A new method of snowmelt sampling for water stable isotopes

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Abstract:

We modified a passive capillary sampler (PCS) to collect snowmelt water for isotopic analysis. Past applications of PCSs have been to sample soil water, but the novel aspect of this study was the placement of the PCSs at the ground-snowpack interface to collect snowmelt. We deployed arrays of PCSs at 11 sites in ten partner countries on five continents representing a range of climate and snow cover worldwide. The PCS reliably collected snowmelt at all sites and caused negligible evaporative fractionation effects in the samples. PCS is low-cost, easy to install, and collects a representative integrated snowmelt sample throughout the melt season or at the melt event scale. Unlike snow cores, the PCS collects the water that would actually infiltrate the soil; thus, its isotopic composition is appropriate to use for tracing snowmelt water through the hydrologic cycle. The purpose of this Briefing is to show the potential advantages of PCSs and recommend guidelines for constructing and installing them based on our preliminary results from two snowmelt seasons. Copyright © 2014 John Wiley & Sons, Ltd.

KEY WORDS   passive capillary sampler; snowmelt; water isotopes; snow core; snowmelt lysimeter

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INTRODUCTION

Snow cover affects hydrological processes in many regions of the world. Water stored in the snowpack limits water availability during the cold season, but snowmelt contributes significantly to river discharge and groundwater recharge. For high-elevation mountain streams, the largest portion of the annual streamflow occurs during melting of snow that accumulated during late autumn to early spring (Jin *et al.*, 2012). In these environments,

meltwater from snow cover was estimated to be critical to downstream water resources for over 1 billion people worldwide (Barnett *et al.*, 2005) and can contribute as much as 75% of annual flow in some northern regions (Callaghan *et al.*, 2011). Recent observations and climate change predictions suggest that there will be significant changes in snow water equivalent and snow cover duration in some regions (Callaghan *et al.*, 2011). Thus, the volume, timing and duration of snowmelt are expected to change as well (Barnett *et al.*, 2005), raising concern about water supply security (Quevauviller *et al.*, 2012). Monitoring the impacts of climate change on water resources will require techniques capable of identifying and quantifying the relative contribution of snowmelt in surface water and groundwater.

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Water stable isotopes have been used to assess the contribution of snowmelt to runoff and groundwater since the 1970s (e.g. Herrmann *et al.*, 1979; Hooper and Shoemaker, 1986; Rodhe, 1987; Laudon *et al.*, 2002; Earman *et al.*, 2006). Despite the uncertainties associated with two-component or multi-component separation methods (Burns, 2002), the use of oxygen and hydrogen isotopes has become a standard tool in many hydrological studies. A significant challenge in using these methods to identify the snowmelt contribution is determining the appropriate isotopic composition of snowmelt. The isotopic composition of the snowpack is different from that of snowmelt (Taylor *et al.*, 2001; Dahlke and Lyon, 2013). Isotopic fractionation that occurs during evaporation from the snowpack, water vapour diffusion in snowpack accompanied by snow metamorphism, and alternating melting/refreezing before and during the snowmelt period can result in significant isotopic offsets between the original snowpack composition and snowmelt (Friedman *et al.*, 1991; Zhou *et al.*, 2008; Sokratov and Golubev, 2009). In addition, the high spatial variability in the isotopic composition of the melting snowpack, also due to the complex snow stratigraphy present at both small and large scales, further complicates estimation of representative values for the isotopic composition of snowmelt. Information on snowmelt isotopic composition is useful for modelling hydrological processes at differing spatial and temporal scales in snow-dominated systems (e.g. hydrograph separation for small catchments, interpretation of large river catchment synoptic surveys). Isotope-based hydrological models (e.g. Cable *et al.*, 2011; Stadnyk *et al.*, 2013) require that snowmelt isotopic compositions are representative of the spatially variable isotopic composition of meltwater at the time of melting and infiltration that are difficult to measure and monitor *in situ*. Indeed, true characterization of the temporally and spatially variant isotopic composition of snowmelt is critical for these applications.

