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REPORT 89-8



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Ice-water partition coefficients for RDX and TNT

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Cover: Experimental setup.

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April 1989



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Susan Taylor



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19. ABSTRACT (Continue on reverse if necessary and identify by block number) An ice-water partition experiment using RDX and TNT was conducted to determine the efficiency with which the formation of ice excludes nonvolatile organic compounds. RDX and TNT are being used by CRREL as substitutes for volatile organics to see if freezing can move organics in saturated soils. Knowledge of the behavior of RDX and TNT, i.e., diffusivity and partition coefficient, is important for determining the conditions under which they, and the volatile organics of interest for hazardous waste cleanup, might be moved. TNT and RDX are excluded from the ice structure at freezing rates of up to 9×10^{-5} cm/s (3.1 in./day). An upper limit for the partition coefficient, <i>K</i> , was estimated using the measured effective partition coefficient and the growth rate of the ice.			
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PREFACE

This report was prepared by Susan Taylor, Geologist, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. The project was funded through DA Project 4A161102AT24, *Research in Snow, Ice and Frozen Ground*; Task SS, *Combat Service Support*; Work Unit 020, *Prediction of Chemical Species Transport in Snow and Frozen Ground*.

The author thanks Dr. Gordon Cox, Thomas Jenkins and Daniel Leggett for their help (and equipment), which made this study possible. Thanks also go to Nancy Perron for demonstrating use of the microtome and Dr. Olufemi Ayorinde, Daniel Leggett and Dr. Gordon Cox for reviewing the paper.

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Ice-Water Partition Coefficients for RDX and TNT

SUSAN TAYLOR

INTRODUCTION

The purpose of this study was to measure the partition coefficients (between water and ice) of RDX and TNT and to determine how rapidly these substances can diffuse away from a freezing front. Partition coefficient is used here in a nonrigorous sense and describes how much TNT or RDX is in the liquid versus the ice phase at nonequilibrium conditions. Studies of this kind have been done using brine (Cox and Weeks 1975), but no data exist on the partition coefficient^{*} between ice and water for organic molecules.

This work was conducted as part of a research program investigating the use of artificial freezing for decontamination of soils. Since RDX and TNT are being used to see if freezing can move organics in saturated soils, knowledge of their behavior, i.e., diffusivity and partition coefficient, would help determine the conditions under which they, and the volatile organics of interest for hazardous waste cleanup, might be moved. An ice-water partition experiment using RDX and TNT was conducted to determine the efficiency with which the formation of ice excludes nonvolatile organic compounds. An upper limit for the freezing rate needed to exclude large, nonvolatile organic molecules, i.e., TNT, RDX etc., from the ice structure was calculated for this experiment.

EXPERIMENTAL METHODS

A 1-mg/L solution of RDX and TNT in reagent grade water was prepared using production grade RDX and TNT purchased from Eastman Kodak. The solution was made up in two 20-L jugs and was mixed continuously for two days. The jugs were covered with tinfoil to exclude light. The solution was then transferred to a 30-cm-wide by 40-cm-long by 30-cm-high reservoir and subjected to a

0.367°C/cm temperature gradient (11°C/30 cm). The base of the Plexiglas container was maintained at 1°C and the freezing plate, which also served as the top of the container and was in contact with the solution, was kept at -10°C. Two holes at the base of the container served as overflow conduits for solution pushed out during ice formation. The sides of the container were insulated with polystyrene insulation board. This experimental setup (see Fig. 1) resulted in a horizontal ice/water boundary, indicative of unidirectional freezing, in which the ice grew from the top downward.

The freezing rate was not constant, being faster at the beginning than at the end of the experiment. The ice thickness was periodically marked on the Plexiglas container and an estimate of the freezing rate was obtained by plotting the ice thickness versus time. Unfortunately, the ice growth was not monitored until the second day (when I discovered that the data logger connected to the thermocouples was not working properly), so information on the fastest ice growth is not available. Based upon information derived from ice growth in brines,^{*} a 3rd order polynomial curve was fit through the points and the origin (Fig. 2) to project ice growth on the first day.

