Using Passive Capillary Samplers to Collect Soil-Meltwater Endmembers for Stable Isotope Analysis

Marty D. Frisbee, Fred M. Phillips, Andrew R. Campbell, Jan M.H. Hendrickx

Abstract

Snowmelt is the primary source of streamflow generation and recharge in much of the southwestern United States, so the stable isotopic composition of snowmelt recharge is a critical endmember in the hydrograph separation of streamflow generation. However, the methodologies available to collect meltwater for stable isotope analysis are limited due to the remote and often seasonally inaccessible nature of the terrain where snowpacks develop. To address this problem, a robust methodology using passive capillary samplers (PCAPS) was developed. Lab results indicated that (1) the wicking process associated with PCAPS does not fractionate water, but precautions are necessary to prevent exchange between the wick and atmosphere, and (2) PCAPS effectively tracked the changing isotopic composition of a soil reservoir undergoing evaporation. To test this methodology in the field, twelve PCAPS were installed at remote sites within the Saguache Creek watershed, a large subwatershed of the Rio Grande in the San Juan Mountains of southern Colorado, during October 2007 prior to the onset of snow accumulation. Bulk and modified-bulk snow collectors were installed at each PCAPS installation site to quantify the isotopic evolution of the snow and snowmelt. Field results indicate that the stable isotopic composition of infiltrating meltwater collected via PCAPS had evolved relative to the isotopic compositions obtained via modified-bulk snow collectors. This outcome may be the result of mixing of evaporated soil-water present before snow accumulation with intermittent and (or) late season pulses of isotopically depleted snowmelt water within the soil matrix. The information on the stable isotopic evolution of infiltrating meltwaters cannot be obtained from bulk and modified-bulk snow collectors. For example, this PCAPS design can be deployed at multiple depths within the same soil profile, thus providing greater insight into the processes controlling the isotopic evolution of deep percolation. Therefore, the PCAPS methodology is particularly useful in collecting soil-meltwater endmembers in remote, seasonally inaccessible watersheds and can provide much needed information on the processes that affect subsurface runoff and the consequent geochemical evolution of the infiltrating waters. This design may also be useful in remote, snowbound areas such as the Sierra Nevada where base cation loss and acidification are concerns during the snowmelt season.

Keywords: snowmelt, soil-water, PCAPS, wick sampler, stable isotope

Introduction

Many of the river basins in the southwestern United States depend upon snowmelt for streamflow generation (Winograd et al. 1998, Rango 2006), so an understanding of the processes which control streamflow generation in the headwaters of these basins is critical for the sustainability of future agricultural, domestic, and municipal water demands. Research into these processes has historically employed a variety of techniques including isotopic hydrograph separation. However, quantification of the snowmelt-infiltration endmember is problematic due to the rugged, remote, and seasonally inaccessible nature of these mountainous watersheds. These conditions often preclude frequent sampling intervals and as a

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consequence, eliminate certain vadose-zone sampling techniques. Nonetheless, it is critical that the snowmelt-infiltration endmember be correctly identified. The isotopic composition of snowpacks can be altered by vapor exchange processes occurring between the snowpack and atmosphere and by exchange between meltwater infiltrating through the snowpack and the remnant snowpack (Clark and Fritz 1997). Previous work has shown that for these reasons the isotopic composition of fresh snow and (or) remnant snowpack can differ greatly from the isotopic composition of the snowmelt runoff (Herrmann et al. 1981, Hooper and Shoemaker 1986, Taylor et al. 2001). Therefore, assuming that the isotopic composition of fresh snow and (or) surface runoff from snowmelt is the same as that of the end-season snowpack can result in errors in the hydrograph separation and (or) in estimation of recharge contributions—most commonly the overestimation of pre-event water sources and underestimation of event water (Feng et al. 2002, Taylor et al. 2002, Liu et al. 2004, Earman et al. 2006). In order to increase the accuracy of isotopic separations, Earman et al. (2006) suggested that the isotopic composition of water collected via modified-bulk collectors may be more representative of actual snowmelt recharge. They used the isotopic compositions of fresh snow and that from the modified-bulk collector to calculate the contribution of snowmelt to recharge. The fresh snow endmember resulted in a contribution of 32 percent while the modified-bulk collector endmember resulted in 53 percent. This outcome illustrates the discrepancy between these two endmembers. Therefore, a robust method requiring little maintenance or monitoring is needed to sample the isotopic signature(s) of snowmelt infiltration in these watersheds and further refine our predictions of the contribution of snowmelt to recharge and streamflow generation.