Here, we present the results of a coordinated research project 'Use of environmental isotopes in assessing water resources in snow, glacier, and permafrost dominated areas under changing climatic conditions' managed by the International Atomic Energy Agency, Vienna. We evaluate the use of passive capillary samplers (PCSs) for snowmelt sampling for water stable isotope (oxygen and hydrogen) analysis over a wide geographical range of sites where snowmelt is an important part of the hydrologic cycle. To our knowledge, this is the first application of the PCS approach to collect exclusively snowmelt water at the ground-snowpack interface. We specifically aim to (i) present this new method of snowmelt sampling to the hydrological community and (ii) assess the potentials and limitations of PCS compared with more traditional approaches for snowmelt sampling

for isotopic analyses. Our results indicate that estimates of the isotopic composition of snowmelt obtained by PCS are equivalent to other methods with the advantage that their low cost and ease of installation allow for improved characterization of the range and variation of snowmelt isotopic composition.

MATERIALS AND METHODS

Manufacture of passive capillary samplers

Passive capillary samplers were developed to collect soil water samples (e.g. Holder *et al.*, 1991). Our PCS (Figure 1) was modified from the design of Frisbee *et al.* (2010). The PCS was made from an 80-cm long, 9.5-mm diameter fibreglass wick that was soaked and rinsed in deionized water and allowed to dry before deployment. One end of the wick (about 20-cm length) was rolled into a tight coil of about 40 mm diameter and secured with a plastic band (Figure 1). The remaining length was encased in plastic tubing and led into a sample collection bottle, sealed except for a small hole (<1 mm) to allow air escape. The coil, where snowmelt water enters the wick, was placed on top of a plastic barrier and secured to the ground with U-shaped pins. Snowmelt was collected in 0.5-l to 5-l bottles, sized for expected snowmelt volumes. The bottles were buried beneath the ground (typically in a plastic box) to prevent the sample from freezing. The sample was collected by removing the bottle from the ground. The type of wick used is critical, and it should be made of fibreglass with a central core, and we recommend that its ability to collect water be tested in the lab prior to field deployment. The effect of different braiding patterns of outer strands of the wick on permeability is not clear, and we advise that consistent wick material be used throughout a given study.

Field deployment and sampling campaigns

All PCSs were built in 2011 in the same lab, to ensure consistent construction. We installed prototypes in the field in six countries during the 2012 snowmelt season as a preliminary test of the applicability and reliability of the method. After data analysis and discussion of first results, we deployed the PCSs in the field during the 2013 snowmelt season in ten partner countries at 11 sites worldwide representing a broad range of climate conditions (Figure 2, Table I). In most countries, we deployed multiple arrays of PCSs, where a typical array had five PCSs in close proximity with the five collection bottles placed together in a water-tight box (Figure 1). Arrays were deployed in various landscape settings depending on specific research questions and requirements of the site. In nearly all cases, the PCSs collected
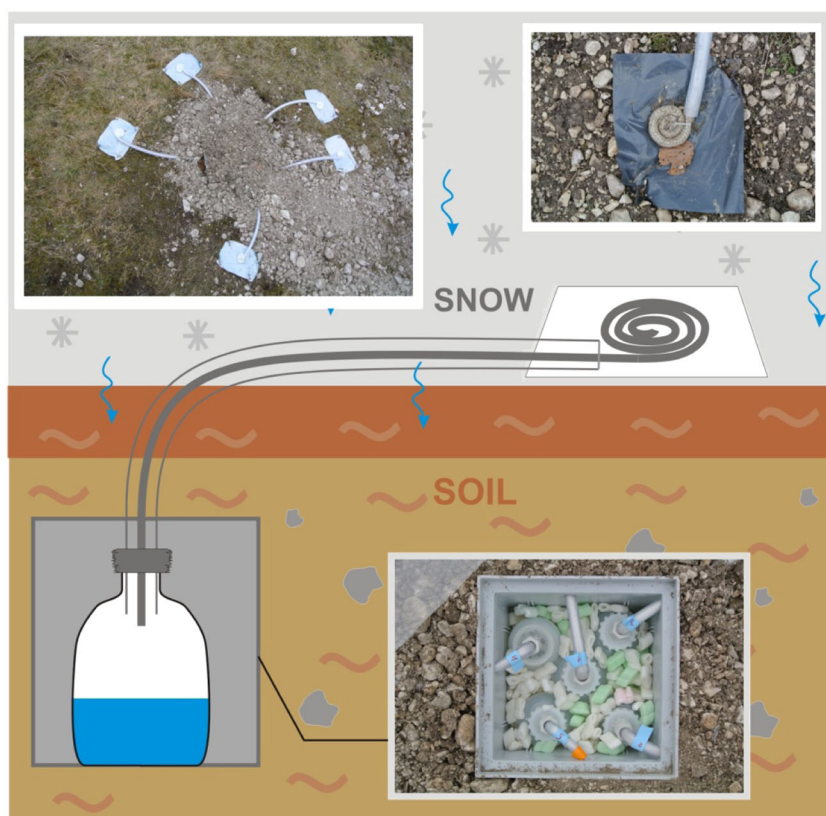
Figure 1. Drawings and photos of the passive capillary sampler showing details of the construction and deployments

