Organic Chemical Permeation and Storage in Seasonal Snow

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ABSTRACT

Experiments were conducted near the laboratory, where shallow trays or inverted containers containing nitroaromatic compounds as vapor sources were placed in contact with the surface prior to snowfall. Snow was allowed to accumulate over the sources, and the temperature profile within the adjacent snow and soil was recorded. After several days snow blocks were collected at 5-cm intervals above the trays. Snow densities, particle sizes, and grain character were determined on site. Nitroaromatic compounds in the meltwater were determined in the laboratory by liquid chromatography. Their concentrations were examined with respect to temperature gradient, snow density, and grain size distribution and found to vary systematically with distance from the source. None of the specimens analyzed contained the equivalent of a monolayer of compound based on the estimated specific surface of the snow. The front of instrumental detection of nitroaromatics was a function of the vapor pressure of the particular source compound; DNT permeated about 1 cm/day in “dry” snow.

Key Words: Nitroaromatics, Permeation, Seasonal snow

INTRODUCTION

The research described in this paper combines an applied experiment in contaminant exploration with a fundamental investigation of a dynamic aspect of geochemistry. There are places where chemical contaminant disposal occurred prior to current waste disposal regulation, and remediation of these contaminants must be completed before the land can be returned to use. Soil sampling and analysis required to examine the nature and extent of soil contamination prior to selection of remediation processes is expensive and may generate secondary wastes. An earlier experiment showed that organic compounds would permeate upward from soil into snow above (Legget and Hogan 1994). The extent to which this process provides noninvasive exploration into the nature and extent of soil contamination is of some interest.

Goldberg (1978) and more recently Wania and MacKay (1993) suggested that Arctic snow acts as a “cold trap” for semivolatile atmospheric contaminants generated in more temperate regions. The air/snow interface is also usually colder than the snow/soil interface (Munn 1966), and thus could act as a trap for evolved soil vapors. Our previous experiments have shown upward permeation of several compounds within the snowpack, which is regulated by their source strength. We found that 2,4-dinitrotoluene (DNT) concentrations in a series of snow blocks over contaminated soil decayed as the log (or square root) of height over the source. The profile of trinitrotoluene (TNT) appeared to be similar, but the absolute concentrations were smaller, corresponding to its lesser vapor pressure. Compounds with greater vapor pressures than DNT (p-nitrotoluene, bromoform, and naphthalene) were not as regularly detected in the samples. We were unable to measure the horizontal dispersion of compounds in that experiment, although we had previously detected lateral movement of TNT in wet snow. The mechanism of contaminant movement in prior experiments was not clearly defined. The experiment described here was conducted during the winter 93–94, and through a combination of favorable field conditions and improved sampling design, provides a more definitive description of contaminant flux.

EXPERIMENTAL METHODS

We used explosives and related nitroaromatic compounds as vapor sources, as before. In addition to being of practical interest as contaminants, they have characteristics which make them excellent tracers as well: these compounds are not found in nature, are easily measured, and cover a wide range of vapor pressures. The compounds used as vapor sources in these experiments are tabulated in Table 1. The vapor sources were usually spiked in dried and sieved local silt soil at concentrations of approximately 1 g/kg in the form of small grains or crystals. Nitroglycerin (NG) was added in the form of smokeless powder, a blend of nitroglycerin and nitrocellulose.

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### Table 1. Sources of vapor.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vapor pressure at 0°C (torr)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paranitrotoluene (PNT)</td>
<td>$4.9 \times 10^{-3}$</td>
<td>Submillimeter grains in silt (1 g/kg)</td>
</tr>
<tr>
<td>2,4-dinitrotoluene (DNT)</td>
<td>$6.2 \times 10^{-6}$</td>
<td>Submillimeter grains in silt (1 g/kg)</td>
</tr>
<tr>
<td>2,4,6-trinitrotoluene (TNT)</td>
<td>$1.8 \times 10^{-8}$</td>
<td>Recrystallized Eastman TNT in silt (1 g/kg)</td>
</tr>
<tr>
<td>Nitroglycerin (NG)</td>
<td>$1.9 \times 10^{-4}$</td>
<td>Double base smokeless powder in silt (-5 g/kg)</td>
</tr>
</tbody>
</table>