Passive capillary samplers (PCAPS) may be useful in collecting snowmelt infiltration in these remote, seasonally snowbound watersheds. The PCAPS concept was developed by Brown et al. (1986) and was subsequently evaluated by Holder et al. (1991) and Knutson and Selker (1994). The samplers are constructed from fiberglass wicks, with the length and diameter chosen to match the matric potential of the soil to be sampled. The wicks behave essentially like hanging water columns, thus allowing water to be drawn from the surrounding soil with little or no maintenance, no application of external suction, and, unlike the zero-tension lysimeter, no dependency upon positive pressure (Boll et al. 1992). They have since been used quite extensively in vadose-zone studies.

Passive capillary samplers have also been deployed to collect soil water for stable isotope analysis in agricultural settings (Landon et al. 1999, Landon et al. 2000, Delin and Landon 2002). These studies used a standard PCAPS design described in the work of Brown et al. (1986) that may not be feasible in mountainous, subalpine settings where soils are often thin and rocky. Therefore, a modification of the standard design was necessary to accommodate the soils encountered in mountainous watersheds, and a simple laboratory experiment was conducted to ascertain the suitability of using PCAPS in these studies (Frisbee et al., in press). The experimental results indicated that the wicking process associated with PCAPS does not fractionate water but that certain precautions are necessary to prevent exchange between the wick and atmosphere. Also, the modified PCAPS design effectively tracked the changing isotopic composition of a soil reservoir undergoing evaporation (Frisbee et al., in press). In order to thoroughly field test this design modification, twelve PCAPS were installed in remote locations of the Saguache Creek watershed in the San Juan Mountains of southern Colorado prior to the onset of snow accumulation in October 2007. This field evaluation was designed to answer important questions regarding the deployment of modified PCAPS to collect snowmelt for stable isotopic analyses: (1) Is the isotopic composition of water collected via modified-bulk snow collectors similar to that of the actual infiltrating snowmelt? (2) Does the modified PCAPS design preserve the stable isotopic composition of actual infiltrating meltwater or is it affected by kinetic processes?

Methods

A 50-ft coil of fiberglass wick having a diameter of 9.5 mm (3/8 inch, Pepperell Braiding Company SKU # 1380) was used in this study. The wicks were thoroughly pretreated by soaking and rinsing the wicks in deionized water several times daily for a duration of 3 weeks to ensure that manufacturing residues were removed. The degree of cleanliness was ascertained by measuring the electrical conductivity of the rinse water after each soak. Samples of the final rinse water were also subjected to standard chemical analyses to provide chemical benchmarks for the field application. The wicks were cut 60.9 cm (2 ft) long resulting in a wick

