

## The Fate of Organic Contaminants in Melting Snow

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### Introduction

Snow and ice influence in a multitude of ways the fate of organic contaminants in the environment<sup>1</sup>. Snow melt in particular controls the extent and timing of the delivery of organic contaminants to aquatic and terrestrial ecosystems. During snow melt, contaminants are being released that have accumulated by precipitation and dry atmospheric deposition, sometimes over time periods of many months. Snow melt thus has the potential to cause temporary concentration maxima in water, air and soil environments. Such maxima may have implications for the exposure of aquatic and terrestrial organisms, especially if the concentration peaks are timed to coincide with particularly vulnerable stages of the organisms' development. The mechanisms of organic contaminant delivery to various ecosystems during snow melt are thus of considerable interest.

Whereas investigations of the melting behaviour of inorganic chemicals in snow and ice have been quite common in both the field and the laboratory, the melting behaviour of organic contaminants is very poorly understood. Field-based research on organic chemicals in snow is rarely aimed at providing a quantitative understanding of the processes that organic contaminants undergo during snow melt<sup>2-6</sup>. Field studies are difficult because snow properties and melting conditions are not controllable, and the concentrations of organic chemicals in natural snow are low and possibly quite variable on a small spatial scale. Here we describe an ongoing project that seeks to gain a quantitative understanding of snow melt related processes by using controlled experiments in a temperature programmable cold room. The questions addressed in the project include: What fraction of the organic contaminants present in a snow pack is transferred with the melt water to the underlying medium or the receiving water body and how much is lost by degradation or evaporation to the atmosphere? Does relocation of organic chemicals occur within a deeper snow pack during freeze-thaw cycles? What is the timing of chemical release with the melt water? Are the chemicals transported while dissolved in the melt water or sorbed to particles? How do the properties of the organic chemical, the properties of the snow pack, and the meteorological conditions during the time of melting influence these processes?

### Materials and Methods

**Experimental Design.** Both natural and artificial snow in rectangular stainless steel vessels (0.45 and 0.25 m<sup>3</sup>) is melted under predetermined temperature conditions within a large cold room. (Fig. 1). A refrigerated cooling liquid is circulated through the double-walled bottom of the vessel, which makes it possible to control the temperature at the bottom of the snow pack separately from the rest of the cold room, enabling the simulation of more realistic temperature gradients within the snow pack. During the melting of snow, changes in physical and chemical snow properties are recorded as a function of snow depth using time domain reflectometry (TDR) and chromatographic techniques. Melt water fractions are collected in a drain at the bottom of each vessel and are sampled using a fraction collector which is rotating at fixed time steps enabling measurements of melt water volume and contaminant quantities released per time unit. Experiments vary in terms of (i) the type of snow and initial snow properties, (ii) the melting conditions, and (iii) the chemical properties. Several PAHs comprising a wide range of partitioning properties are used as model substances.

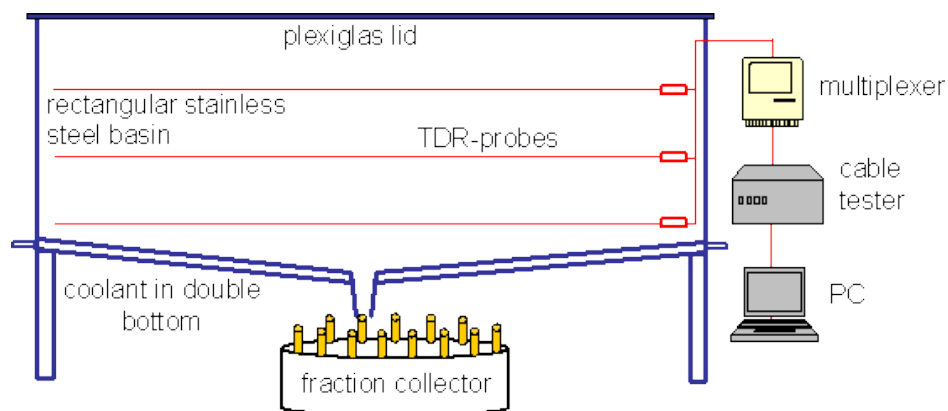


Figure 1: Experimental setup of a snowmelt vessel.

**Snow-Making.** The necessity to have large amounts of snow with constant and comparable properties for the experiments led to the development of a method for producing artificial snow by means of a “snowgun”. Air compressed at 50 psi (Air compressor - Porter Cable Delcpl6025) and tap water are mixed and forced through a nozzle (size 3/32”) into the cold room. The mixture consisting of tiny water droplets within a high pressure environment rapidly cools down due to expansion, convection, and evaporation and falls as pellet snow into the experimental vessel. To keep the wet bulb temperature sufficiently low, a temperature of -20 °C is maintained within the chamber. The produced snow exhibits snow properties similar to recently deposited natural snow with a density below 0.2 g/cm<sup>3</sup>. Mixtures of solutions containing defined concentrations of PAHs either in the dissolved phase or attached onto fine particles are injected into the water stream leading to the snowgun.

