

A SIMULATION OF THE ENRICHMENT OF ATMOSPHERIC POLLUTANTS IN
SNOW COVER RUNOFF

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ABSTRACT

The soluble impurities contained in a snow cover can be concentrated as much as five fold in the first fractions of snowmelt runoff. In addition, daily impurity surges are possible. Melt-freeze cycles concentrate the impurities in the lower portion of the snow cover hence prepare the impurities for rapid removal. Environmental damage can occur due to the concentration and rapid release of atmospheric pollutants from the snow, especially in areas of "acid precipitation." The enrichment of the soluble impurities is explained and the results of laboratory experiments are given.

INTRODUCTION

Snowflakes are nucleated in the atmosphere by micron size particles. These nucleating particles can be either water soluble or insoluble and other particles can be collected by the crystals during their growth (Fletcher, 1962). Further attachments of impurities may take place by scavenging as the flakes move through the atmosphere. During deposition and between snow storms, dry atmospheric fallout and local sources of contamination add to the impurities contained in and on the surface of the snow cover.

Although the average concentration of soluble impurities in a snow cover is generally quite low, the first fractions of meltwater runoff from the snow cover are enriched with the soluble impurities which are swept out with the first infiltrating liquid. Thus, the snow cover can store and suddenly release chemicals which can do appreciable environmental damage, especially by increasing the acidity of runoff in areas subject to acid precipitation (Leivestad and Muniz, 1976; Johannessen and Hendriksen, 1978). The insoluble impurities are also important since they tend to collect on the snow surface and reduce the albedo. However, it is the soluble impurities which limited to the discharge from the snow cover and does not deal with the buffering and mixing which can occur in the soils.

The principles of water flow through snow are fairly well understood (Colbeck, 1978; Wankiewicz, 1979) and both theoretical considerations (Colbeck, 1977) and laboratory observations (Johannessen and Hendricksen, 1978) of impurity movements have been made. The phenomenon of impurity concentration deserves further investigation, however, because of the increasing problem of acid precipitation in industrialized areas and the potential for environmental disruption in areas where intense energy development may take place in the future.

Here we describe the processes of impurity movement through snow examining the effects of the distribution of an impurity within the snow, snow depth, and freeze-thaw cycles. Since snow covers in temperate regions are usually deposited in discrete storm sequences separated by rain and/or melt events, the pollutants are not usually

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distributed uniformly in the snow cover. Furthermore, the snow cover itself may be quite heterogeneous resulting in channeling of the flow down distinct flow paths (Gerdel, 1954). Large portions of the snow cover may be bypassed during the initial phase of runoff thus reducing the concentration of the impurities in the first melt fractions. Also, the distribution of snow and snowmelt may vary substantially over an entire drainage basin thus dispersing the pollutants over a larger portion of the seasonal runoff. Nevertheless, the initial meltwater fractions can carry a concentrated load of the pollutants in a manner which needs further investigation.

SNOW METAMORPHISM AND WATER FLOW

Once a layer of snow is deposited, the individual snowflakes disappear as the snow grains undergo continuous metamorphism characterized by increasing grain size and grain rounding (de Quervain, 1945). Thus the specific surface area of the snow is continuously reduced and the grain boundaries continuously migrate. Grain growth and grain boundary migration cause a segregation of impurities in all crystalline materials because the impurities are not readily incorporated into the crystalline lattice during recrystallization. Ammonia and flouride salts are most readily accepted into the ice lattice but only in molar ratios of about 1 to 5000 (Hobbs, 1974, p. 112). Other chemicals are rejected more completely and, due to the constant evaporation of smaller particles and the migration of grain boundaries, the snow grains are continuously purified. These processes concentrate the impurities on the grain surfaces; hence, most of the impurity load is carried where the liquid water moving through the snow can readily remove the solubles.

Once liquid infiltration wets the snow, the processes driving grain growth accelerate (see Fig. 1) and new equilibrium conditions are established for the most stable configuration of the grains (Colbeck, 1979). These dynamic processes help prepare the snow cover for rapid removal of the soluble impurities by further concentrating the impurities on the grain surfaces and in the liquid fillets and veins where they can be removed with the first rain or meltwater runoff.