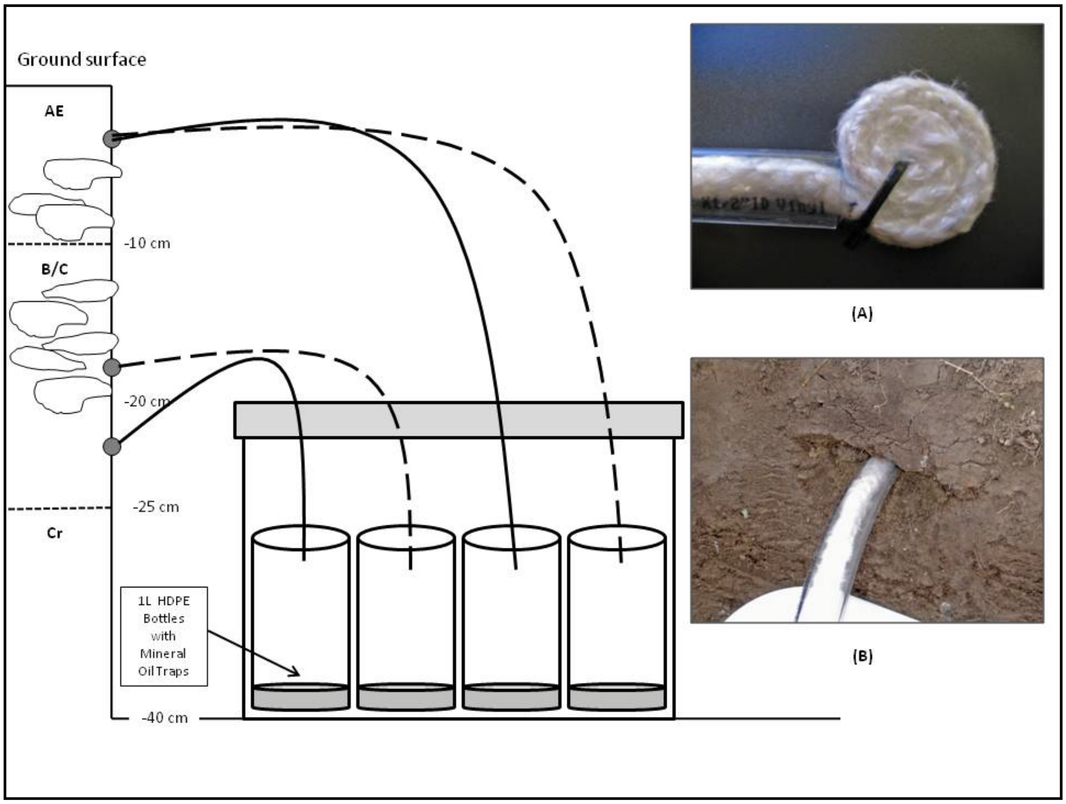

Figure 1. Diagram of typical PCAPS installation. Two PCAPS were installed at shallow depths and two were installed deeper in the soil profile. Dashed and solid lines represent paired PCAPS. Inset A is a close-up photo of "fiddlehead" and tubing assembly. Inset B is a close-up photo of an actual installation in a soil profile.

matric potential (ψ_{wick}) of -60.9 cm at soil fluxes equal to 0 (Knutson and Selker 1994). One end of each wick was coiled into a "fiddlehead" shape and then securely yet loosely fastened in place using zip-ties (Figure 1, Inset A). Typically a straight length of 7 inches (17.8 cm) could be coiled tightly to produce a collection surface of approximately 3 to 4 cm in diameter.

Soil pits were dug in three remote locations in the watershed. All pits were installed to a depth of approximately 40 cm. A weathered bedrock layer (Cr) was encountered at 15 to 25 cm below the surface. Most soils have little organic development, thin AE horizons, and are broadly classified as stony to cobbly or gravelly loams. The locations of these pits were based on the aspect of the slopes, elevation, and typical snowpack accumulation (Figure 2). For example, all sites were located in high elevation meadows, which should have been conducive to snowpack accumulation and persistence. The elevations of these sites ranged from 9,370 ft (2,857 m) to 10,250 ft (3,124 m). Four lateral, horizontal holes were then dug into the walls of each soil pit using gardening spades and pocket knives to a lateral depth of approximately 5 to 7 inches (12.7 to 17.8 cm). The wick assembly was pulled through flexible PVC tubing with an outer diameter of 1.59 cm (5/8 inch) and an inner diameter of 1.27 cm (1/2 inch). The "fiddlehead" was then inserted into the hole and the hole was backfilled with native soil in an attempt to maintain soil hydraulic properties. Thus, the "fiddlehead" was placed in direct contact with the soil while the remainder of the wick was entirely enclosed within flexible PVC tubing (Figure 1, Inset B). Passive capillary samplers typically comprise a water collection plate that has wick fibers glued to the top of it and a wick draining from the center of the plate down to a collection bottle, resulting in overall assembly lengths up to 100 cm (Brown et al. 1986). Our design modification was necessary because the shallow, rocky soils common in this mountainous watershed cannot accommodate the assembly length associated with the standard PCAPS design. Each soil pit contained two shallow PCAPS located at depths less than 10 cm and two deep PCAPS located at depths of approximately 20 cm (Figure 1).

