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Diffusion and Drive-Point Sampling to Detect Ordnance-Related Compounds in Shallow Ground Water Beneath Snake Pond, Cape Cod, Massachusetts, 2001–02

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CONVERSION FACTORS, VERTICAL DATUM, WATER-QUALITY INFORMATION, AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	Ву	To obtain
foot (ft)	0.3048	meter (m)
inch (in.)	2.54	centimeter (cm)
millimeter (mm)	0.03937	inch (in.)
mile (mi)	1.609	kilometer (km)
liter (L)	0.2642	gallon (gal)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: $^{\circ}F = (1.8 \text{ x }^{\circ}C) + 32$

VERTICAL DATUM

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called the Sea Level Datum of 1929.

Altitude, as used in this report, refers to distance above or below sea level.

WATER-QUALITY INFORMATION

Chemical concentration is given in units of milligrams per liter (mg/L) or micrograms per liter (μ g/L). Milligrams and micrograms per liter are units expressing the mass of the solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 milligram per liter. Micrograms per liter is approximately equivalent to "parts per billion" and milligrams per liter is approximately equivalent to "parts per million" in dilute water.

ABBREVIATIONS

ARNG	Army National Guard	RDX	Hexahydro-1,3,5-trinitro-1,3,5-
GPS	Global positioning system		triazine
HMX	Octahydro-1,3,5,7-tetranitro-	STL	Severn Trent Laboratory
	1,3,5,7-tetrazocine	USGS	U.S. Geological Survey
mL	milliliter	USEPA	U.S. Environmental Protection
mm	millimeter		Agency
MMR	Massachusetts Military	VOC	Volatile organic compound
	Reservation	μg/L	microgram per liter
MWCO	Molecular-weight cutoff	μm	micrometer
PDA	Photo diode array	μS/cm	microsiemens per centimeter at
PETN	Pentaerythritol tetranitrate		25 degrees Celsius
PVC	Polyvinyl chloride		

Diffusion and Drive-Point Sampling to Detect Ordnance-Related Compounds in Shallow Ground Water Beneath Snake Pond, Cape Cod, Massachusetts, 2001–02

By Denis R. LeBlanc

ABSTRACT

Diffusion samplers and temporary drive points were used to test for ordnance-related compounds in ground water discharging to Snake Pond near Camp Edwards at the Massachusetts Military Reservation, Cape Cod, MA. The contamination resulted from artillery use and weapons testing at various ranges upgradient of the pond.

The diffusion samplers were constructed with a high-grade cellulose membrane that allowed diffusion of explosive compounds, such as RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), into deionized water inside the samplers. Laboratory tests confirmed that the cellulose membrane was permeable to RDX and HMX. One transect of 22 diffusion samplers was installed and retrieved in August-September 2001, and 12 transects with a total of 108 samplers were installed and retrieved in September–October 2001. The diffusion samplers were buried about 0.5 feet into the pond-bottom sediments by scuba divers and allowed to equilibrate with the ground water beneath the pond bottom for 13 to 27 days before retrieval. Water samples were collected from temporary well points driven about 2-4 feet into the pond bottom at 21 sites in December 2001 and March 2002 for analysis of explosives and perchlorate to confirm the diffusion-sampling results.

The water samples from the diffusion samplers exhibited numerous chromatographic peaks, but evaluation of the photo-diode-array spectra indicated that most of the peaks did not represent the target compounds. The peaks probably are associated with natural organic compounds present in the soft, organically enriched pond-bottom sediments. The presence of four explosive compounds at five widely spaced sites was confirmed by the photo-diode-array analysis, but the compounds are not generally found in contaminated ground water near the ranges. No explosives were detected in water samples obtained from the drive points. Perchlorate was detected at less than 1 microgram per liter in two drive-point samples collected at the same site on two dates about 3 months apart. The source of the perchlorate in the samples could not be related directly to other contamination from Camp Edwards with the available information.

The results from the diffusion and drive-point sampling do not indicate an area of ground-water discharge with concentrations of the ordnance-related compounds that are sufficiently elevated to be detected by these sampling methods. The diffusion and drive-point sampling data cannot be interpreted further without additional information concerning the pattern of ground-water flow at Snake Pond and the distributions of RDX, HMX, and perchlorate in ground water in the aquifer near the pond.