Clearly the rate at which the impurities are removed depends upon the atmospheric conditions under which the snow was deposited as well as the degree and type of metamorphism the snow cover has experienced. The sequence and intensity of rain and/or melt events is also important. Therefore we describe the nature of water flow through snow before presenting the experimental evidence.

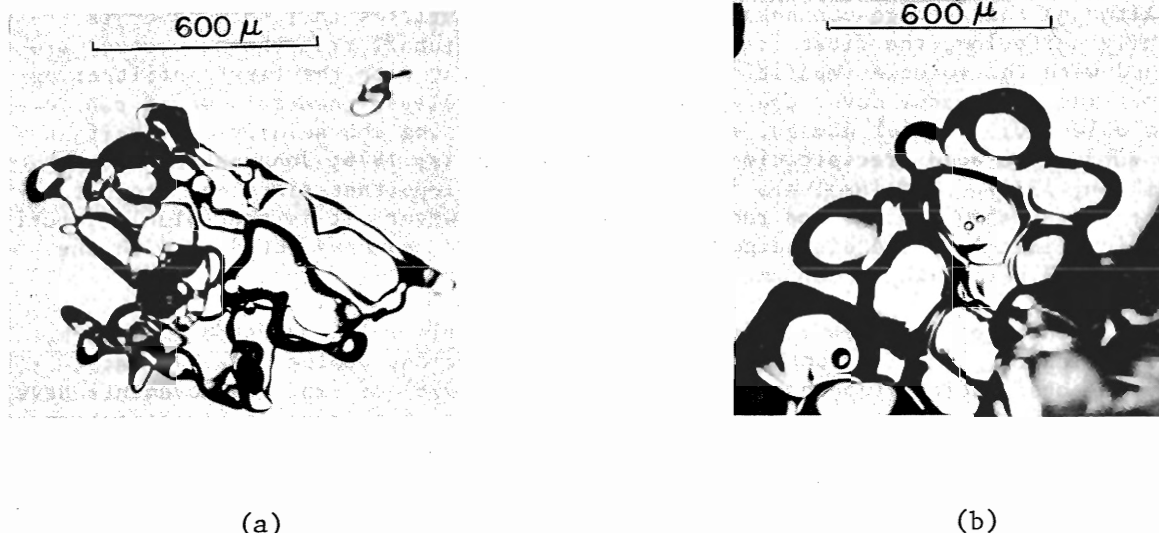


Figure 1. a. Dry snow grains before melting begins. These grains were stored at a low temperature for two years before being used in these experiments.
b. Snow grains on second day of melting.

Meltwater is mostly produced at and rainwater falls on the snow surface from which it percolates downward. When liquid water enters a dry snow cover (snow at a subfreezing temperature), part of the infiltrating liquid freezes in order to raise the snow temperature to the melting point but most of the retained liquid is held by capillary attraction (Colbeck, 1976). This is particularly true in the case of a fresh snow cover which has not experienced much grain rounding and still has minute crystalline branches with small radii of curvature (see Fig. 2). As the "wetting front" propagates into the dry snow, there is a general demarkation between the overlying wet snow and the underlying dry snow (Yosida, 1973). When sufficient rain and/or melt occurs, this wetting front arrives suddenly at the base of the snow cover and the first portion of the infiltrating liquid is available for immediate runoff and/or infiltration. Where only a small quantity of liquid is available, the wetting front may not reach the soil and the infiltrating liquid may be entirely retained in the snow. The sudden arrival of the wetting front and the daily meltwater wave are illustrated on Figures 3, 4 and 5 by a sudden increase in the volume of discharge. The basic reason for these sudden arrivals is the nonlinear relationship between water flux and concentration (Colbeck, 1978).

Depending on subsequent weather events, the retained liquid will either freeze in place or be available for flow during the next melt or rain event. If the snow freezes, the impurities are excluded by the freezing process and are pushed to the surface of the newly formed ice where they are available to enrich the next wave of