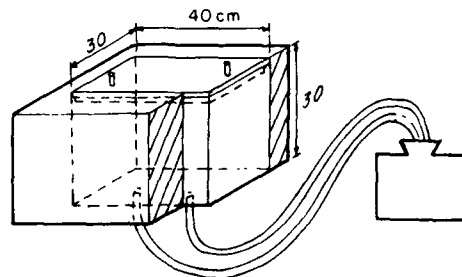


Figure 1. Experimental setup.

^{*}Personal communication with Dr. Gordon Cox, CRREL, June 1988.

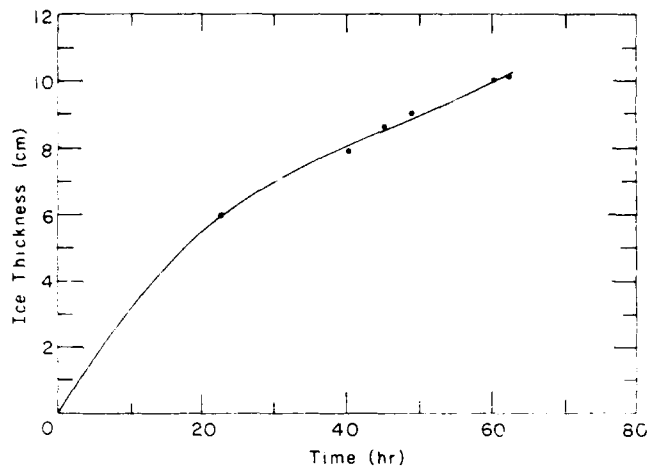


Figure 2. Plot of ice thickness versus time.

Roughly one-third (10.1 cm) of the reservoir was frozen by the end of the experiment. A 3-cm section was removed from each edge of the ice block to minimize any effects the side wall might have had on the growth and hence the concentration of the ice. The central section was used for the analyses. Figure 3 illustrates the manner in which the original ice block was subdivided. To obtain a general idea of the distribution of RDX and TNT in the ice, 1-cm-thick sections of block H were cut with a band saw and analyzed. After the analysis of these initial samples indicated that the results looked promising, a more careful sampling of the ice block was obtained by shaving blocks B and E with a microtome. A series of very thin layers was removed from the ice and placed in bottles of known weight. Weights of the sample were obtained and just enough sample was collected to fill the 2-mL HPLC autosampler vials. Samples of the starting solution and the final solution were also analyzed.

All the chemical analyses were conducted using a Reversed-Phase, High Performance Liquid Chromatography (RP-HPLC) instrument composed of a Spectra Physics detector (SP8490) and pump (SP8810) coupled to a Dynatech autosampler (model LC 241), a Hewlett-Packard integrator (HP3393A)

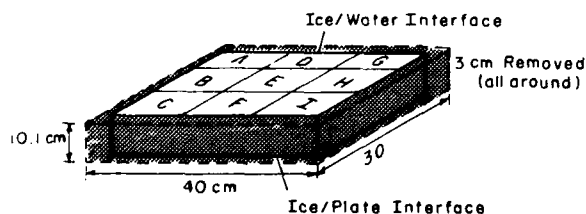


Figure 3. Sectioning of the ice block.

Table 1. Concentrations measured for known standards and explosive controls. The variation between the known value and those measured is about 5%. The analyses of the initial and final solutions are also tabulated.

	RDX ($\mu\text{g/L}$)	TNT ($\mu\text{g/L}$)
Explosive standard	2006	365
Explosive standard (measured)	1915 2095 2028	337 354 342
Explosive control	220	207
Explosive control (measured)	236 227	193 186
Initial solution (measured)	1181 1223	1160 1192
Final solution (measured)	1831 1831 1822	1696 1670 1683 1676

and a Cole Parmer chart recorder. An LC-18 column (Supelco, Inc.) was eluted with 1:1 methanol-water at a flow rate of 1.5 mL/min. The variable wavelength detector was set at 254 nm. Retention times for RDX and TNT were 4.3 and 9.4 minutes respectively. Peak heights of 2 cm for RDX and 5 mm for TNT at a range setting of 0.001 absorbance units, full scale, corresponded to the detection limits and could be measured accurately by hand. At the low concentrations of interest to this study, manual peak height measurements proved to be more reliable than automated peak areas from the integrator.