Figure 2. World map showing the sampling sites (red dots) where passive capillary samplers were installed

sufficient water for analysis, and there were few problems with bottle overflow and incorporation of soil water (as indicated by colour and electrical conductivity). We report here on sampling results from 194 individual PCSs.

At eight of the 11 sites where PCSs were installed either traditional snow cores (using snow tubes) or snowmelt samples from snowmelt lysimeters were also collected. Snowmelt lysimeters have a plastic or metal plate beneath the snowpack, slightly sloped so that meltwater flows into a collection vessel. Some snowmelt lysimeters have a plastic tube for meltwater to drain from the plate to the collection vessel (e.g. Shanley *et al.*, 2002), whereas in other snowmelt lysimeters the sample is collected directly at the base of the plate (e.g. Holko *et al.*, 2013). Like PCSs, snowmelt lysimeters are effective at collecting snowmelt, and they have the potential advantage of integrating small-scale variability over a discrete area (e.g. 1 m^2). Only in two countries (Slovakia and USA) were samples from all three types of devices (snow tubes, snowmelt lysimeters and PCSs) taken at the same time in a consistent way so that a sound comparison could be made only for those two sites.

Table I. Sampling site characteristics

Country (region)	Altitude (m a.s.l.)	MAT (°C)	MAP (mm)	Cold period precipitation (mm)	Max snow depth (cm)	Max SWE (mm)	Land cover type	Climate
Argentina	2580–2800	5	450	300–400	150	150–250	Bare rock	Dry summer subtropical
Canada	231	3	519	110	6	100	Grass	Warm summer continental
Georgia	1676	14	154	90	103	160	Grass	Mountain continental
Italy	1950–1990	4	1220	158	>150	>700	Grass	Mountain continental
Morocco	3229	10	600	45	<50	300	Bare rock	Dry summer subtropical
Pakistan	2002–2539	—	2200	700–950	45	—	Grass	Dry summer subtropical
Russia (Moscow)	192	5	727	246	77	236	Grass	Warm summer continental
Russia (Siberia)	210	−10	230	75	40	75	Forest taiga	Continental subarctic
Slovakia	560–2494	7	700–2000	60–450	>200–	>600	Grass, forest	Mountain continental
Slovenia	735–742	7	1839	380	191	—	Grass	Mountain continental
USA	550	5	1250	450	120	272	Forest	Mountain continental

SWE, snow water equivalent; MAT, long-term mean annual temperature; MAP, long-term mean annual precipitation.
Cold period: days with average temperature below 0°C. The climate description is based on the Köppen – Geiger Climate Classification (Kottek *et al.*, 2006). Meteorological data were derived from the nearest weather stations available at each site.