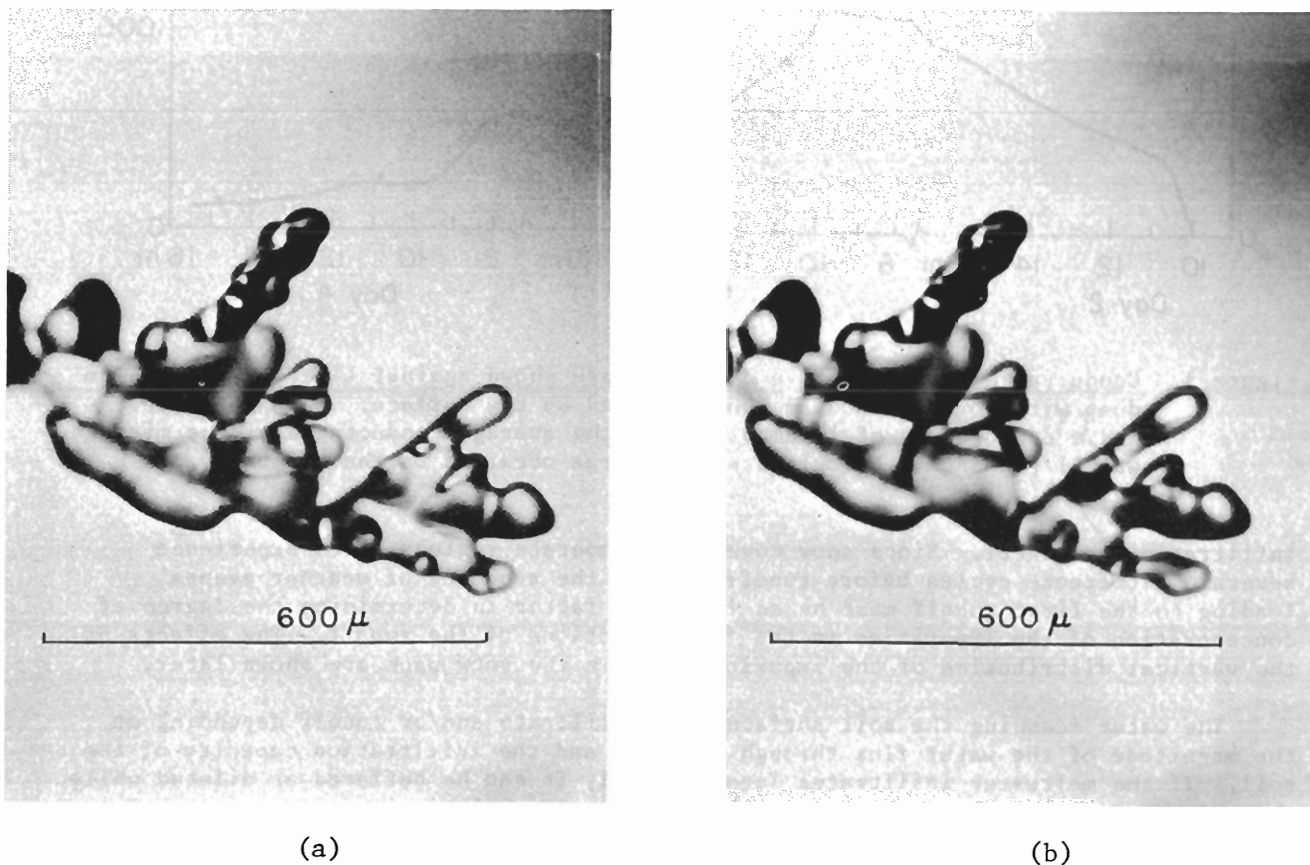


Figure 2. As meltwater reaches the grains in dry snow, much of the liquid is retained between ice surfaces as shown here. Grain rounding proceeds rapidly once the snow is wetted and some of the water will soon be released. Although liquid does not cover the entire ice surface at this point, soluble ions on the ice surface are quite mobile so both the retained liquid and mobile liquid (in the form of discrete drops or flowing films) become enriched in the soluble impurities. As melting and drainage proceed, the liquid meniscus jumps between the two positions shown in a and b.