The melt water from the ice, the starting solution and the unfrozen final solution contained no solids and were run on the HPLC without diluting or filtering. Table 1 lists the concentrations measured for the starting solution (average 1.202 mg/L for RDX and 1.176 mg/L for TNT) and for the final solution (average 1.829 mg/L for RDX and 1.681 mg/L for TNT) using the HPLC. Explosive standards and an explosive control were analyzed along with the samples to ensure that the instrument was operating properly.

As the solubilities of RDX and TNT in water are low—30 mg/L for TNT, 40 mg/L for RDX (Leggett 1985)—an original concentration of 1 mg/L was chosen to ensure that any increase in TNT and RDX

concentration in the water, resulting from their exclusion from the ice, would not result in precipitation of the solutes. The concentration selected also made sample dilution unnecessary when RDX and TNT were determined by RP-HPLC.

RESULTS AND DISCUSSION

The majority of the ice block was columnar growth ice, with a 7-mm-thick transition zone at the freezing plate interface (Fig. 4). The columnar ice had fairly equidimensional grains (Fig. 5), whereas the transition zone had grains that had unequal dimensions (Fig. 6). Many small bubbles within the transition ice made this region opaque. Tubular, vertical bubbles were found in the columnar ice (see Fig. 7). The different bubble patterns are a function of the rates of freezing and the rates of diffusion of gas in water (Halde 1979). At high freezing rates, numerous small bubbles form, whereas lower freezing rates give the dissolved gases time to diffuse to existing bubbles. At very slow freezing rates, the dissolved gas has



Figure 4. Vertical thin section of the ice block.

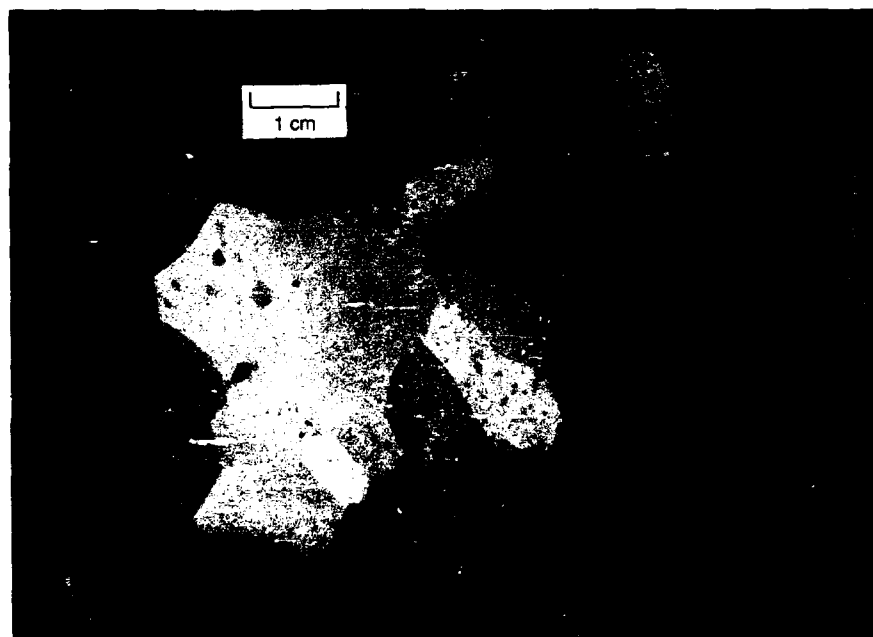


Figure 5. Horizontal section through the columnar ice.