In most of the experiments, aluminum trays, 0.2 × 0.3 × 0.05 m, were used to contain a 3- to 5-mm layer of spiked soil. This served to isolate the contaminated soils while providing thermal contact with the soil below. A small thermistor bead was attached to the bottom of each tray. Some additional sources consisted of a few milligrams of pure compound in a ventilated bottle or short open-sided cylinder. These were suspended in the snowpack to examine horizontal permeation. A diagram describing the experimental geometry and instrumentation is given in Figure 1.

Tray locations were marked by stakes early in the winter. Thermistors were inserted to depths of 0.1 and 0.3 m in the soil proximate to several trays prior to ground freezing. An additional thermistor was suspended in the thatch just above the soil to measure the undisturbed interface temperature at the same elevation as the tray bases. Another thermistor was fixed at 0.3 m above the surface in anticipation of providing an in-snowpack temperature.

Semi-shielded, air temperature thermistors were placed at 8, 4, and 2 m above the soil surface. A gantry was provided central to the tray locations to allow thermistors to be adjusted to elevations 0.3 and 1.0 m above the snow surface. A "float" was fabricated to provide a sky-shielded thermistor mount 0.01 m above the snow surface. Other thermistors were placed in the soil, and atop the soil within 100 m of the experiment, to aid in diagnosing dynamic freezing and thawing events.

### SPECIMEN COLLECTION AND ANALYSIS

The sample collection protocol was designed to obtain chemical profiles in the snow following extended periods in which snowpack temperatures remained below freezing. This was to avoid potential complications that would have been introduced by the presence of liquid water. A chronology of soil, soil/snow interface, and air temperatures within and at the surface of the snowpack was maintained to provide a record of temperature transients and to use as a forecast tool to conduct sampling.

Snow samples were collected with a 5-cm nominal La Chapelle stainless steel rectangular corer, weighed, and immediately transferred to pre-cleaned, 16-ounce, wide-mouth jars with Teflon-lined screw caps. They were maintained at −30°C until analyzed. Analyses were completed within 24 hours of removal from cold storage. The melted snow was analyzed for the tracer compounds by high-pressure liquid chromatography (HPLC)/UV spectrometry using well-established methods developed in-house (Jenkins et al. 1986). Mass/volume concentrations in water obtained from HPLC analysis were practically equivalent to mass/mass concentrations. The volumetric concentration in the original snow was found by multiplying this number by the snow density as calculated from the experimentally measured snow mass and known dimensions of the La Chapelle corer.

### RESULTS AND DISCUSSION

A chronology of temperatures and snow conditions at the experiment site is given in Figure 2. The tracer-spiked soil sources were placed on 3 January 1994, and were covered to a depth of 60 cm in a few days. The snows that occurred during early January 1994 precipitated from relatively cold air and were made up of unrimed crystals characteristic of cold clouds. The air
Figure 2. Chronology of snow cover and soil, snow and air temperature at the experiment site. Stellars denote snowfall, hexagons surface frost, and filled circles rain. Plotted lines are isotherms.

above the snow was consistently less than 0°C and was quite frequently −20° to −30°C through 21 January.

A column of specimens was collected just after local sunrise on 21 January 1994, under ambient air temperature of −30.3°C, in 61 cm of natural snow. The tracer source was located from the pre-placed stakes defining the tray corners. Working space was excavated about 15 cm west of the tray and the wall was sheared for examination. The air had remained quite cold and calm during the accumulation period, and there were no glaze or dust crusts. The chronology of snow accumulation was discernible from visible and strength differences at interfaces. Snow grain type and size were examined with a hand lens, and Formvar replicas were made for later microscopic analysis.