INTRODUCTION

Military activities at Camp Edwards at the Massachusetts Military Reservation (MMR) on western Cape Cod (fig. 1) since the early 1900s have resulted in contamination of the ground water by ordnance-related compounds such as RDX, HMX, and perchlorate (Army National Guard Bureau, 2002). The U.S. Army National Guard (ARNG) is conducting studies to locate and describe the contaminants, and to develop methods to remediate contaminated soils and ground water at the military reservation (Army National Guard Bureau, 2003). The studies have shown that the contaminants are present in various plumes that extend from the reservation toward ground-water discharge areas at ponds and the coast.

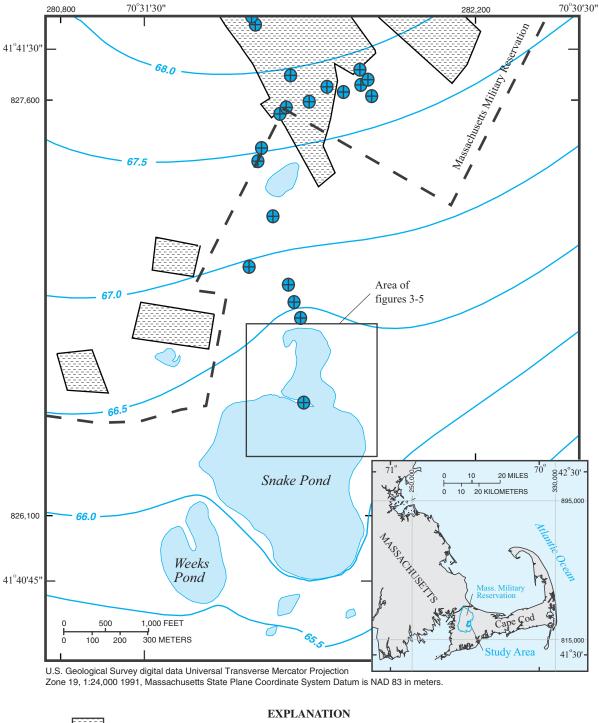
In November 2000, RDX was detected in monitoring wells near Snake Pond, which is an 83-acre glacial kettle-hole pond that is located southeast of the Camp Edwards training area (fig. 1) and has a maximum depth of about 33 ft (Massachusetts Division of Fisheries and Wildlife, 1993). The suspected source of the contamination is various artillery ranges, also known as the J-ranges, on the southeastern section of the reservation (AMEC, 2002a).

Ground water in this area flows southeastward from the top of the water-table mound that underlies western Cape Cod toward Snake Pond, which is a ground-water flow-through pond (Winter and others, 1998) that has no surface-water inlet or outlet. Snake Pond is in direct hydraulic contact with the aquifer, which is composed of permeable sand and gravel glacial outwash (Masterson and others, 1996). Ground-water-flow modeling of the area (Walter and others, 2002; AMEC, 2001, 2002b) indicated that the contaminants could discharge into the northern half of Snake Pond, including a shallow northern cove that is separated from the larger southern area of the pond by a low peninsula that is submerged during periods of high water levels (fig. 1). Test drilling in May 2001 indicated that RDX was present in the ground water beneath the peninsula (AMEC, 2001).

Various contaminant plumes of volatile organic compounds (VOCs) from the MMR that intersect ponds near the base discharge to these ponds near their shorelines. There were concerns that the ordnance-related compounds might similarly discharge near the northern shore of Snake Pond. Diffusion samplers buried in pondbottom sediments had been used successfully to detect and delineate the discharge areas of the VOC plumes at the other ponds (Savoie and others, 2000). Therefore, the U.S. Geological Survey (USGS), in cooperation with the Army National Guard Bureau, used diffusion samplers to test for the presence of the ordnance-related compounds in shallow ground water beneath Snake Pond during 2001-02. The results of this investigation were used to guide additional test drilling near Snake Pond (AMEC, 2002b) This report describes the construction and testing of the diffusion samplers, the application and results of diffusion sampling at Snake Pond, and subsequent drive-point sampling to confirm the diffusion-sampler results.