RESULTS AND DISCUSSION

Comparison among different sites

The collective PCS results from all sampling sites spanned a large range of isotopic values ($\delta^{18}O$ from −32.1 to −4.3‰, δ^2H from −239 to −22‰) and plotted along the global meteoric water line (Figure 3). The sites grouped into distinct isotopic populations by climate. The mountain continental group included five of the 11 sampling sites and plotted in a tight band in the range from −18.0 to −10.7‰ for $\delta^{18}O$ and from −129 to −76‰ for δ^2H. The three dry subtropical and semi-arid
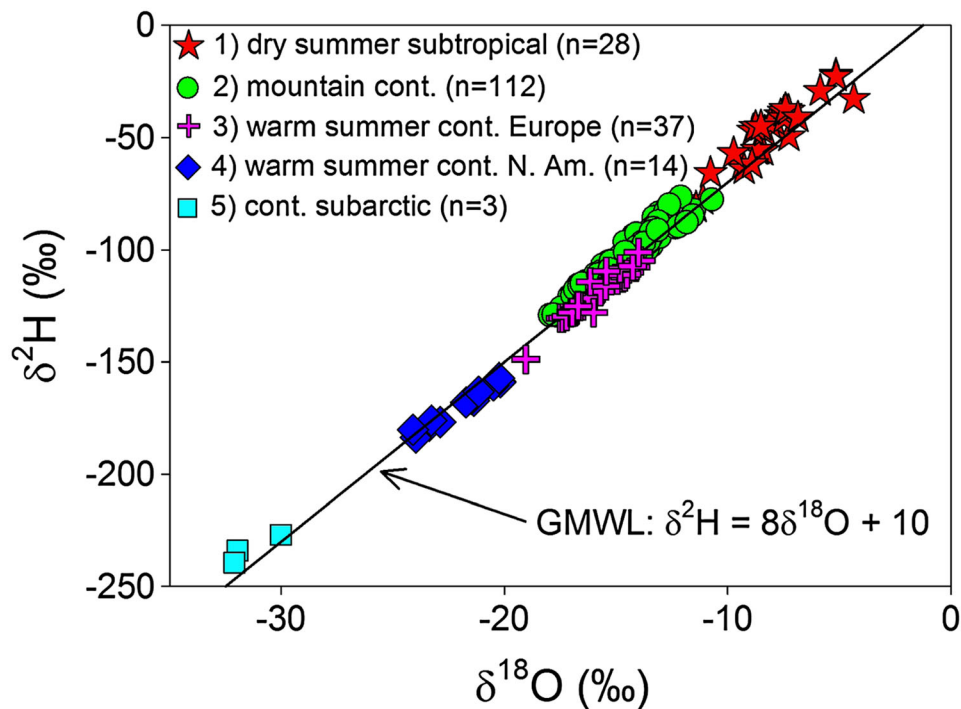

Figure 3. Relation between $\delta^{18}O$ and δ^2H of snowmelt sampled by passive capillary samplers in different climatic regions in the world. The global meteorological water line is also plotted. Countries represented in each group are: (1) dry summer subtropical (Argentina, Morocco, Pakistan); (2) mountain continental (Georgia, Italy, Slovakia, Slovenia, USA); (3) warm summer continental – Europe – (Russia); (4) warm summer continental – North America – (Canada); and (5) continental subarctic (Russia-Siberia). Site characteristics are presented in Table I

sites (Argentina, Morocco and Pakistan) included our lowest latitude but highest elevation sites and were relatively more isotopically enriched. Snowmelt from Russia (Moscow, warm summer continental) partially overlapped with the mountain continental group and plotted at its lower limit. Canada (warm summer continental but at the border with the continental subarctic zone) and Russia (Siberia, continental subarctic) formed distinct individual groups and were progressively more isotopically depleted.

To quantify the contribution of snowmelt to the hydrologic cycle, and to get an accurate isotopic signal of the meltwater, hydrologists must capture the water that actually infiltrates the soil. The position of the PCS at the base of the snowpack enables collection of the percolating meltwater, and the fidelity of the points to the global meteoric water line confirms that the PCS design prevents evaporation from the sample without the need for added measures such as mineral oil in the sample bottle. In fact, the lack of evidence for sample evaporation is noteworthy considering that the 11 sites varied widely in snow amount and characteristics and that details of the field deployment differed from site to site. The lack of evaporation is also confirmed by deuterium excess calculated for all PCS measurements (Dansgaard, 1964). Deuterium excess for the 11 sites was on average 12.3‰ (standard deviation = 4.8‰, $n = 194$) and took on typical values of each climatic zone. The distribution of deuterium excess for our measurements was not skewed toward low or high values but was very close to the normal theoretical distribution (Figure 4), suggesting that no significant evaporation (which would lower the values, even to negative ones) or other secondary processes had occurred in the samples.