The temperature within the snowpack was determined at 5-cm intervals with a fast-response, air-temperature thermistor. The shield was 1 cm in diameter, and the snow column was still in shade when measured. Some warming of the upper 10 cm of the pack occurred during sample collection concurrent with an air temperature increase to −23°C.

The wall was sheared vertically along the west edge of the source tray and sampling begun, with vertical dimensions gauged with a meter stick imbedded in the pack adjacent to the sample column. Sampling of a single stratum is sometimes difficult because of its thinness or slope of the bedding. Snow may slump or collapse as the sampling wall is exposed or deform in the path of the corer. For these reasons the geometric sampling uncertainty is estimated to be about ±2 cm on each of the three axes. This should be kept in mind when examining sample heights, temperatures, and strata ages in Figure 3.

The dotted line at 6.5 cm in Figure 3 is the snow surface of 5 January, and the center of height of the lowest collectable specimen. A sample collected at or below the tray lip at 4.0 cm might contain pure source material. The DNT concentration above this minimum level diminishes with the logarithm (or square root) of distance; within the 2-cm resolution of collection, the minimum height point also lies along the same line.

Peranitrotoluene (PNT) is just detectable in the layers below 18 cm, which is the snow that fell prior to 11 January. The snow that fell on 17 and 18 January was overlain by −25°C or colder air until collected on 21 January, at −30.3°C. The PNT vapor apparently permeated the relatively warm snow present before 17 January, but was captured by the relatively cold upper snow layers of 17–21 January. In the center panel of Figure 3, the PNT concentration can be seen to increase concurrently with the increasing negative temperature difference.

The right panel of Figure 3 shows that the DNT concentration diminishes as the log of vertical distance
above the source. Near the snow/air interface the DNT concentration just exceeds the threshold of detection, and there is a hiatus in the progression at around 30 cm where no DNT was detected. The nitroglycerin (NG) concentration is less than the DNT concentration although NG has a greater vapor pressure. This is believed to be due to our use of smokeless powder as the source material, which probably has less source strength than pure compound.

The air temperature at the experiment site remained quite cold through 28 January. Air temperatures near -40°C were observed on 27 January, followed by a rapid warming and more than 1 cm of liquid precipitation on 29 January. This liquid precipitation thoroughly infiltrated the snowpack in some places. The temperature profiles on those days, at the primary sensor array, indicated that the snowpack was 0°C throughout as was the soil to 30 cm below. The liquid precipitation produced quite variable changes in the snow cover. Several places within a few kilometers of the site had continuous glaze upon the surface. Pit analysis in the vicinity of the experiment found discontinuous and scattered ice lenses about 1 mm in thickness and a few centimeters in length. Some temperatures at the snow/soil interface in the vicinity of the sensors indicate liquid water had pooled there for several days without refreezing. Other snow/soil interface temperatures remained subfreezing through the period, indicating that no liquid had penetrated to that level in those places.

A strong flow of cold air resumed following this brief thaw. The surface temperature approached 0°C for the first time on 15 February, and a second snow column was collected for analysis on 17 February 1994. The results of this collection are presented in Figure 4. The concentrations of DNT and NG again diminished proportionally to the logarithm or square root of distance from the source. TNT was now detectable adjacent to the source, but no PNT was detectable in any stratum.

The concentration profiles in Figure 4 are quite similar to profiles obtained from other collections in which native snow has overlain spiked soil for 30 days or more. The characteristics of these profiles are:

1. The concentrations of compounds with vapor pressures of greater than $10^{-3}$ torr are below the threshold of detection of the HPLC method.

Figure 3. Snow stratigraphy, temperature structure, and tracer chemistry, 21 January 1994.

Figure 4. Snow stratigraphy, temperature structure, and tracer chemistry, 17 February 1994.
2. The concentrations of compounds with vapor pressures in the range $10^{-4}$ to $10^{-6}$ torr lie along an orderly gradient proportional to the logarithm or square root of distance from the source. The concentration at a specified distance from the source increases with time.

3. The concentrations of compounds with vapor pressures less than $10^{-6}$ torr appear to have the same distance dependence, but are confined to layers a few (<20) centimeters from the source.

