

# PERFORMANCE CHARACTERISTICS OF A BULK PRECIPITATION COLLECTOR WITH RESPECT TO MEASUREMENT OF WATER ISOTOPES OXYGEN-18 AND DEUTERIUM

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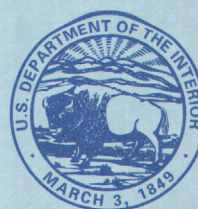
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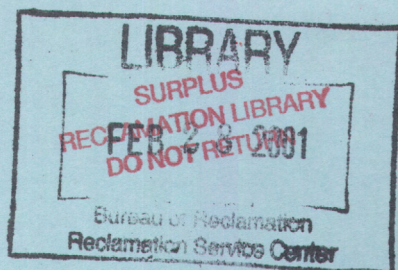


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# **Performance Characteristics of a Bulk Precipitation Collector with Respect to Measurement of Water Isotopes Oxygen-18 and Deuterium**

by Hans C. Claassen and Douglas R. Halm

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## CONVERSION FACTORS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
liter (L)	0.2643	gallon
meter (m)	3.281	foot







# Performance Characteristics of a Bulk Precipitation Collector with Respect to Measurement of Water Isotopes Oxygen-18 and Deuterium

By Hans C. Claassen and Douglas R. Halm

## Abstract

Samples of precipitation were exposed to onsite ambient conditions in order to evaluate the effectiveness of a specific bulk precipitation collector design to obtain reliable precipitation samples for isotope analysis. Although the samples were subjected to conditions expected to provide greater isotopic modification than samples during ordinary collection, little isotopic modification was observed. The bulk collector design should provide reliable samples of precipitation for isotopic analysis.

## INTRODUCTION

Watershed studies commonly require knowledge of the isotopic composition of precipitation for use as a tracer or indicator of climate. Although many processes may modify the isotopic composition of precipitation as it becomes ground water (Fritz and Fontes, 1980), little knowledge of the quantitative effect of these processes may be gained without accurate amount and isotope data for the incident precipitation.

Two areas of concern are evident in design of an effective precipitation collection device: (1) the collector should obtain a representative sample of precipitation, and (2) the sample should remain effectively unmodified while residing in the collector. Although the first concern is a problem common to any precipitation measurement and has been addressed by various rain-gage modifications (Gray and Male, 1981), proper siting of the collector can avert many of the complications related to catch efficiency. Evaporation and isotopic exchange are presumed to be the processes most likely to affect samples residing in the collector prior to removal.

Vogeli and Claassen (1971) reported on the design of a bulk precipitation collector intended to minimize the effects of evaporation and isotopic exchange that might occur during exposure of the collector. This paper presents results of a field experiment designed to demonstrate the effectiveness of this design in obtaining representative samples of precipitation from high-altitude mountain sites in Colorado.

## Collector Design and Installation

The collector consists of a 40-cm-diameter, 18-gage galvanized cylinder of a length sufficient to remain above the maximum snow-accumulation level expected at the site. The site is chosen to minimize turbulence at the collector orifice. Clearings in forested watersheds are suitable if the nearest trees are located at least a distance equal to their height from the collector. Wind velocities in overly large clearings may be too high for efficient collection. Ten-year measurements of collector performance relative to a standard U.S. Weather Bureau rain gage in an acceptable location shows an efficiency of 98 percent; in a poor location, 88 percent (H.C. Claassen, U.S. Geological Survey, unpublished data). Both locations were in western Colorado at altitudes of 1,400 and 3,400 m.

A set (generally three) of nested polyethylene bags are hung inside the cylinder, with the innermost bag having a 2-cm-diameter restriction placed about one-third of the way up from the bottom. The restriction minimizes evaporation in addition to providing limited access to atmospheric vapor, which minimizes isotopic exchange. The length of the bags should be nearly equal to the height of the cylinder. The bag redundancy provides insurance against samples being lost through leakage.