Comparison of different sampling techniques

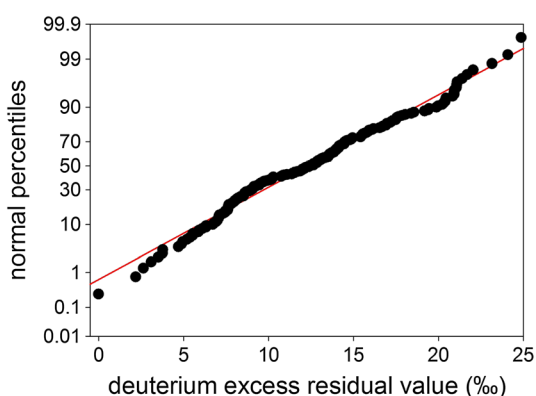An ANOVA applied to snow cores and snowmelt data collected from PCSs and snowmelt lysimeters in Slovakia and USA showed that the mean values of the PCS, snowmelt lysimeter and snow core sample populations were statistically different (at the 0.05 significance level). The PCS and snowmelt lysimeter samples were statistically similar and were both statistically different and isotopically more enriched compared with the snow core samples (Figure 5). These results are as we expected; because the snowpack progressively fractionates through the ablation period, the resulting meltwater (as collected by PCSs and lysimeters) is relatively isotopically enriched (Taylor et al., 2001; Unnikrishna et al., 2002; Zhou et al., 2008; Dahlke and Lyon, 2013). At the Canadian and Siberian sites, however, the isotopic composition of snow cores and snowmelt from the PCSs was identical, presumably because the entire snowpack melted too rapidly for significant fractionation to occur. Particularly, our observations at the Canadian and Siberian sites are in agreement with the results by Lee et al. (2010), who found that the mean isotopic values of snowpack and meltwater (although the latter were not collected by snowmelt lysimeters) for a mountain site in Sierra Nevada (USA) were not significantly different. Moreover, they noticed that the standard deviations from the snowpack to snowmelt decreased, indicating that the variability of isotopic composition decreased during snow metamorphism and melting, as shown at other sites (Taylor et al., 2001; Unnikrishna et al., 2002). Consistent with these studies, we observed larger variability in snow core data (longer whiskers in Figure 5) compared with snowmelt data from snowmelt lysimeters and PCSs.

On the basis of these first tests on PCS and the experience of our group in using more traditional snowmelt lysimeter and snow core approaches, we can provide some comparative information about the potential and the limitations of PCS for the isotopic characterization of snowmelt (Table II). First of all, PCS was shown to yield representative values of snowmelt isotopic composition at all sites, unlike snow cores, which are still commonly used in hydrograph

Figure 4. Normal probability plot for deuterium excess data derived from the passive capillary sampler measurements
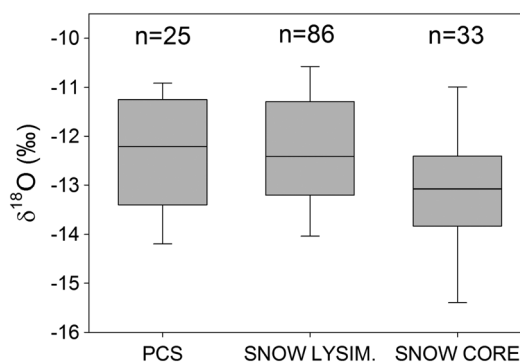

Figure 5. Box-plots of snowmelt composition collected by passive capillary samplers, snow lysimeters and of snow cores at the two sites (Slovakia and USA) where data were collected in a comparative way in spring 2012. The boxes indicate the 25th and 75th percentiles, the whiskers indicate the 10th and 90th percentiles, and the horizontal line within the box indicates the median

Table II. Comparison of strengths and weaknesses of different sampling methods for the determination of the snowmelt isotopic composition

	PCS	Lysimeter with tube[a]	Lysimeter without tube[b]	Snow core
Representativeness of the snowmelt isotopic composition	3*	3**	2**	1***
Cost	3	2	3	3
Installation	3	1	2	—
Ease of sampling	3	3	3	3
Collection of samples at multiple locations	3	2	3	3
Collection of season-integrated samples	3	2	2	—
Collection of day-integrated samples	2	3	3	—
Snowpack disturbance	3	3	1	2
Risk of malfunctioning due to ice clogging or leakage	3	1	3	—

PCS, passive capillary sampler.
Legend: 1: poor performance; 2: fair performance; 3: good performance; -: not applicable.
[a]: according to Shanley *et al.* (2002);
[b]: according to Holko *et al.* (2013).
*: this study;
**: this study plus personal experience;
***: Taylor *et al.*, (2001) plus personal experience.

