Geophysical Research Abstracts
Vol. 18, EGU2016-15992, 2016
EGU General Assembly 2016

An assessment of the isotopic (^{2}H/^{18}O) integrity of water samples collected and stored by unattended precipitation totalizers

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The IAEA-WMO Global Network of Isotopes in Precipitation (GNIP) provides worldwide δ^{18}O and δ^{2}H data for numerous hydrological and climatological studies. The traditional GNIP sample collection method relies on weather station operators to accumulate precipitation obtained from manual rain gauges. Over the past decades, widespread weather station automatization resulted in the increased use of unattended precipitation totalizers that accumulate and store the rainwater in the field for up to one month. Several low-tech measures were adopted to prevent *in situ* secondary evaporative isotopic enrichment (SEE) of totalized water samples (i.e. disequilibrium isotopic fractionation after precipitation is stored in the collection device). These include: (a) adding a 0.5-1 cm floating layer of paraffin oil to the totalizer bottle, (b) using an intake tube leading from the collection funnel and submerged to the bottom of the totalizer bottle, or (c) placing a table tennis ball in the funnel aiming to reduce evaporation of the collected water from the receiving bottle to the atmosphere.

We assessed the isotopic integrity of stored rainwater samples for three totalizers under controlled settings: each aforementioned totalizer was filled with a 100 or 500 mL of isotopically known water and installed in the field with the intake funnels sheltered to prevent rainwater collection. Potential evapotranspiration (PET) was obtained from on-site meteorological recordings. Stored evaporative loss from each totalizer was evaluated on a monthly basis; gravimetrically and by analysing δ^{18}O and δ^{2}H of the stored water, for a period of 6 months and a cumulative PET of $\sim$500 mm.

The gravimetric and isotope results revealed that for smaller water volumes (100 ml, corresponding to ca. 5 mm of monthly precipitation), negligible isotope enrichment (δ^{18}O) was observed in the paraffin-oil based totalizer, whereas unacceptable evaporative isotope effects were observed for the ball-in-funnel collector. For the submerged-tube sampler, the evaporative effect depended on the amount of stored water: 100 ml showed unacceptable isotopic enrichment, whereas the SEE of 500 ml stored water was acceptable.

These data allowed us to estimate the impact of secondary evaporative enrichment on a device-specific basis as a function of PET. Based on global PET grids (e.g. CGIAR data), and benchmarking the expected SEE against the reasonable uncertainty of isotope spectrometry ($< \pm 0.1‰$ for δ^{18}O), these findings reveal the most suitable totalizer device for any given climatic condition. Under extreme conditions (e.g. high aridity, little precipitation vs. high PET), a paraffin-oil based rain totalizer is most appropriate for monthly collections. Submerged-tube samplers may be considered if either a higher frequency of collection were possible, or monthly under pluvial/temperate climate conditions. The use of ball-in-funnel type totalizers are not recommended at all, unless samples could be collected on a daily basis.