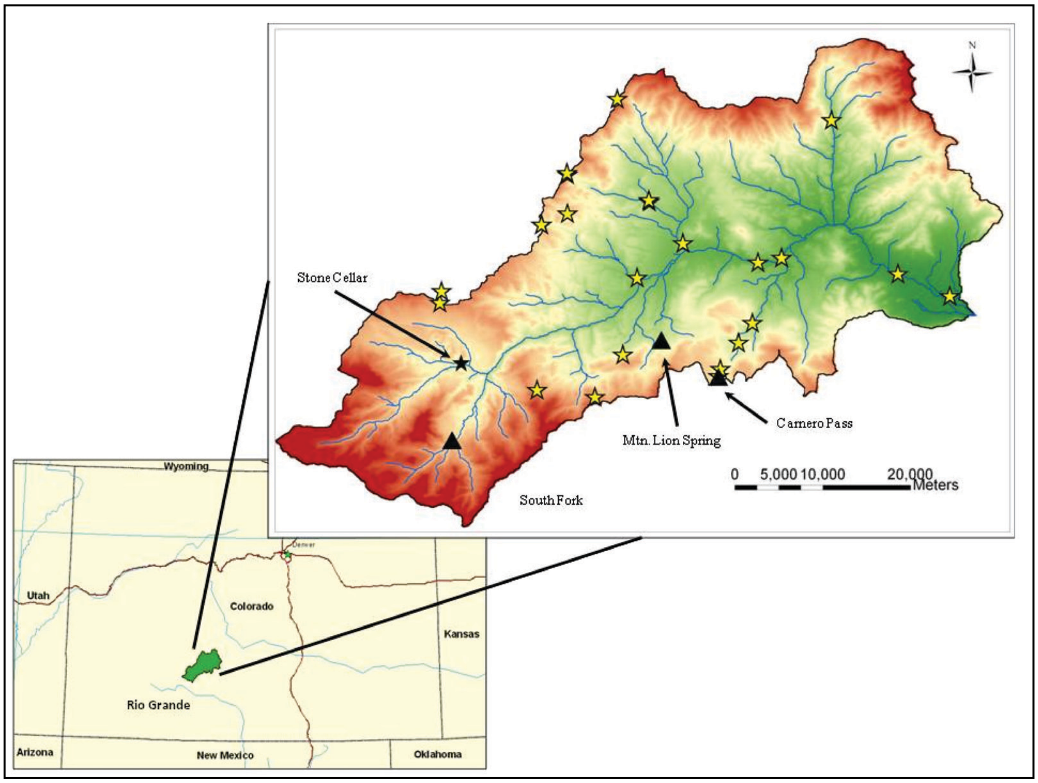

Figure 2. Map of Saguache Creek watershed. Yellow stars indicate locations of snow and (or) snowmelt runoff sampling sites, black triangles indicate locations of PCAPS installations and snow collectors, and the black star indicates the location of a stand-alone snow collector site.