ACKNOWLEDGMENTS

Access to Snake Pond was graciously granted by Faith Willard of Camp Good News. The diffusion samplers were installed and retrieved with the assistance of Timothy McCobb, Michael Columbo, Jennifer Savoie, Andrew Massey, Joshua Koch, Kathryn Hess, Dann Blackwood, Kenneth Parolski, Barry Irwin, and Michael Casso of the U.S. Geological Survey. Analysis of the water samples was completed with the assistance of James Madison of Severn Trent Laboratories and Mark Grant, Elizabeth Wessling, Timothy Dwyer, and Herbert Colby of AMEC Earth & Environmental, Inc. David Hill and Benjamin Gregson of the Camp Edwards Impact Area Groundwater Study provided valuable technical and financial support. The review comments concerning this report of Don Vroblesky, Peter Church, and Gail Moede of the U.S. Geological Survey also are appreciated.



MILITARY RANGE WATER-TABLE CONTOUR—Shows model-simulated altitude of water table, in feet above sea level. Contour interval 0.5 feet (Walter and others, 2002) TEST BORING WITH VALIDATED DETECTIONS OF EXPLOSIVE COMPOUNDS OR PERCHLORATE AS OF APRIL 2002 (AMEC, 2002a)

Figure 1. Locations of Camp Edwards military ranges, Snake Pond, test borings with validated detections of explosives and perchlorate, and altitude of the water table, Cape Cod, Massachusetts, 2001–02.

FIELD INVESTIGATION AND RESULTS

Diffusion samplers operate on the principle of chemical diffusion. A sampling fluid, such as deionized water, that is free of the contaminants of concern is placed inside a sealed tubular membrane that is permeable to the targeted contaminants. When buried in pond-bottom sediments in areas of ground-water discharge, the sampler is immersed in pore water about to discharge to the pond. The sampler is left in place long enough for contaminants dissolved in the ground water flowing past the sampler to diffuse through the membrane into the enclosed water; thus, concentrations inside and outside the sampler become equal. The sampler is then retrieved, and the water is decanted into a container for shipment to the laboratory for analysis.

Vroblesky and others (1996) describe the development and application of diffusion samplers to identify the discharge of VOC plumes to streams. Savoie and others (2000) describe the use of diffusion samplers to locate two VOC plumes that are discharging to Johns Pond near the MMR. Additional studies in which diffusion samplers were used to describe the discharge of VOC plumes to surface waters are described by Church and others (2002). In these studies, polyethylene was used as the membrane in the diffusion samplers because VOCs can diffuse through this type of plastic.

Diffusion-Sampler Design

The diffusion samplers in this study were intended to test for the presence of RDX and HMX. These large organic molecules are not VOCs and would not pass through the polyethylene membrane used in the earlier investigations. The use of cellulose-based membranes for diffusion sampling of higher molecular-weight organic compounds is being tested by the USGS (Vroblesky and others, 2002). The effectiveness of these membranes for sampling RDX and HMX was tested in the Snake Pond study. Prototype diffusion samplers were constructed of various parts, including a rigid inner core, the diffusion membrane, and an outer protective mesh (fig. 2). The fluid in the samplers was deionized water.

A 1-ft-long section of 2-in. nominal diameter butyrene tubing served as the inner core of the sampler. About 100 holes (0.25-in. diameter) were drilled through

the tubing. Polyethylene slip-on caps were placed over the ends of the tubing and were also perforated with three 0.25-in. holes. The holes in the tubing and caps allowed for ready exchange of water inside and outside of the tubing.

The rigid inner core of the sampler is necessary to prevent the collapse of the tubular cellulose membrane during the diffusion process. The membrane is permeable to water, and the deionized water inside the sampler diffuses through the membrane into the surrounding ground water as contaminants diffuse in the opposite direction into the sampler. Without the rigidity provided by the inner core, the membrane would collapse over time until chemical equilibrium was established. A rigid inner core is unnecessary in samplers made with polyethylene, which is not permeable to water.