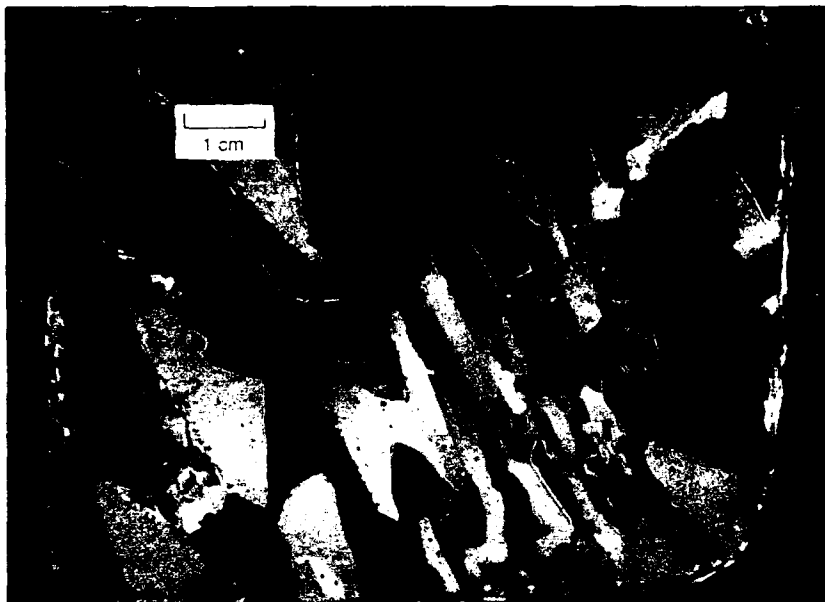


Figure 6. Horizontal section through the transition zone.

time to diffuse away from the freezing front and no bubbles form. This was the case for the bottom 10 mm of the ice.

Preliminary chemical analyses using 1-cm-thick sections (120-mL volumes) indicated that only the ice at the two interfaces—the ice/freezing plate interface and the ice/water interface—had any measurable RDX and TNT. Note that the method

detection limit is 12 $\mu\text{g/L}$ for RDX and 2.6 $\mu\text{g/L}$ for TNT (Jenkins et al. 1988).

A detailed chemical analysis of the ice at the two interfaces was then made. Small samples (2 mL) were obtained by microtome sectioning. Figure 8 is a plot of RDX and TNT concentration versus position of the ice below the freezing plate obtained from the latter analysis. Concentrations were below the detection limit adjacent to the freezing plate, increased to a maximum at about 4 mm, fell below the detection limits at 1 cm and then increased right at the ice/water interface.

The low concentration seen in the first millimeter is interpreted as resulting from a low

freezing rate experienced briefly between the time the freezing plate was turned on and when it equilibrated at -10°C . Once the plate was cold, however, the freezing rate increased, entrapping up to 15% TNT and RDX. The progressive decrease in concentration after the maximum reflects a gradual decrease in the freezing rate brought about by the ice insulating the freezing plate.



Figure 7. Appearance of the ice during the course of the experiment.

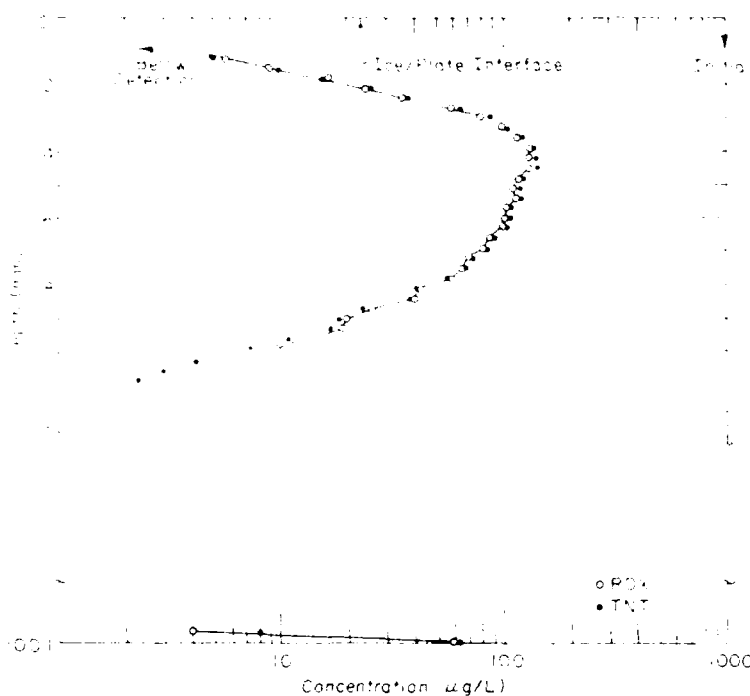


Figure 8. Measured concentrations of RDX and TNT as a function of depth within the ice block.