## Factors Affecting Isotopic Composition of Precipitation Samples

A sample in the collector may evaporate as a consequence of the normal vapor-pressure gradient outward. When snow is collected, it resides for a time in the upper two-thirds of the collector where it is more likely to sublime than precipitation held below the restriction. Sunny, warm days cause melting of this snow, which drains into the volume below the restriction. The effect of retention of snow in the upper, less protected, part of the collector is mitigated by the lower vapor pressure of the sample associated with cool, cloudy conditions that normally persist during the period prior to translocation to the volume below the restriction.



Change in air mass from that which was the source of the precipitation may subject the precipitation in the collector to isotopic exchange and, in some cases, condensation (dew or hoarfrost). It is difficult to assess the importance of these processes on the modification of the sample, but circumstances that minimize evaporation also should serve to minimize exchange. Both evaporation and exchange involve transport of vapor, and the restriction in the polyethylene collection bag tends to restrict vapor transport. Condensation may be important in altering the precipitation isotope composition if it occurs in sufficient quantities. In the semiarid West, this is unlikely most of the time.

## DESIGN OF THE ONSITE EXPERIMENT

A collection cylinder was modified to exclude the entry of precipitation by placing a rain cap over the open end. This cap was about 15 cm larger in radius than the cylinder and was placed about 5 cm above the collector rim to exclude all vertically falling precipitation, while allowing air to circulate freely over the opening. Samples of precipitation representing the previous 1- to 3-month period were placed in the collector bag. These samples were analyzed for their oxygen-18 and deuterium content at the U.S. Geological Survey Laboratory in Reston, Virginia (Tyler Coplen, U.S. Geological Survey, written commun., 1993). The volume of water introduced varied from 8 L to 20 L, to simulate varying amounts of precipitation, and was exposed to onsite conditions for periods of 1 month to

slightly over 3 months. All seasons were represented by precipitation and exposure times.

## ANALYSIS OF DATA

Eight samples were exposed over a 3-year period. Table 1 presents the results. The data are reported in parts per thousand (per mil) relative to Vienna Standard Mean Ocean Water (VSMOW). Analytical uncertainty ( $1\sigma$ ) is 0.1 per mil for oxygen-18 and 1.0 per mil for deuterium. The uncertainty in the difference between two values is:

$$2\sigma = 2(\sigma_1^2 + \sigma_2^2)^{1/2}$$

All samples showed some gain or loss during exposure, and all samples were isotopically modified, though only about one-half of them were modified significantly at the 95-percent confidence level.

It was expected that samples might lose varying amounts of water, summer-exposed samples the most; it was surprising that four (half) of the samples gained volume (samples 2, 4, 5, 8). Those samples that gained volume were exposed during the coldest period (Dec., Jan., Feb.), when precipitation is primarily in the form of small snowflakes that are easily affected by wind. The cap on the cylinder was designed to exclude vertically falling precipitation, but apparently also created sufficient turbulence at the collector orifice to allow some snow to enter. Although it is possible that even

**Table 1.** Data derived from precipitation samples exposed to environmental conditions

[VSMOW, Vienna standard mean ocean water]

Sample number	Sample represents season	Sample exposure season	Exposure time (days)	Nominal isotopic composition (per mil, VSMOW)		Volume change (percent)	Change in isotopic composition <sup>1</sup> (per mil, VSMOW)	
				Oxygen-18	Deuterium		Oxygen-18	Deuterium
1	Summer	Early fall	61	-18.32	-124.9	-0.9	-0.56	-4.6
2	Late fall	Fall/winter	37	-16.44	-119.5	+2.5	+0.06	-.4
3	Late winter	Spring	98	-15.86	-116.0	-.2	+0.01	-.2
4	Summer	Fall/winter	103	-9.88	-66.8	+2.5	-.96	-9.3
5	Early winter	Winter	78	-25.48	-190.6	+4.4	+0.20	+1.4
6	Winter/late winter	Spring	91	-17.96	-130.0	-2.9	+0.13	+4.1
7	Spring	Summer	90	-11.16	-73.5	-.09	+0.12	+3.0
8	Summer	Fall/winter	91	-14.04	-97.4	+6.4	-.37	-3.9

<sup>1</sup>Changes in isotopic composition statistically significant at the 95-percent confidence level are 0.28 per mil for oxygen-18 and 2.8 per mil for deuterium.

samples with net volume loss have allowed some snowfall or rainfall to be admitted, the seasonal distribution during only the coldest season of samples experiencing gains minimizes this possibility. Because test samples that gained volume do not directly address the effect of evaporation or exchange on precipitation samples, the following discussion focuses on the four samples that had decreases in volume.