Figure 2 shows that the snow/soil interface temperature remained near 0°C throughout the experiment. The −5°C isotherm is present in snow 30 cm above the snow/soil interface for extended periods, and was relatively constant for 5 days prior to both snow samplings. The plotted points above the snow chronology show that the temperature difference from the 30-cm level to the surface was greater than 20°C during the 48 hours preceding the sampling of 21 January, but less preceding the sampling of 17 February. We propose that the characteristic concentration gradient found in the lower 30 cm of snowpack is associated with the relatively constant temperature and temperature gradient found there. The absence of tracer in the layers above 30 cm may be due to midday warming (Colbeck 1989, Jordan 1991) accompanying the greater incoming solar radiation of February.

The sampling of 21 January (Fig. 3) is the only successful detection of PNT in several sampling attempts. The air above the experiment was −30°C at the start of sampling and just slightly above −20°C at completion. The characteristic odor of PNT was discernible during excavation of the access pit, but little PNT was found adjacent to the source. The PNT was found only in the layers near the surface with least temperature. The PNT concentration was proportional to temperature decrease in the layer, rather than to distance from the source.

These and prior experiments have found concentrations of NG, DNT, and TNT in snow above a spiked soil source to diminish with elevation directly over the source. A parallel sampling obtained on 17 February, 40 cm northeast of the edge of the source tray showed no detectable amounts of NG, TNT, DNT, or PNT in any layer. Prior experiments in shallower snow also provided a null at 30-cm horizontal distance. The consensus of these experiments is that NG, DNT, and TNT permeate from soil to surface along the temperature gradient, although a spread of only 0.25 cm horizontal for each centimeter of vertical rise would give a similar concentration gradient. The pseudo-permeation rate is roughly 1 cm per day for DNT, and 1 mm per day for TNT. NG appeared to permeate more slowly in these experiments, which could be due to the lower source strength of the smokeless powder source or to greater affinity of NG molecules for the ice surface, or both.

DNT appears to permeate at about 2 cm per day in the experiment shown in Figure 3, which could be due to the lesser snow density and larger temperature gradient during that exposure.

While we cannot uniquely identify all the processes responsible for permeation from these few experiments, we can eliminate some from consideration. Unrestricted vapor diffusion through the air within the snowpack would distribute the tracer upward through a 1-m pack in a day, while nearly the total winter would be required for tracer to move 1 mm through solid ice by diffusion. These two limiting cases aside, we propose that diffusion through the porous medium retarded by molecular interactions with the snow particles, under the influence of temperature, is the most reasonable hypothesis that explains the experimental results. The observed volumetric tracer concentrations in snow would be a function of source strength, distance from source, the surface area of snow per unit volume and, apparently, temperature. Presumably, the preferential movement of tracer along the temperature gradient results from the temperature dependence of the vapor/snow sorption coefficient (per unit surface area) under the quasi-equilibrium conditions prevailing in the stratum. Vapor/ice sorption coefficients and heats of adsorption have recently been measured for a few organic compounds (Goss 1993). Heats of adsorption of several compounds on ice were similar to their heats of (self)condensation, which qualitatively accounts for the nitroaromatic permeation patterns' relationship to vapor pressure and snow temperature observed here. A more precise and general model for organic compound sorption on ice will require a consideration of the specific interactions of the ice surface with individual chemical species. The concentrations of compounds detected in our experiments were less than would be required for monolayer coverage on the available surface of any stratum analyzed.

CONCLUSIONS

We have found that the permeation of organic tracers in native snow is a dynamic process, probably dominated by the vapor pressure of the tracer and the temperature gradient in the snowpack. It will be necessary to further refine the resolution of snow sampling, and further examine dynamics of temperature gradients within snowpack, to uniquely describe the permeation process. The cold-trapping of airborne organic compounds by snow may provide only temporary storage. The dynamic movement of these chemical tracers in snow was sufficiently orderly to continue to consider snow sampling as a method of exploration for soil contaminants.
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REFERENCES