The measured concentration (60 g/L for each compound) in the ice at the ice/water interface is attributed to the adherence of a small amount of the final liquid to the ice surface. This interpretation is supported by my having observed drops of water on the surface of the ice as the water was drained from the base of the tank. As the ice was kept below freezing, the drops were not produced by melting. Originally, I thought the spike in concentration at the ice/water interface was attributable to an adhered monolayer. The 120 g/L (60 g/L of each compound) observed is, however, less than the 2.35 mg/L predicted for a monolayer (see Appendix A).

In order to calculate the effective partition coefficient, $K_{\text{eff}} = C_i/C_w$, not only is the concentration of TNT and RDX in the ice required but that in the remaining water is also needed. Since direct sampling of water in the reservoir was not possible during the course of the experiment, the initial and final concentrations of TNT and RDX in the water and the measured TNT and RDX concentrations for each sampled ice layer were used to calculate the changing TNT and RDX concentrations in the bulk water. The following equation from Cox and Weeks (1975) was used.

$$C_w = [C_o h - C_i t] / h - t \quad (1)$$

where C_w = changing concentration of the water
 C_o = initial water concentration
 C_i = average concentration of the ice
 h = tank depth
 t = ice thickness.

When the concentration of TNT and RDX in the ice was below the detection limit, the detection limit for each organic was used as the contaminant concentration in the ice. The calculated final concentration for RDX compared well with the value measured with the RP-HPLC (1820 g/L calculated, 1829 g/L measured) but for TNT there was a 6% difference between the calculated and the measured value (1787 g/L calculated, 1681 g/L measured). Because the concentration of TNT and RDX is so much larger in the water than the ice, the calculated, final concentration is not sensitive to the value chosen for the below-detection ice concentration.

In the future the liquid expelled out the tube will be sampled with time and analyzed.

From the C_i measured and the C_w calculated, the effective partition coefficient K_{eff} was determined (Table 2). Following Cox and Weeks (1975), the equation of Burton et al. (1953) was used to relate the effective partition coefficient (K_{eff}) to the "theoretical" partition coefficient experienced at an ice growth velocity $v = 0$

$$K_{\text{eff}} = \frac{K_o}{K_o + (1 - K_o)e^{-\delta v/D}} = \frac{C_i}{C_w} \quad (2)$$

where K_{eff} = effective partition coefficient
 K_o = partition coefficient when freezing front is static, $v = 0$
 v = velocity of freezing front
 D = diffusion coefficient of RDX and TNT in water
 δ = thickness of the boundary layer.

By rearranging eq 2 in linear form

$$\ln\left(\frac{1}{K_{\text{eff}}} - 1\right) = -v\delta/D + \ln\left(\frac{1}{K_o} - 1\right) \quad (3)$$

Table 2. Calculated values of K_{eff} for TNT and RDX at different ice layers. The ice growth velocity and the position of each layer within the ice block are also tabulated.

Ice thickness (cm)	Ice growth velocity (cm/s)	TNT K_{eff}	RDX K_{eff}
0.1	1.08×10^{-4}	2.54×10^{-3}	4.57×10^{-3}
0.2	1.04×10^{-4}	1.52×10^{-2}	1.65×10^{-2}
0.3	1.08×10^{-4}	7.41×10^{-2}	6.60×10^{-2}
0.4	1.04×10^{-4}	1.16×10^{-1}	1.07×10^{-1}
0.5	1.16×10^{-4}	1.00×10^{-1}	9.82×10^{-2}
0.6	1.08×10^{-4}	9.01×10^{-2}	8.57×10^{-2}
0.7	1.01×10^{-4}	6.65×10^{-2}	6.51×10^{-2}
0.8	1.02×10^{-4}	3.81×10^{-2}	4.05×10^{-2}
0.9	1.00×10^{-4}	1.53×10^{-2}	1.62×10^{-2}
1	1.02×10^{-4}	5.43×10^{-3}	9.66×10^{-3}
2	9.09×10^{-5}	1.59×10^{-3}	9.32×10^{-3}
3	7.70×10^{-5}	1.53×10^{-3}	8.99×10^{-3}
4	7.10×10^{-5}	1.47×10^{-3}	8.65×10^{-3}
5	6.40×10^{-5}	1.41×10^{-3}	8.31×10^{-3}
6	4.74×10^{-5}	1.36×10^{-3}	7.79×10^{-3}
7	3.79×10^{-5}	1.30×10^{-3}	7.64×10^{-3}
8	3.13×10^{-5}	1.24×10^{-3}	7.30×10^{-3}
9	2.63×10^{-5}	1.18×10^{-3}	6.96×10^{-3}
10	2.86×10^{-5}	1.12×10^{-3}	6.62×10^{-3}