The diffusion membrane was a high-grade, regenerated-cellulose tubular membrane obtained from Membrane Filtration Products, Inc. (Item No. 0810-100, Seguin, TX). The lay-flat tubing was shipped in a 20-percent ethanol preservative solution (the tubing can also be purchased in a dry form that requires additional processing before use). The membrane has a width of 100 mm, an expanded diameter of about 64 mm (2.5 in.), a thickness of 65 μm , and a nominal molecular-weight cutoff (MWCO) of 6,000 to 8,000 Daltons (nominal pore size of 18 angstroms).

The tubular membrane was cut into sections about 2 ft long, then rinsed thoroughly in tap water, followed by deionized water, to remove the storage solution. A knot was tied in one end of the membrane, deionized water was added to partially fill the membrane and expand it to its full diameter, and the inner core was slipped inside of the membrane, which was then filled to the top with deionized water. A knot was tied in the top of the membrane to seal in the deionized water. The entire assembly was then slipped into a flexible plastic mesh (Flexguard II, 2- to 2.5-in.-diameter, M-Line, Inc., Brunswick, OH) to protect the membrane from abrasion and tears. A completed sampler contained about 500 mL of deionized water. The samplers were stored in deionized water until their deployment, unlike the samplers made with polyethylene, which can be stored in air.

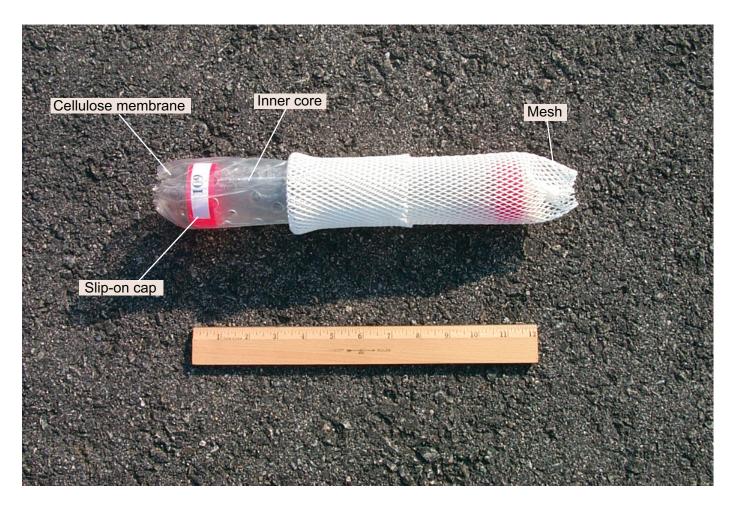


Figure 2. Diffusion sampler showing inner core, slip-on end caps, cellulose membrane, and outer mesh. Mesh is pulled back to show inner components.

Laboratory Test of Diffusion Samplers

The effectiveness of the cellulose-membrane diffusion samplers for sampling RDX and HMX was tested in the laboratory prior to their use in the field. Three test chambers were constructed from 5.5-ft-long sections of 3-in.-diameter PVC pipe with rubber end caps. The chambers were filled with ground water collected on July 12, 2001, from three wells on Camp Edwards. These wells had been sampled previously and had contained the target compounds at concentrations that were suitable for the laboratory tests.

The test chambers were secured in an upright position, rinsed thoroughly, and filled with ground water from the wells. A diffusion sampler filled with deionized water was suspended inside each chamber, and the chambers were stored in a dark walk-in refrigerator at

about 4°C for about 12 days. The prototype diffusion samplers were constructed with 1.25-in.-diameter, 1.5-ftlong cores and 75-mm lay-flat cellulose tubular membrane that had been purchased in the dry form. The total volume of the test chambers was about 8 L, and the volume of the diffusion samplers was about 0.35 L. About once a day, the chambers were shaken to ensure that the water inside the chambers remained mixed.

At the end of the 12-day test period, the samplers were retrieved from the test chambers, and the water inside the diffusion samplers was decanted into sample bottles and shipped to the laboratory for analysis. Samples of the water in the annuluses of the test chambers were also sent for analysis. The ground water originally used to fill the test chambers was not sent to the laboratory for analysis.

There was reasonable agreement between the measured concentrations of RDX and HMX in the water collected from the diffusion samplers and the test chambers (table 1). The concentrations from the diffusion samplers were about 75 to 80 percent of the corresponding concentrations from the water in the chambers at the end of the test period. This difference probably was caused by the absence of flow in the sealed chambers.