A plastic collection box was then assembled which contained four 1-L LDPE bottles. Each bottle contained a small reservoir of mineral oil to prevent evaporation and atmospheric exchange. The mouth of each bottle was covered with a Ziploc® sandwich bag that was securely wrapped around the bottle using zip-ties. Each tubing/wick assembly was pushed through an access hole in the lid of the plastic collection box and the open end of the wick assembly was pushed through the Ziploc® and into the mouth of the bottle (Figure 1). Silicon sealant was applied at the juncture of the tubing and the box to prevent leaking and flow along the outside of the tubing. Each pit was then covered with a heavy duty plastic drop cloth and wooden covers were placed over the drop cloth to prevent overburden failure.

The PCAPS were installed prior to the onset of snowpack accumulation during October 2007. Each soil pit location was accompanied by the installation of a bulk and modified-bulk snow collector. Bulk collectors preserve the integrated isotopic composition of fresh snow. Modified-bulk collectors delay the snow from falling into the mineral oil trap and consequently, allow atmospheric exchange processes to occur. This collector is thought to preserve an integrated composition similar to actual recharge. The bulk collector was constructed from a 6-ft (1.83-m) length of 4-inch (10.2-cm) PVC pipe. A flat cap was cemented to the bottom of the pipe and a small reservoir of mineral oil was poured into the pipe. The modified-bulk snow collector was constructed from two 3-ft (0.92-m) lengths of 4-inch (10.2-cm) PVC pipe. Two 4-inch circular sections of fine mesh, 10 grids per inch, were cut and placed inside a PVC coupling fitting. The two lengths of PVC were then affixed to the coupling fitting, a flat termination cap was cemented to the lower PVC, and a mineral oil reservoir was poured inside the pipe assembly. These large-scale modifications to the designs used in the work of Earman et al. (2006) were necessary due to the possibility of snowpacks exceeding 4–5 ft (1.22–1.52 m) in the backcountry. The snow collectors were also installed prior to the onset of snowpack accumulation during October 2007.

All water samples captured by the snow collectors and the water samples obtained from the PCAPS were removed during the first week of June 2008. Each water sample was analyzed for $\delta^{18}O$ and δD. The $\delta^{18}O$ composition was measured on 1 mL samples of water using the CO_2 / H_2O equilibration method described in Clark and Fritz (1997) using a Thermo Finnigan Gasbench operated in continuous flow mode. The δD composition was measured by metal reduction with powdered chromium at 850°C in an H-Device (Nelson and Dettman 2001) and analyzed in dual inlet mode. Both CO_2 and H_2 were analyzed on a Thermo Finnigan Delta^{PLUS} XP Stable Isotope Ratio Mass Spectrometer. At the time of sample retrieval, two soil samples, one shallow and one deep, were removed from the Carnero Pass installation. Water was vacuum distilled from the soil samples using the vacuum distillation method described in the work of Araguás-Araguás et al. (1995) and later analyzed for $\delta^{18}O$ and δD. The variability in $\delta^{18}O$ and δD was ascertained by analyzing 21 duplicates. Variability in $\delta^{18}O$ ranged from 0.0 to 0.5 ‰ (only one duplicate varied by 0.5 ‰). The duplicates of δD varied from 0 to 2 ‰ (only one duplicate varied by 2 ‰).

Results

Samples of early season and late season (fresh) snow, late season remnant snowpack, and late season surface runoff were collected during the winters and snowmelt seasons of 2006, 2007, and 2008. These samples were fit with a linear trendline resulting in the equation $\delta D = 7.7\delta^{18}O + 5$ ($R^2 = 0.97$). In Figure 3, that snow evolution line (SEL) is compared with the local meteoric water line (LMWL) for all precipitation samples in the watershed and the global meteoric water line (Craig 1961). The LMWL is given by the equation $\delta D = 8.3\ \delta^{18}O + 19$ ($R^2 = 0.99$). As can be seen in Figure 3, evaporation (sublimation) does not appear to be the primary process controlling isotopic fractionation as the slope of the SEL is close to 8. Shallow and deep PCAPS samples from the South Fork and Carnero Pass installations are also plotted in Figure 3. As expected, the PCAPS samples plot within the area separating early season snow from late season snowpack and surface runoff. The PCAPS samples do not exhibit any significant kinetic alteration due to evaporation or sublimation since they plot along the SEL.