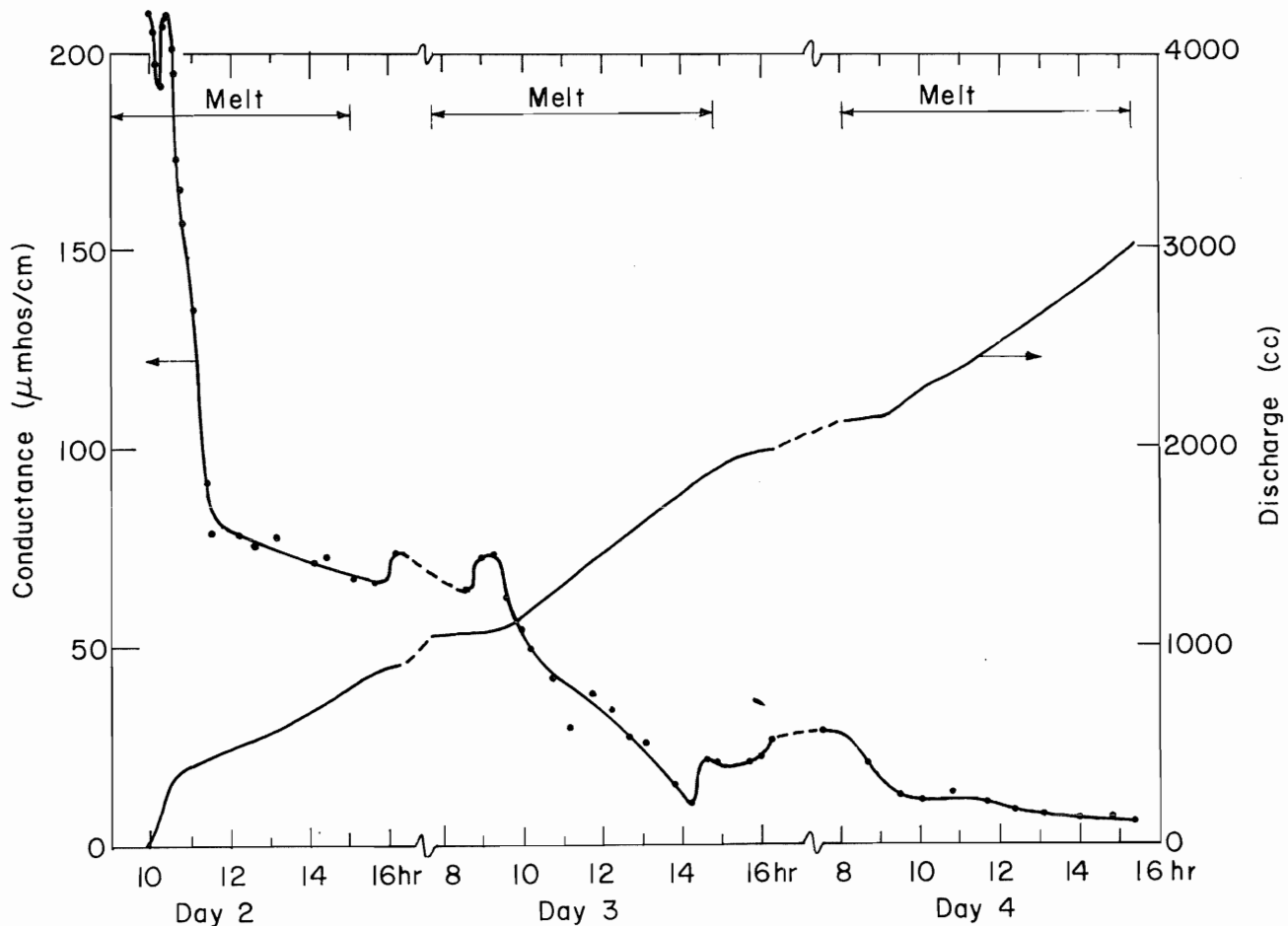


Figure 3. Conductance and cumulative discharge are shown against time for snow 35 cm deep with powdered sodium chloride added on the surface. The snow itself had a conductance of 12 $\mu\text{mhos/cm}$ and the average conductance of the mixture was 41 $\mu\text{mhos/cm}$. No meltwater discharge occurred on the first day of melting.

infiltrating meltwater. Since snow covers in temperate regions often experience several melt-freeze cycles before runoff begins, the sequence of weather events leading to the first runoff must be an important factor in determining the degree of concentration of the impurities in the first fractions of the runoff. The effects of the vertical distribution of the impurities within the snow pack are shown later.