**Time Domain Reflectometry (TDR).** The water content of wet snow and the density of dry snow are measured on-line using TDR<sup>7,8</sup>. This technique depends on measuring the travel time of an electromagnetic pulse through a probe, which is dependent on both the probe characteristics and the dielectric permittivity of the medium around the probe. Six handcrafted TDR probes consisting of aluminum tubes, an epoxy resin probe head, and coaxial cables are attached within the snowmelt vessel and embedded into the snow pack during the experiments. A short rise-time cable tester (Textronik 1502B) sends electromagnetic pulses along the probes while a multiplexer (SDMX50, Campbell Scientific Inc.) is alternately switching between them. The signals are sampled and evaluated using the TDR software WinTDR<sup>9</sup>. While the water content is measured during melting periods, the dry snow density can only be acquired in “night-time” refrozen snow.

Both parameters are calculated using approximations from a review by Frolov et al.<sup>10</sup>. The density of dry snow was determined with:

$$\epsilon_d' = (1 + 0.845 \rho_s),$$

where  $\epsilon_d'$  is the real part of the dielectric permittivity of dry snow and  $\rho_s$  is the bulk snow density. The apparent permittivity was assumed to correspond to the real part of the permittivity leaving its imaginary part negligible<sup>8</sup>. The water content was calculated using:

$$\epsilon_s' = \epsilon_d' + \Delta\epsilon_s' = \epsilon_d' + (16.7 W + 42.5 W^2)$$

where  $\epsilon_s'$  is the dielectric permittivity of the bulk wet snow,  $\Delta\epsilon_s'$  is the incremental dielectric permittivity accounting for the water content  $W$ . The average bulk snow density is additionally controlled on the basis of the level of the snow surface during the experiments. Sublimation and evaporation of snow was assumed to be negligible because an air tight lid was covering the snow vessel during the experiments.

**Chemical Analysis.** The meltwater samples are analyzed for PAHs by HPLC with fluorescence detection. Particles are extracted with a solvent and also analyzed for PAHs by HPLC. Furthermore, the meltwater fractions are

characterised in terms of conductivity and pH upon leaving the snowmelt vessel.

## Results and Discussion

Figure 2 present first results from two experiments deploying natural snow.

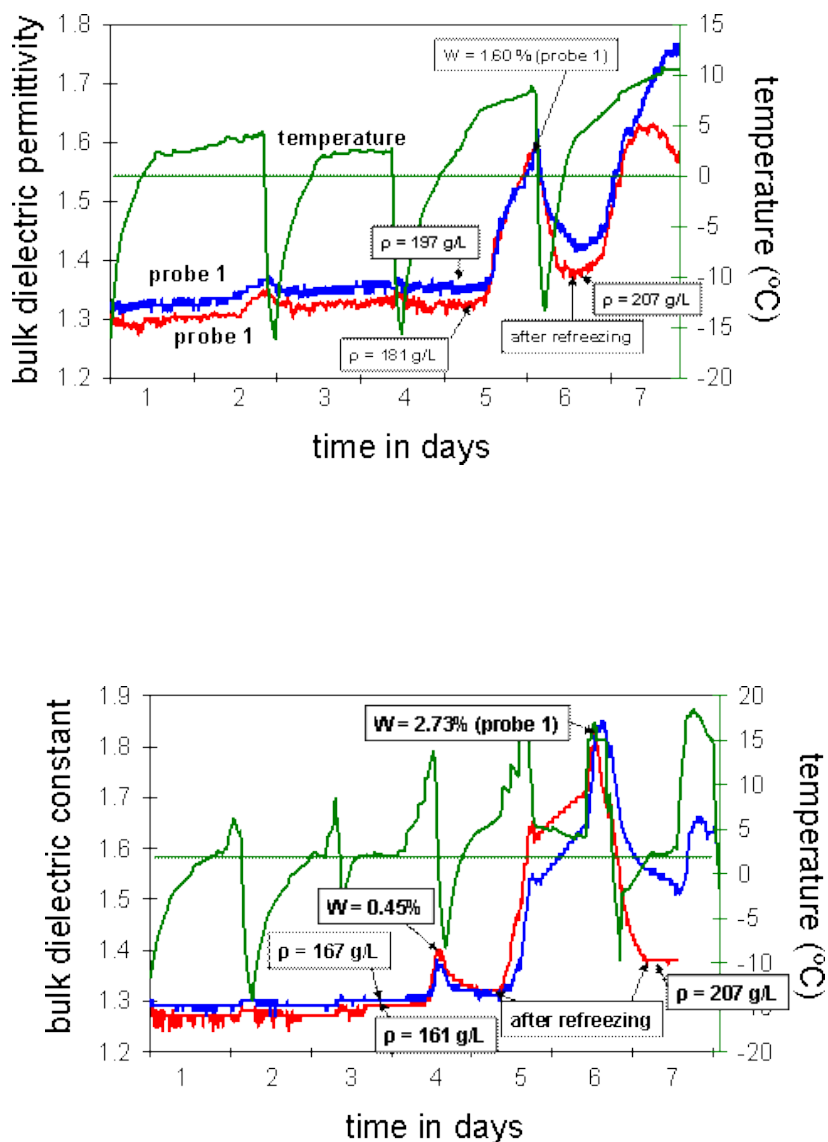


Figure 2: Temperature and bulk dielectric permittivities of two vertically stacked TDR probes during two snow melt experiments.