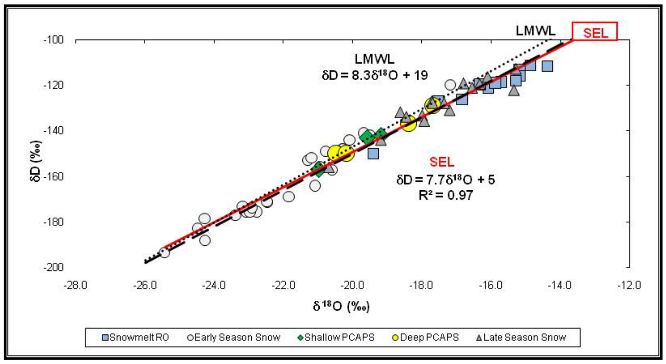

Figure 3. The solid red trendline represents the evolution of early season snow, late season snow, and surface runoff from snowmelt—the snow evolution line (SEL). The dashed line is the global meteoric water line given by Craig (1961). The dotted line is the local meteoric water line fit to all precipitation samples (rainfall and snow) in the Saguache Creek watershed.

Three of the four PCAPS pairs show some degree of isotopic mixing with depth (Figure 4). The isotopic composition of the fourth pair, South Fork–A, is the same, within error. Interestingly, the individual trendlines shown in Figure 4 as arrows effectively bracket the SEL shown in Figure 3. These results are, at first, encouraging since kinetic fractionation within the soil pit between the wick and the atmosphere was an initial concern. However, the wicks are essentially in a closed system as long as there are no leakage points along the length of the tubing that houses the wick between the soil pit wall and the collection bottle (Frisbee et al., in press). It should be noted that a short length of tubing should also be installed inside the lateral holes of the soil pit wall to limit the possibility of wick exposure outside the soil pit wall (see Figure 1, Inset B). It is also encouraging to note that the shallow PCAPS do appear to preserve the isotopic composition of the bulk and modified-bulk snow collectors. However, since little if any isotopic evolution occurred between the bulk and modified-bulk snow collectors, it would seem that answering question 1 would be problematic. We think, on the other hand, that these results clearly illustrate that the isotopic composition of infiltrating meltwater may be significantly different than that which is measured on the soil surface. This evolution takes place within a relatively shallow soil profile and the consequences of this evolution may have serious implications for endmember mixing analyses aimed at quantifying the contributions of snowmelt recharge to streamflow generation in these landscapes.

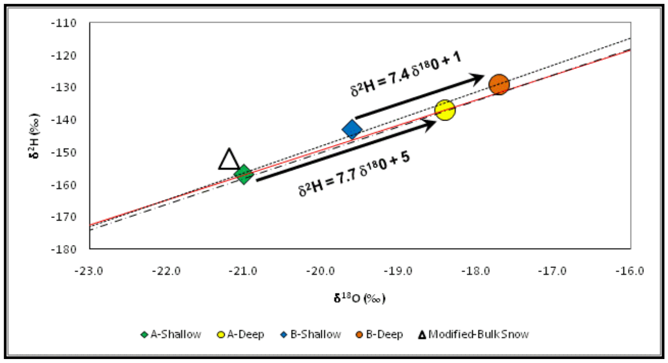

Figure 4. Evolution of PCAPS water samples in Carnero Pass. Open triangle is Modified-Bulk Snow, diamonds represent shallow PCAPS samples and circles represent deep PCAPS samples. Isotopic evolution in each pair is indicated by arrows. The red line is the SEL, the dotted line is the LMWL, and the dash-dot line is the GMWL given by Craig (1961).