The water reaching the soil surface will infiltrate and/or runoff depending on the magnitude of the water flux through the snow and the infiltration capacity of the soil. If the meltwater infiltrates into the soil, it can be buffered or diluted while the meltwater moving along the soil surface can remain relatively concentrated. The overland flow component of snowmelt runoff has been measured to be as high as 100% (Dunne et al., 1976) and as low as 0% (Price et al., 1979). The overland component travels through the bottom layer of the snow. The water moves through a liquid saturated layer in a mode of flow which differs significantly from that of the unsaturated infiltration in the overlying snow. During this lateral movement over the soil surface, the runoff could be further enriched if soluble impurities from atmospheric fallout had accumulated on the soil surface prior to the emplacement of the seasonal snowcover. Likewise, the runoff could be buffered by chemical reactions between the moving water, the vegetation, and the soil. Hornbeck and Likens (1974) also suggest that leaching from the organic matter in the snow can be important. We do not treat these considerations because they are site and season specific, but turn over attention to the movement of the impurities in the snow.

The movement of the impurities with the water in snow has not been as thoroughly investigated as the movement of the water itself. Nevertheless, we can use the information available about impurity movements on other porous media (e.g. Greenhorn and Kessler, 1970; Bear, 1972) to achieve a general understanding of how impurities should move through snow.

We are concerned with soluble impurities which are quickly dissolved by the infiltrating water. Since the infiltration is not completely uniform, there will be some bypassing of impurities (these impurities will be picked up by subsequent flow). In general there are two types of mixing as the impurities move with the meltwater through the snow:

- (1) Molecular diffusion due to local differences in the concentration of impurities.
- (2) Mechanical dispersion caused by velocity variations in the flowing liquid.

Molecular diffusion tends to spread the impurities so that the moving water can pick up impurities from local sources or, if the lower levels of the snow are relatively pure, molecular diffusion will raise the impurity levels in the lower layers by reducing the concentration of the flowing water. Molecular diffusion increases with the liquid water content (Colbeck, 1977). Mechanical dispersion increases with the speed of the flowing water and is highly dependent on the geometry of the pore space. The relative significance of these two dispersive mechanisms is characterized by the Peclet number ($P_e = vd/D$ where v is the velocity of the flowing water, d is the grain size, and D is the coefficient molecular diffusion).

The appropriate values of this dimensionless number for the flow of water through snow suggest that at high fluxes ($10^{-6} \text{ m}^3/\text{m}^2/\text{sec}$), hydrodynamic dispersion is dominated by mechanical dispersion whereas molecular diffusion becomes relatively more important at low flow rates ($10^{-7} \text{ m}^3/\text{m}^2/\text{sec}$). The consequences of this are illustrated later.

EXPERIMENTAL PROCEDURES AND RESULTS

Powdered sodium chloride crystals were added to sieved snow to raise the average level of soluble impurities to that observed for acid precipitation in Scandinavia (Johannessen and Hendriksen, 1978). The snow samples with varying impurity distributions and snow depths were then melted with varying melt-freeze cycles in a container in a temperature controlled cabinet ($\approx 0.1^\circ\text{C}$). The melting was by radiation absorption on the snow's surface (at a rate comparable to intense natural melt) and the meltwater discharge was collected at the bottom for frequent volume and conductivity measurements. It is important to note that a "liquid tension" was drawn on the bottoms of the snow samples by keeping the bottoms in contact with a semi-permeable ceramic plate. The "liquid tension" is necessary to prevent the accumulation of meltwater in a saturated layer at the base of the sample. In spite of this procedure some dilution of the initial meltwater fractions took place by mixing in the bottom of the experimental apparatus. Also, the initial concentration of the discharged water may have been reduced by the large size of the sodium chloride particles (10 to 100 μm) used in these experiments (the smaller, more evenly distributed atmospheric particles would probably be dissolved more rapidly by the infiltrating water). These factors tend to offset the fact that the melting and flow are more uniform in the experiments than in nature. At the impurity concentrations used in these experiments, the impurities had little effect on the melt rate or meltwater movement.