Diffusion Sampling of Ground Water

August-September 2001 Transect

A single transect of 22 diffusion samplers was placed in Snake Pond in August 2001 to test the sampling method before a larger sampling effort was undertaken. The transect was located along the simulated path of ground-water flow that intersected the screened interval of the monitoring wells on the peninsula where RDX was detected in May 2001 (AMEC, 2001, 2002b). The simulations indicated that ground water from this interval could discharge to Snake Pond as far as 500 ft south of the peninsula, so the transect extended from this point northward, across the peninsula, to the northern shore of the cove (fig. 3).

The samplers were set in the pond by using the method described by Savoie and others (2000). The transect line was prepared by using fisherman's sinking pot-warp rope with the samplers attached by short strings and clips at 50- to 75-ft intervals along the line (table 2). Small stainless-steel weights were attached to the slightly buoyant samplers so they would sink to the bottom. A boat and compass were used to lay the line on the pond bottom. The line end points were located with a global-positioning system (GPS) unit. Scuba divers swam along each line and buried the samplers about 0.5 ft into the pond-bottom sediments by hand with a trowel.

To retrieve the samplers, divers swam along the lines and pulled the samplers out of the sediments. The lines were hauled into a boat, where the diffusion samplers were unclipped from the line and rinsed with pond water to remove mud clinging to the sampler. The

water inside the samplers was then poured into 500-mL amber glass bottles through a small hole snipped in the cellulose membrane. The bottles were chilled onsite and later shipped to the Severn Trent Laboratory (STL) in Burlington, VT, for analysis.

Three quality-control water samples also were sent for analysis. The sample identified as the RDX control in table 2 was obtained from a diffusion sampler that was kept in a 20-L container of water from well MW34M1, known to contain RDX, for 7 days. The sample identified as the distilled-water control in table 2 was obtained from a diffusion sampler that was kept for 14 days in a 20-L container of deionized water. The sample identified as the water blank in table 2 was obtained directly from the deionized water supply used to fill the diffusion samplers.

The diffusion samplers were buried in the pond-bottom sediments on August 24, 2001, and retrieved on September 7, 2001. This 13-day period was considered sufficient for contaminant concentrations to equilibrate between the diffusion-sampler water and the pore water in the sediments. During retrieval, the membrane of sampler WWD-P016 (P16 in fig. 3) was punctured and the sample was lost. The scuba divers reported that the bottom sediments in the cove were generally fine grained and soft except close to the northern shore of the cove and near the peninsula. They also reported that the sediments were similarly fine grained and soft in the main pond basin farther than about 200 ft south of the peninsula.

Table 1. Results of laboratory tests of prototype diffusion samplers constructed of tubular cellulose membranes, July 2001

[Analysis by Severn Trent Laboratories, Burlington, Vermont. HMX, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; No., number; RDX, Hexahydro-1,3,5-trinitro-1,3,5-triazine; $\mu g/L$, microgram per liter; <, actual value is less than value shown]

	Annulus of	test chamber	Diffusion sample		
Well No.	RDX (µg/L)	HMX (µg/L)	RDX (µg/L)	HMX (µg/L)	
MW142M2	< 0.25	< 0.25	< 0.25	< 0.25	
MW34M1	1.2	<.25	.89	<.25	
MW76M2	47	5.7	36	4.6	