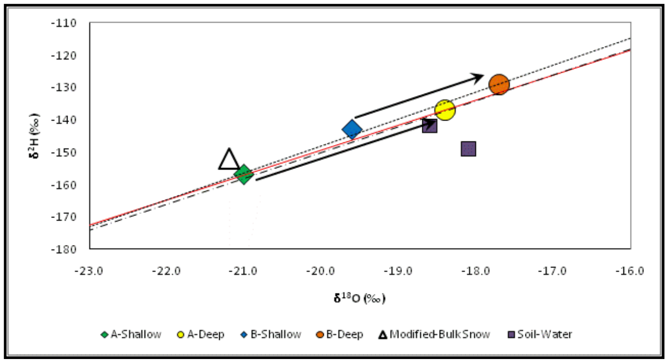

Figure 5. Evolution of Carnero Pass samples. Soil-water samples (purple squares) were obtained only at the Carnero Pass site.

It is readily apparent from Figure 4 that the shallow PCAPS samples appear to preserve the isotopic composition of the bulk and modified-bulk snow samples while the isotopic composition of infiltrating meltwater can be significantly different at a relatively shallow depth of 20 cm as compared to the meltwater collected in the shallow subsurface. To further examine this phenomenon, we can focus on the Carnero Pass samples and plot the snow, PCAPS, and soil water samples from that site only (Figure 5). The infiltrating water samples do not appear to be heavily evaporated since the slopes of the trendlines are very near 8. If, for example, evaporation had occurred in the soil or during the wicking process, a slope of between 3 to 5 in the trendlines of the PCAPS samples would be apparent. The soil in the Carnero Pass soil pit was still moist when the samples were retrieved yet the soil samples were taken from the pit face that had likely undergone evaporation. Thus, the two soil samples plot away from the SEL (Figure 5). The shallow soil sample plots on a trendline with a slope of 6.3 relative to the preserved isotopic composition of the shallow PCAPS while the deep soil sample plots on a trendline with a slope of 2.8. All other soil pits were dry at the time of retrieval. It is more plausible that the PCAPS trendlines are the result of mixing in the soil profile whereby persistent diffuse melting from the snowpack and (or) intermittent periods of melt occurring over the course of winter create periods of sporadic infiltration into the soil. Therefore, mixing can occur between newly infiltrating meltwater and soil water that reflects previous infiltration, and which may create conditions where subsequent meltwater infiltration can mix with soil water that has already undergone isotopic alteration with depth (Merlivat 1978).

Conclusions

We initially designed this field evaluation to test the suitability of a modified passive capillary sampler design for collecting the integrated isotopic composition of snowmelt-infiltration. We were interested in testing the assumption that the isotopic composition of water collected by modified-bulk snow collectors is similar to that of actual infiltration during snowmelt. While the modified-bulk collectors employed during the 2007–2008 winter season did not experience significant isotopic alteration, it is apparent that the assumption may not be valid in all cases. Isotopic evolution of infiltrating meltwater did occur in these shallow, rocky subalpine soils to such an extent that the deep PCAPS samples were not similar to the isotopic composition of the waters retrieved from the snow collectors. In addition, if properly installed in the soil, the wicking process associated with the PCAPS design does not fractionate water. Thus, the isotopic compositions of the infiltrating meltwaters are preserved. Overall, the performance of the modified PCAPS design was encouraging, and we conclude that this design may be particularly useful in collecting snowmelt infiltration endmembers in remote, seasonally inaccessible watersheds. This design can provide much needed information on the processes that affect subsurface runoff and the consequent isotopic evolution of the infiltrating waters. This design may also be useful in remote, snowbound areas such as the Sierra Nevada where base cation loss and acidification are concerns during the snowmelt season.

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References

Araguás-Araguás, L., K. Rozanski, R. Gonfiantini, and D. Louvat. 1995. Isotope effects accompanying vacuum extraction of soil water for stable isotope analyses. Journal of Hydrology 168:159–171.

Boll, J., T.S. Steenhuis, and J.S. Selker. 1992. Fiberglass wicks for sampling of water and solutes in the vadose zone. Soil Science Society of America Journal 56:701–707.