Table 3. Organic substances whose diffusivities and molecular weights were used in Figure 10.

Substance	Diffusivities* ($D_a \times 10^5$)	Molecular** weight (a.m.u.)	\sqrt{M}
Lactose	0.43	342.3	18.50
Sucrose	0.45	342.3	18.50
Caffeine	0.63	194.2	13.94
Mannitol	0.58	182.18	13.50
Glucose	0.6	180.16	13.42
Pyrogallol	0.7	126.11	11.23
Rosorcinol	0.8	110.11	10.49
Hydroquinone	0.77	110.11	10.49
Phenol	0.84	94.11	9.70
Pyridine	0.76	79.1	8.89

* Thibodeaux (1979, p. 462-463).

** Atomic mass units.

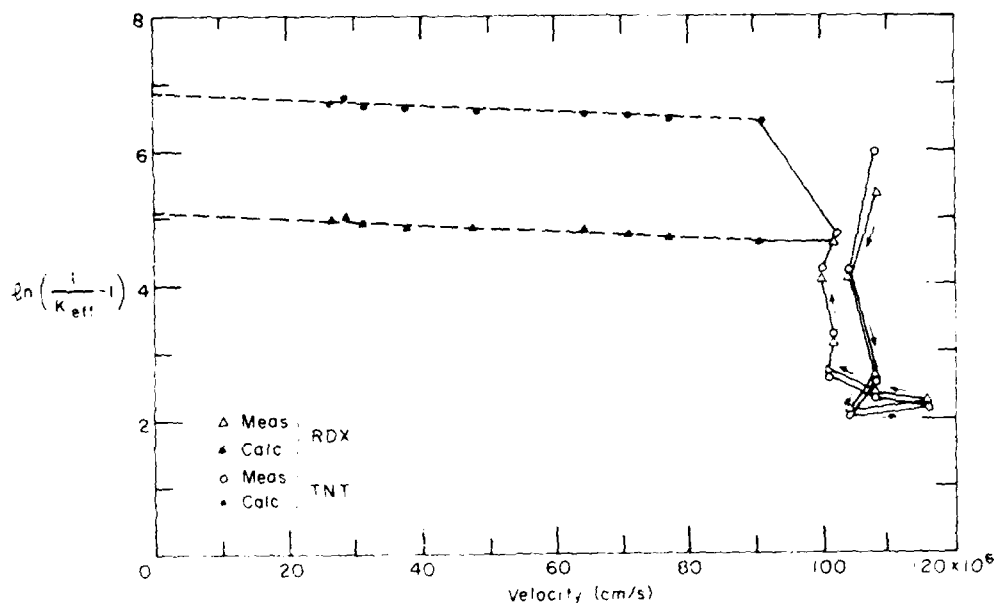


Figure 9. Plot of the natural log of $\left[\frac{1}{K_{eff}} - 1 \right]$ versus ice growth velocity.

one can see that by plotting the natural log of $K_{eff}^{-1} - 1$ against the ice growth velocity, v , the slope of the resulting line is the value of δ/D with K_0 being the intercept (Cox and Weeks 1975). Figure 9 is such a plot and yields an upper limit for K_0 , the partition coefficient at $v = 0$, of 6.06×10^{-3} for RDX and 1.07×10^{-3} for TNT. These values are only upper

limits, the values obtained for K_0 being very sensitive to the value chosen for C_i when the concentration of the organics in the ice was below the detection limit.