The results of three experiments are shown on Figures 3, 4, and 5. The large initial concentration shown on Figure 3 is typical of the results and is analogous to the increased acidity of the first fractions of snowmelt runoff observed in nature. The initial concentration of the meltwater discharge is about five times as large as the average impurity concentration in the snow, a figure which falls within the range of values (three to seven) of Johannessen and Henriksen (1978). Although the concentration drops rapidly during the first few hours of discharge, the average concentra-

tion throughout the first day of runoff (second day of melt) is about two and one-half times the average concentration of the mixture itself. Thus the entire first day's snowmelt runoff would present an enhanced threat of pollution, especially in situations where the runoff is not diluted by simultaneous groundwater flow. For this particular example, the concentration decreases rapidly throughout the second day of discharge, dropping below the average of the original snow-salt mixture. On the third day of discharge, the concentration of dissolved impurities falls below the impurity level of the original snow, indicating that most of the added impurity and some of the indigenous impurities, such as the snowflakes nuclei and surface adsorbed ions, have been removed.

In the experiment shown on Figure 3 the salt was dissolved at the melting surface and carried into the snow where refreezing during the first night concentrated the salt solution. On the second day of melting, those concentrated droplets were removed with the runoff. In the experiment shown on Figure 4, meltwater was produced on the first day of melting because of a lesser snow depth (the melting rate was the same throughout all experiments).

Although the average concentration of the snow-salt mixture was greater in the second experiment, the concentration of the initial runoff was significantly less, apparently because the meltwater was not concentrated by refreezing overnight before the discharge began. The first day's runoff shown on Figure 4 has an average concentration of only two and one-half times the average of the original snow-salt mixture and the maximum value observed was much less than that observed in the first experiment.

The results of a third experiment are shown on Figure 5. The only difference between the second and the third experiments was the initial distribution of the added sodium chloride; in the second experiment the salt was distributed evenly in four, equally spaced layers and in the third experiment the same amount of salt was placed in the bottom 2 cm of the 17 cm sample. While placing the salt at the bottom may seem to prejudice the experiment, it must be remembered that melt-freeze cycles (which often precede snowmelt runoff) concentrate the soluble impurities at the base of the snowpack. In fact, this is shown by the results on Figure 3. Also, atmospheric fallout preceding the onset of snow accumulation could place soluble impurities on the soil surface where they would be picked up by the first snowmelt runoff. Concentrating the impurities at bottom of the snowpack enhances the effect of the snow on the impurity content of the runoff. The initial fraction of the runoff carries a larger impurity load than seen in the previous experiments although the concentration drops rapidly throughout the first day of runoff. After melt ceases on the first day, runoff slows markedly and molecular diffusion of the impurities becomes relatively more important (as stated earlier molecular diffusion is more important at low flow rates). The impurities spread by diffusion throughout the lower portion of the snow column such that the next day's meltwater wave is enriched and a second spike of concentrated meltwater is discharged. Again the concentration drops rapidly following the arrival of the daily meltwater wave. A similar phenomenon occurs on the third day but by then the snow is largely depleted of its impurity load.

The release of daily slugs of enriched runoff shown on Figure 5 indicates a patterned release of impurities with short duration pulses of concentrated solution. The concentration begins dropping shortly after the arrival of the daily meltwater wave so the highest concentrations on the second and third day are initiated during the periods of the lowest flow rates. Therefore, the amount of impurity being discharged is not as great on the second day as on the first day, even though the concentration itself is greater on the second day.

DISCUSSION AND CONCLUSION

It is well known that snowmelt occurs in a variety of circumstances with significant variations from year-to-year and place-to-place. The sequence of snow storms, rain, and melt events combine to form a situation which may favor either slow or sudden release of the soluble ions contained in the snow cover.