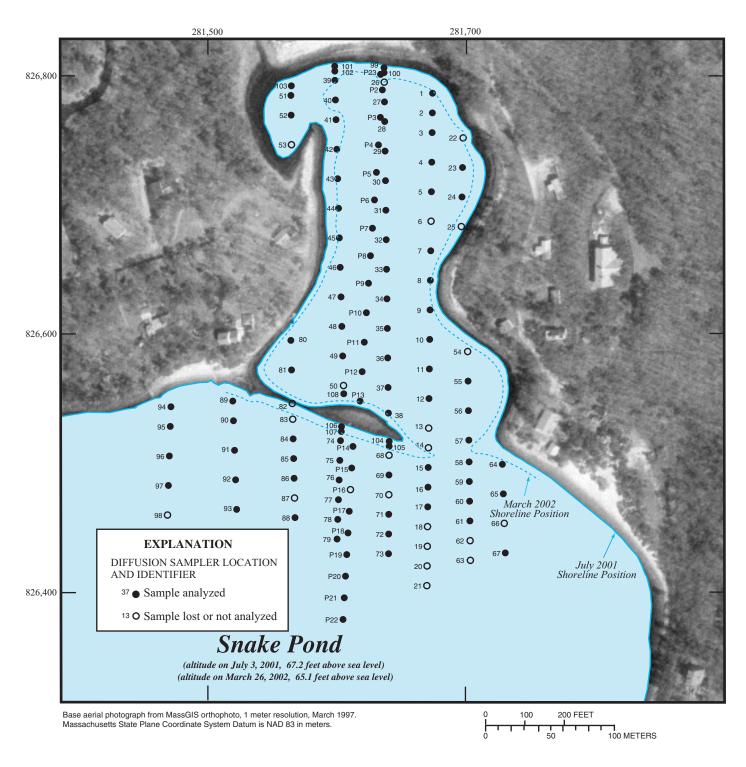


Figure 3. Locations of diffusion samplers set in the bottom sediments of Snake Pond, Cape Cod, Massachusetts, August-October 2001. (Pond altitudes from Rose Forbes, Air Force Center for Environmental Excellence, written commun., 2003.)

Table 2. Locations, site identifiers, and installation and retrieval dates of diffusion samplers set in the bottom sediments of Snake Pond, Cape Cod, Massachusetts, August—October 2001

[USGS sample ID: Samples retrieved September 7, 2001, preceded by SNP/RDX/0901. Samples retrieved October 17, 2001, preceded by SNP/RDX/1001. State-plane coordinates given as easting and northing, NAD 83. ID, identification number; No., number; RDX, Hexahydro-1,3,5-trinitro-1,3,5-triazine; STL, Severn Trent Laboratories; USGS, U.S. Geological Survey; --, sample lost or not analyzed]

Site identifier (fig. 3)	STL control No.	USGS sample ID	Distance from shore (feet)	Easting (meters)	Northing (meters)
	Diffusion s	amplers installed August 24, 20	001, and retrieved Se	eptember 7, 2001	
P23	GS08-023	WWD-P023	36	281,633.0	826,799.7
P2	GS08-002	WWD-P002	75	281,634.3	826,787.6
P3	GS08-003	WWD-P003	145	281,632.8	826,766.4
P4	GS08-004	WWD-P004	215	281,631.3	826,745.1
P5	GS08-005	WWD-P005	285	281,629.7	826,723.8
P6	GS08-006	WWD-P006	355	281,628.2	826,702.5
P7	GS08-007	WWD-P007	427	281,626.7	826,680.6
P8	GS08-008	WWD-P008	497	281,625.1	826,659.3
P9	GS08-009	WWD-P009	567	281,623.6	826,638.1
P10	GS08-010	WWD-P010	642	281,622.0	826,615.3
P11	GS08-011	WWD-P011	717	281,620.3	826,592.5
P12	GS08-012	WWD-P012	792	281,618.7	826,569.7
P13	GS08-013	WWD-P013	867	281,617.1	826,546.9
P14	GS08-014	WWD-P014	50	281,611.6	826,511.8
P15	GS08-015	WWD-P015	105	281,610.6	826,495.1
P16		WWD-P016	160	281,609.6	826,478.4
P17	GS08-017	WWD-P017	215	281,608.7	826,461.6
P18	GS08-018	WWD-P018	270	281,607.7	826,444.9
P19	GS08-019	WWD-P019	325	281,606.8	826,428.1
P20	GS08-020	WWD-P020	380	281,605.8	826,411.4
P21	GS08-021	WWD-P021	435	281,604.8	826,394.7
P22	GS08-022	WWD-P022	490	281,603.9	826,377.9
	GS08-024	RDX control from well MW	/34M1		
	GS08-025	Water blank from deionized	water used to fill diff	usion samplers	
	GS08-026	Distilled-water control			
	Diffusion sam	plers installed September 20-2	1, 2001, and retrieve	ed October 17, 2001	
64	GS11-064	WWD01-0050	50	281,727.3	826,497.9
65	GS11-065	WWD01-0125	125	281,728.1	826,475.1
66		WWD01-0200	200	281,728.8	826,452.2
67	GS11-067	WWD01-0275	275	281,729.6	826,429.4
54		WWD02-0050	50	281,700.5	826,585.2
55	GS11-055	WWD02-0125	125	281,700.8	826,562.3
56	GS11-056	WWD02-0200	200	281,701.1	826,539.5
57	GS11-057	WWD02-0275	275	281,701.4	826,516.6
58	GS11-058	WWD02-0330	330	281,701.6	826,499.8
59	GS11-059	WWD02-0380	380	281,701.8	826,484.6