The bulk snow permittivity reflecting dry snow density (at temperatures below freezing) or wet snow water content (at temperature above freezing) was measured with two TDR probes over a period of several melt -freeze cycles during each of the two experiments. Probe 2 was stacked 5 cm below probe 1 within the bulk snow. The dry snow density is clearly higher around the lower probe 2 during both experiments. This difference becomes more pronounced after

major melt events. The water content was calculated by extrapolating the snow densities of the dry snow periods before and after a melting phase. Major melting periods are characterized by snow densification and metamorphism. Interestingly, temperatures around 3 to 5 °C over a time period of an entire day did not result in an increase of either snow density or liquid water content, presumably because air movement around the snow vessel and above the snow surface was extremely limited.

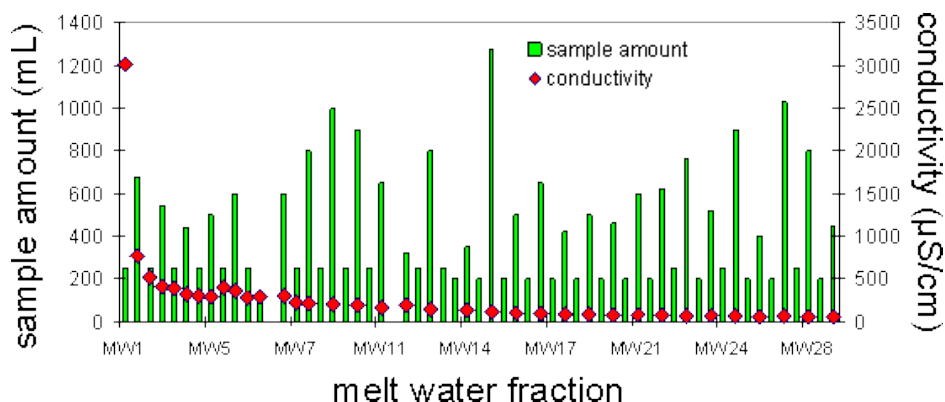


Figure 3: Conductivity of the meltwater leaving the snowmelt vessel.

During the second experiment the conductivity of the meltwater leaving the snowmelt vessel decreased rapidly from an initial maximum (Fig. 3). The first meltwater fraction was sampled after five melt-freeze cycles without any meltwater leaving the vessel. Melt-freeze cycles cause pollutants to freeze out of the snow grain lattice and accumulate in the quasi-liquid layer where they are available to enrich the next wave of infiltrating meltwater. During recrystallization the pollutants are not readily incorporated into the crystalline lattice causing their gradual segregation<sup>11</sup>.

Further refinement of the TDR methods combined with the inclusion of electric conductivity measurements of the bulk snow, and the PAHs analysis of the melt water samples are currently being implemented.

### Acknowledgement

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### References

1. Wania F., Hoff J.T., Jia C.Q., Mackay D. (1998) *Environ. Pollut.* 102: 25-41.
2. Simmler N., Herrmann R., Thomas W. (1986) In: *Modelling snowmelt-induced processes* IAHS Publishing.
3. Simmler N., Herrmann R. (1987) *Wat. Air Soil Pollut.* 34: 79-95.
4. Daub J., Herrmann R., Förster J., Robien A., Striebel T. (1994) *Wat. Sci. Tech.* 30: 73-85.

5. Wania F., Semkin R., Hoff J.T., Mackay D. (1999) *Hydrol. Proc.* 13: 2245-2256.
6. Schöndorf T., Herrmann R. (1987) *Nordic Hydrol.* 18: 259-278.
7. Lundberg A. (1997) *Cold Reg. Sci. Tech.* 25: 197-205.
8. Schneebeli M., Coléou C., Touvier F., Lesaffre B. (1998) *Ann. Glaciol.* 26: 69-72.
9. Or D., Jones S.B., VanShaar J.R., Humphries S., Koberstein L. (2004) WinTDR – Version 6.1, Soil Phys. Utah State Univ., Env. Phys, UConn.
10. Frolov A.D., Macheret Y.Y. (1999) *Hydrol. Proc.* 13: 1755-1760.
11. Colbeck S.C. (1981) *Water Res. Research*, 17(5): 1383-1388.