The summer-exposed sample (7) was expected to demonstrate the largest evaporation but instead displayed the smallest volume loss (0.09 percent). It may be assumed that most of the enrichment observed was the result of isotopic exchange. Exposing this spring precipitation sample to summer vapor isotopically enriched relative to the vapor in equilibrium with the precipitation should cause some sample enrichment. The enrichment observed for this sample is not significant for oxygen-18 and is marginally significant for deuterium at the 95-percent level. Sample 3 had a 0.2-percent volume loss and no significant change in isotopic composition. This is in contrast to sample 6, which displayed the largest loss (2.9 percent), although it was exposed during the same season (spring). Winter samples exposed in spring would be expected to be enriched by exchange; it may be that sample 6 was more affected by exchange because it was initially isotopically lighter than sample 3. Both evaporation and exchange have contributed to the slight enrichment observed in sample 6. The result notwithstanding, the enrichment in oxygen-18 is not statistically significant, whereas the deuterium enrichment appears to be marginally so.

The loss of water from sample 1 was intermediate to that of samples 3 and 6 (0.9 percent). The effect of exchange on a summer sample exposed in fall is expected to result in the sample becoming isotopically lighter. This sample appears to have been affected by exchange and possible evaporative enrichment to a statistically significant degree.

The test samples were subjected to one phenomenon that was unintended—addition of precipitation during exposure. In samples subjected to cold-season exposure, this was the dominant effect, overriding any evaporation or sublimation that might have occurred. Comparison of rain-gage data with collector-derived precipitation amounts suggests that evaporation from the collectors is minimal, 2 or 3 percent at most, for properly chosen sites. This evaporation could result in enrichment of the samples; however, the data presented in this report suggest that isotopic exchange is more likely to cause changes in isotopic composition than small amounts of evaporation.

Test samples were exposed for longer periods than the average exposure time of most precipitation samples. Quarterly integrated samples generally would not be exposed for the entire quarter. Even for

long exposure times, the observed changes in isotopic composition either are statistically not significant or are only marginally significant.

## SUMMARY

An experiment to evaluate the performance of a bulk precipitation collector described by Vogeli and Claassen (1971) is presented. The evaluation was limited to determining if the collector obtained representative precipitation samples for oxygen-18 and deuterium analysis. The experiment subjected samples to environmental conditions more likely to isotopically modify the samples than would conditions during ordinary operation of the collector, particularly with respect to exposure time, isotopic exchange, and addition of unwanted precipitation to the sample.

Eight samples of precipitation of known isotopic composition were exposed to environmental conditions for varying amounts of time and during all seasons. The samples were all isotopically different from precipitation that would be derived from the period of exposure. This would result in larger effects of isotopic exchange on the samples than would occur during ordinary collection. The samples were exposed for longer average times than ordinary collection. Although the experimental design intended to exclude all precipitation occurring during the exposure period, this was not completely effective during the coldest exposure period. The cap on the bulk collector allowed some light, windblown, falling snow to enter.

Notwithstanding the extraordinary conditions imposed on the samples, four (half) of the samples were isotopically modified to a statistically nonsignificant extent or nearly so (samples 2, 3, 5, 7). Two samples were modified slightly by blowing snow (samples 4, 8) and two were modified slightly by, primarily, a combination of isotopic exchange and evaporation (samples 1, 6). Samples collected under ordinary environmental conditions and for periods not in excess of 3 months will not be modified to a statistically significant extent and will accurately represent the isotopic composition of precipitation that fell during the exposure period.

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