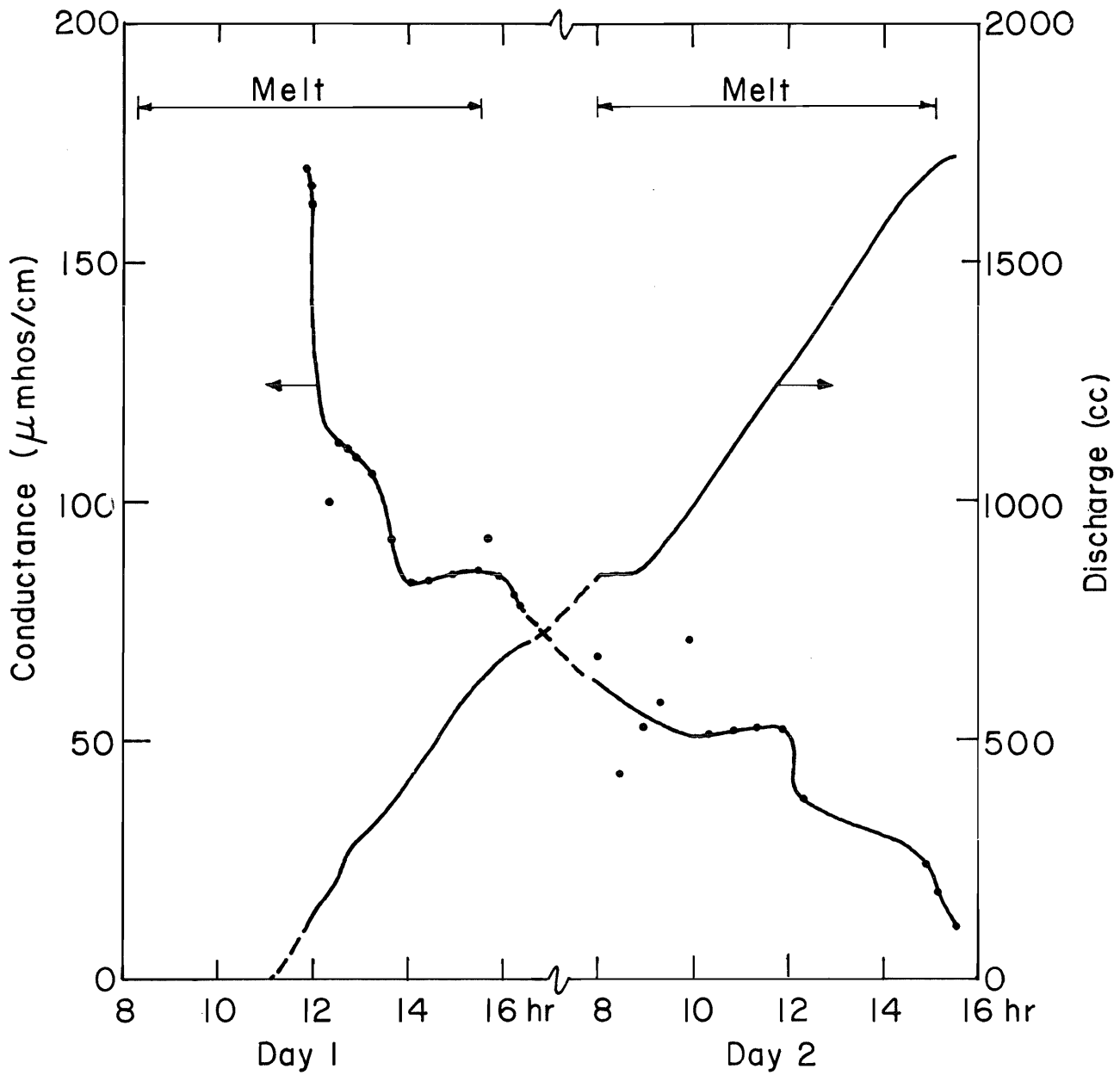


Figure 4. Conductance and cumulative discharge are shown against time for snow 17 cm deep with sodium chloride distributed in four, evenly spaced layers. The snow itself had a conductance of 12 $\mu\text{mhos/cm}$ and the average conductance of the mixture 67.9 $\mu\text{mhos/cm}$. Water discharge began on the first day of melting.