separation studies (see Laudon *et al.*, 2002 and Taylor *et al.*, 2002 for a discussion on how snow core isotopic data can affect hydrograph separation results). In addition, PCS has the significant advantage, compared with snowmelt lysimeters, of being relatively inexpensive and easy to produce and install in the field. Thus, it is practical to install many PCSs in order to characterize the isotopic composition of snowmelt at different sites in the same research area and at different spatial scales, enabling statistical analyses to assess snowmelt variability and uncertainty in measured compositions. This is particularly important in mountainous areas with accessibility issues and where spatial variability in snow cover isotopic values can be considerable even at the small scale (Dietermann and Weiler, 2013), as also shown in an ongoing study by our group. PCS is especially useful to obtain seasonally integrated samples needed, for instance, to compute the snowmelt contribution to yearly runoff or groundwater recharge (Earman *et al.*, 2006). Moreover, according to our preliminary laboratory and field tests, PCS can also be used to collect samples during individual melt events (e.g. at the daily scale) for hydrograph separation applications. However, further studies are needed in order to develop a robust methodology for proper use of PCS for high-frequency snowmelt sampling. PCS is not prone to problems that can affect snowmelt lysimeters, such as ice clogging the drain tube (in the case of devices such as those reported in Shanley *et al.* (2002)) or disturbance of the snowpack during sampling (in the case of devices such as those reported in Holko *et al.* (2013)). Finally, although we have not tested this, PCS could be also used for the determination of solutes and other geochemical tracers, therefore expanding their usefulness in catchment hydrology studies. Tests and experiments on this aspect are still needed.

During the field campaigns carried out by the different teams, we also noticed a few drawbacks. In some cases, when capturing the winter-integrated snowmelt samples, underestimation of the cumulated depth of the snowpack could lead to the choice of a bottle too small to accommodate the entire sample. Moreover, in some mountain catchments with rugged topography (e.g. Italy), PCSs placed on steep hillslopes could be potentially destroyed by avalanches. Conversely, PCSs installed in riparian areas prone to soil saturation, especially at peak melt, could lead to sampling saturation overland flow in addition to snowmelt. Careful installation procedures and snow depth estimations can significantly reduce these risks. At sites and/or during particular years when snowpack melts, re-accumulates and melts again during the season, leaving the ground almost snow-free for some days (as was the case of Canada in our study), the wick or the sample in the bottle can freeze during very cold periods, despite being installed in a box buried in the soil. Moreover, precipitation during mid-winter thaws or toward the end of the melting season could occur as rainfall that would percolate through the snowpack and affect the isotopic signature of sample (but the overall PCS sample still reflects the integrated winter recharge signal). The amount of rainfall possibly collected in the bottle depends on storm characteristics (e.g. rainfall intensity, storm duration), the volume of water already stored in the bottle and the hydraulic properties of the wick. The latter should be tested especially for application of PCS at sites where direct rainfall on the device may occur.

While our preliminary investigations have shown that PCS gives similar isotopic results to existing methods and has some significant logistical advantages, some aspects of our results are not yet explained, and we are addressing

these in follow-up studies. Although evaporative fractionation appears minimal, there are slight deviations from the GWML, which differ among sites. We plan controlled laboratory analyses to investigate the effects of wick length and sample volume on possible fractionation within the wick. We also will develop methods for sizing the collection bottles to prevent overflow. Finally, we will assess whether the samplers may collect differentially at different melt rates, which could affect the representativeness of the seasonally integrated snowmelt sample.

CONCLUSIONS

In this paper, we present a new approach for obtaining snowmelt for isotopic (and potentially geochemical) analysis. Although additional tests are needed, we found that the PCS method reported here has some significant advantages over existing snowmelt sampling techniques: (1) snowmelt is sampled directly at the base of the snowpack, avoiding artificial ponding and reducing the potential for evaporative enrichment that can occur with other methods; (2) the materials are inexpensive; (3) they are easy to construct and install; (4) unlike snow cores, which may miss mid-season snowmelt and late-season snowfall, PCS will collect integrated snowmelt water throughout the season, and (5) arrays of PCSs can be used to investigate snowmelt variability at scales ranging from sub-metre to many km without prohibitive installation costs.

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