part B: Rainwater Accumulation and Sample Preparation

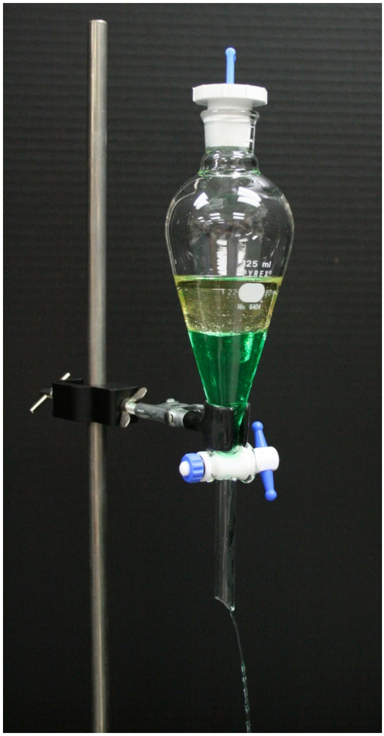
Removal of paraffin oil

While paraffin oil serves well as an evaporation barrier, it can cause serious analytical complications in laboratory handling, particularly when samples are analysed by water isotope laser spectroscopy. Hence, it is very important that paraffin oil is fully removed before a sample bottle is filled, and the analytical laboratory is informed.

- To separate the paraffin oil from the water sample, use a glass or plastic ~500 mL separation funnel. Because paraffin oil forms an emulsion with water when shaken or mixed, be sure to allow for the oil to fully separate from the water sample in the separation funnel (allow about an hour or even more).

- With the water separated, proceed to the step 'Sample preparation from accumulated water'.

- If you did not (or only partly) succeed in removing the oil, please indicate this clearly on any sample bottle which may contain paraffin oil.



Separation funnel (note that the water has been coloured for illustrative purposes only. Source: www.wikipedia.org)

Event-based rainwater collection

- **Every day:** The rain gauge must be read and emptied as soon as possible following each rain event, or each morning. It is essential that water be sampled daily, and that the rain gauge collector is dried before redeploying to its position for the following collection.
  - After reading and recording the gauge, the well-mixed collected water is poured directly into a sample bottle. Usually, event-based samples are only taken for stable isotopes (30 mL or even smaller bottles).
  - The Station name, the collection period and the precipitation amount must be clearly printed on each sample bottle. To avoid confusion each sample bottle should be filled and labelled immediately.
  - Meteorological and other parameters are recorded according to the protocol applied. In many cases, this depends on the project objectives.

For further information and/or technical inquiries on the GNIP sampling programme, or other matters related to IAEA's activities in isotope hydrology, please contact the GNIP team (gnip@iaea.org) or visit the web site of the IAEA Water Resources Programme (http://www.iaea.org/water).