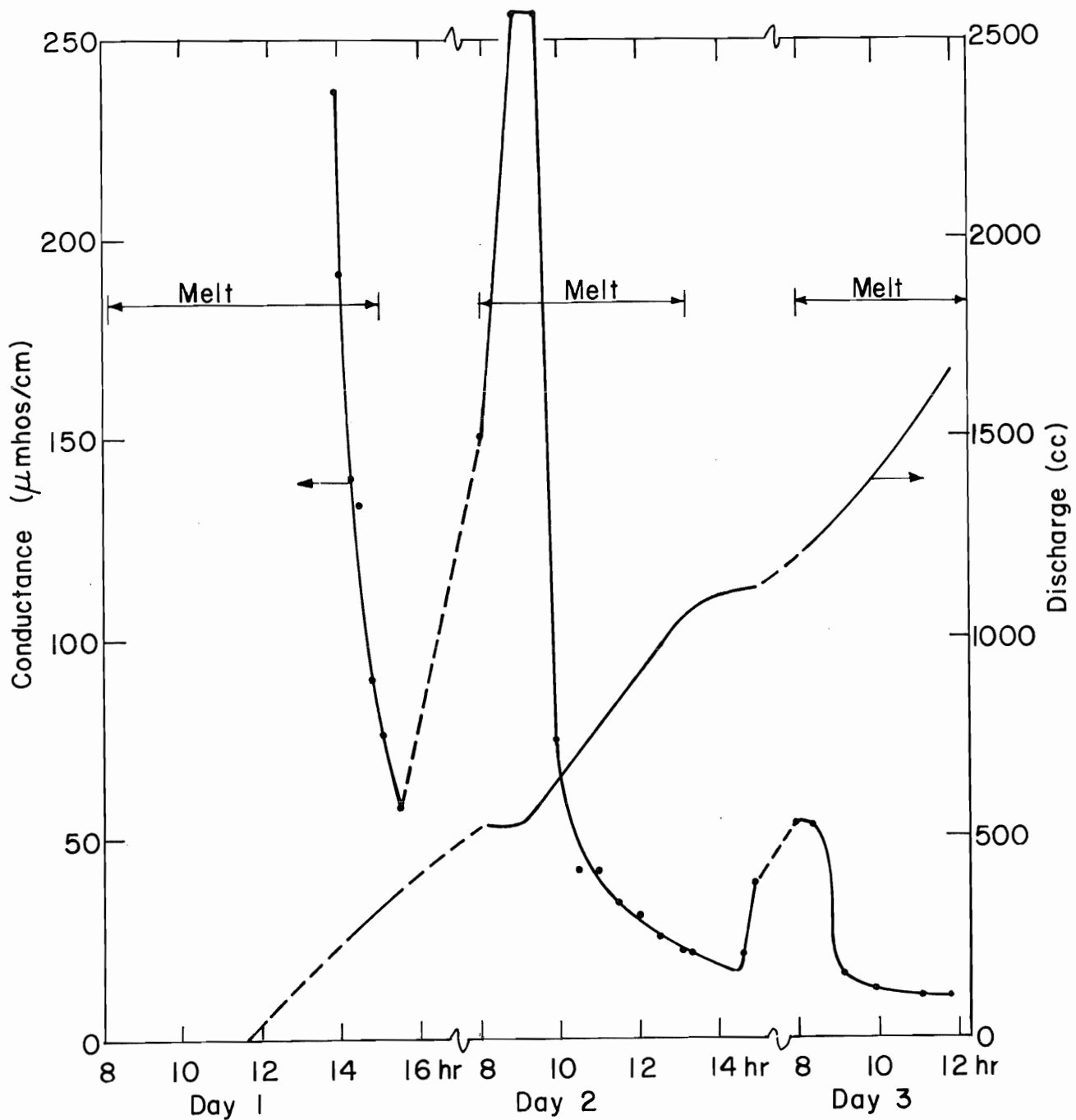


Figure 5. Conductance and cumulative discharge are shown against time for snow 17 cm deep with sodium chloride distribution in the lower 2 cm in the snow. Water discharge began on the first day of melting.

Based on this laboratory study, one of the worst scenarios for environmental damage by the sudden release of atmospheric pollutants from the snow cover would be a sequence of melt-freeze cycles followed by a slow melt ($10^{-7} \text{ m}^3/\text{m}^3/\text{sec}$) or rain. The melt-freeze cycles could remove the impurities from the upper portions of the snow cover and concentrate them in the lower portions where they can be quickly removed with the early water runoff. At the lower flow rates, molecular diffusion is rela-

tively important so the impurities get into the moving water by diffusion away from their discrete sources. The combination of these two conditions could remove the largest quantity of impurity with the minimum quantity of meltwater. This situation could produce the maximum concentration of impurities although at less than maximum flow rates. This scenario would probably be most damaging to an aquatic system with a rapid turnover and minimal groundwater flow.

In other systems the maximum rate of release of the impurities might be most important or the repeated daily releases of sudden bursts of impurities as shown on Figure 5. Whatever the most damaging sequence for a particular location, it is very likely to occur at least on an occasional year because the pattern of weather events leading to snowmelt runoff is quite variable.

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