Since diffusivities of molecules in water depend upon the size of the molecule, a plot of measured diffusivities of various organic molecules (Table 3)

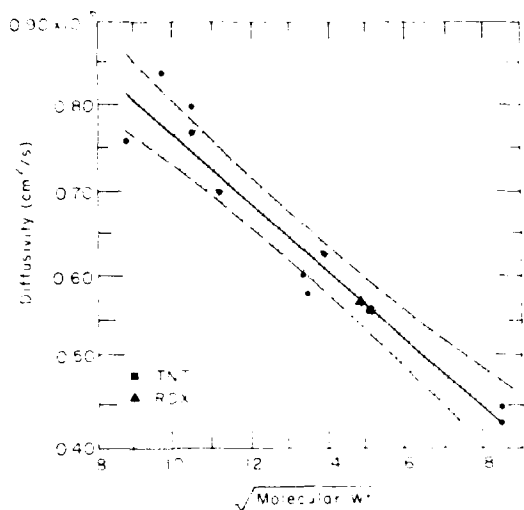


Figure 10. Measured diffusivities of ten organics vs the square root of their molecular weight. Shaded area represents one standard deviation from the best fit line.

against the square root of their molecular weights gives a linear relationship* (Fig. 10). Plotting TNT and RDX on this graph gives an approximate diffusion coefficient for RDX of 5.8×10^{-6} cm²/s and for TNT of 5.7×10^{-6} cm²/s. By multiplying the values obtained for δ/D from Figure 9 (3736 s/cm for RDX, 4396 s/cm for TNT) by their respective values for D , δ was estimated to be 2.2×10^{-2} cm for RDX and 2.5×10^{-2} cm for TNT.

CONCLUSION AND FUTURE RESEARCH

In conclusion, I think that TNT and RDX are suitable for modeling the movement of organics upon freezing, as they are excluded from the ice and are not volatile. An upper limit for the partition coefficient, K_p , was calculated to be 6.06×10^{-3} for RDX and 1.07×10^{-3} for TNT. These values were obtained by calculating the effective partition coefficients (concentration of TNT and RDX in frozen layers versus the changing liquid composition) and plotting these values against the ice growth rate. The thickness of the boundary layer was calculated to be about 2.5×10^{-2} cm.

*Personal communication with Daniel Leggett, CRREL, June 1988.

Freezing excludes TNT and RDX very efficiently at freezing rates up to 9×10^{-5} cm/s (3.1 in./day); at higher freezing rates up to 15% of the solute was entrapped. TNT and RDX behaved similarly in this experiment, which is not surprising given the closeness of their molecular weights (227 for TNT, 222 for RDX). These compounds should be shielded from light to avoid photodegradation. The use of a microtome as a sampling tool was found to provide a detailed record of the distribution of these molecules as a function of freezing rate.

In future experiments, soil or a particulate medium (glass beads) will be used to study the effect particles have on the concentration and distribution of nonvolatile organics. In my opinion, the variables of greatest importance for determining the distribution of the organics are: tortuosity (path length), chemical activity of the particulate material (both organic and inorganic) and the freezing rate. Glass spheres or coarse quartz sand should give information on the effect of tortuosity on the movement of organics. The added complication of surface chemistry would be studied using soils.

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APPENDIX A: CALCULATION OF CONCENTRATION OF MONOLAYER

The concentration of the monolayer was calculated by dividing the area of the ice surface (80.1 cm²) by the surface area of each compound. From the number of TNT or RDX molecules, the number of moles and then the number of grams was calculated. The gram weight of the monolayer was then divided by the volume of the sample. The surface areas of TNT and RDX were estimated using the following equation from Bansal et al. (1982) (Leggett 1985):

$$A = 1.091 \times 10^{-16} [M \times 10^{24} / N]^{2/3} \quad (\text{A1})$$

where A = area in square centimeters
 M = molecular weight
 N = Avogadro's number = 6.023×10^{23} molecules/mole.

Equation A1 yields a surface area for the TNT molecule of 5.7×10^{-15} cm² (5.6×10^{-15} cm² for RDX).

A facsimile catalog card in Library of Congress MARC format is reproduced below.

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