Brown, K.W., J.C. Thomas, and M.W. Holder. 1986. Development of a capillary wick unsaturated zone water sampler. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV, Cooperative Agreement CR812316-01-0.

Clark, I., and P. Fritz. 1997. Environmental Isotopes in Hydrogeology. Lewis, Boca Raton, FL.

Craig, H. 1961. Isotopic variations in meteoric waters. Science 133:1,702–1,703.

Delin, G.N., and M.K. Landon. 2002. Effects of surface run-off on the transport of agricultural chemicals to ground water in a sandplain setting. The Science of the Total Environment 295:143–155.

Earman, S., A.R. Campbell, F.M. Phillips, and B.D. Newman. 2006. Isotopic exchange between snow and atmospheric water vapor: Estimation of the snowmelt component of groundwater recharge in the southwestern United States. Journal of Geophysical Research 111:D09302.

Feng, X., S. Taylor, and C.E. Renshaw. 2002. Isotopic evolution of snowmelt: 1. A physically based one-dimensional model. Water Resources Research 38(10):1,217.

Frisbee, M.D., F.M. Phillips, A.R. Campbell, and J.M.H. Hendrickx. In press. Modified passive capillary samplers for collecting samples of snowmelt infiltration for stable isotope analysis in remote, seasonally inaccessible watersheds: 1. Laboratory Evaluation. Hydrological Processes.

Herrmann, A., M. Lehrer, and W. Stichler. 1981. Isotope input into runoff systems from melting snow covers. Nordic Hydrology 12:309–318.

Holder, M., K.W. Brown, J.C. Thomas, D. Zabcik, and H.E. Murray. 1991. Capillary-wick unsaturated zone soil pore water sampler. Soil Science Society of America Journal 55(5):1,195–1,202.

Hooper, R.P., and C.A. Shoemaker. 1986. A comparison of chemical and isotopic hydrograph separation. Water Resources Research 22:1,444–1,454.

Knutson, J.H., and J.S. Selker. 1994. Unsaturated hydraulic conductivities of fiberglass wicks and designing capillary wick pore-water samplers. Soil Science Society of America Journal 58:721–729.

Landon, M.K., G.N. Delin, S.C. Komor, and C.P. Regan. 1999. Comparison of the stable-isotopic composition of soil water collected from suction lysimeters, wick samplers, and cores in a sandy unsaturated zone. Journal of Hydrology 224:45–54.

Landon, M.K., G.N. Delin, S.C. Komor, and C.P. Regan. 2000. Relation of pathways and transit times of recharge water to nitrate concentrations using stable isotopes. Ground Water 38(3):381–395.

Liu, F., M.W. Williams, and N. Caine. 2004. Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. Water Resources Research 40:W09401.

Merlivat, L. 1978. Molecular diffusivities of $H_2{}^{16}O$, $HD^{16}O$, and $H_2{}^{18}O$ in gases. Journal of Chemical Physics 69:2,864–2,871.

Nelson, S.T., and D. Dettman. 2001. Improving hydrogen isotope ratio measurements for on-line chromium reduction systems. Rapid Communications in Mass Spectrometry 15:2,301–2,306.

Rango, A. 2006. Snow: The real water supply for the Rio Grande Basin. New Mexico Journal of Science 44:99–118.

Taylor, S., X. Feng, J.W. Kirchner, R. Osterhuber, B. Klaue, and C.E. Renshaw. 2001. Isotopic evolution of a seasonal snowpack and its melt. Water Resources Research 37(3):759–769.

Taylor, S., X. Feng, M. Williams, and J. McNamara. 2002. How isotopic fractionation of snowmelt affects hydrograph separation. Hydrological Processes 16:3,683–3,690.

Winograd, I.J., A.C. Riggs, and T.B. Coplen. 1998. The relative contributions of summer and cool-season precipitation to groundwater recharge, Spring Mountains, Nevada, USA. Hydrogeology Journal 6:77–93.