Table 2. Locations, site identifiers, and installation and retrieval dates of diffusion samplers set in the bottom sediments of Snake Pond, Cape Cod, $Mass a chusetts, August-October\ 2001---Continued$

Site identifier (fig. 3)	STL control No.	USGS sample ID	Distance from shore (feet)	Easting (meters)	Northing (meters)
	Diffusion samplers ins	talled September 20-21, 20	01, and retrieved Octo	ober 17, 2001—Cont	inued
60	GS11-060	WWD02-0430	430	281,702.0	826,469.4
61	GS11-061	WWD02-0480	480	281,702.2	826,454.1
62		WWD02-0530	530	281,702.4	826,438.9
63		WWD02-0580	580	281,702.6	826,423.6
1	GS11-001	WWD03-0050	50	281,673.3	826,785.0
2	GS11-002	WWD03-0100	100	281,673.1	826,769.8
3	GS11-003	WWD03-0150	150	281,673.0	826,754.5
4	GS11-004	WWD03-0225	225	281,672.7	826,731.7
5	GS11-005	WWD03-0300	300	281,672.4	826,708.8
6		WWD03-0375	375	281,672.2	826,686.0
7	GS11-007	WWD03-0450	450	281,671.9	826,663.1
3	GS11-008	WWD03-0525	525	281,671.6	826,640.3
9	GS11-009	WWD03-0600	600	281,671.4	826,617.4
10	GS11-010	WWD03-0675	675	281,671.1	826,594.5
11	GS11-011	WWD03-0750	750	281,670.8	826,571.7
12	GS11-012	WWD03-0825	825	281,670.6	826,548.8
13		WWD03-0900	900	281,670.3	826,526.0
14		WWD03-0950	950	281,670.1	826,510.7
15	GS11-015	WWD03-1000	1,000	281,669.9	826,495.5
16	GS11-016	WWD03-1050	1,050	281,669.8	826,480.2
17	GS11-017	WWD03-1100	1,100	281,669.6	826,465.0
18		WWD03-1150	1,150	281,669.4	826,449.8
19		WWD03-1200	1,200	281,669.2	826,434.5
20		WWD03-1250	1,250	281,669.1	826,419.3
21		WWD03-1300	1,300	281,668.9	826,404.1
104	GS11-104	WWD04-0012	13	281,639.7	826,515.7
105	GS11-105	WWD04-0025	25	281,639.7	826,511.9
58		WWD04-0050	50	281,639.6	826,504.9
59	GS11-069	WWD04-0100	100	281,639.5	826,489.7
70		WWD04-0150	150	281,639.5	826,474.5
71	GS11-071	WWD04-0200	200	281,639.4	826,459.2
72	GS11-072	WWD04-0250	250	281,639.3	826,444.0
73	GS11-073	WWD04-0300	300	281,639.3	826,428.7
106	GS11-106	WWD05-0012	13	281,602.8	826,527.1
107	GS11-107	WWD05-0025	25	281,602.7	826,523.3
74	GS11-074	WWD05-0050	50	281,602.1	826,516.3
75	GS11-075	WWD05-0100	100	281,601.6	826,501.0
76	GS11-076	WWD05-0150	150	281,601.0	826,485.8
77	GS11-077	WWD05-0200	200	281,600.5	826,470.6
78	GS11-078	WWD05-0250	250	281,600.0	826,455.3

Table 2. Locations, site identifiers, and installation and retrieval dates of diffusion samplers set in the bottom sediments of Snake Pond, Cape Cod, Massachusetts, August-October 2001—Continued

Site identifier (fig. 3)	STL control No.	USGS sample ID	Distance from shore (feet)	Easting (meters)	Northing (meters)
	Diffusion samplers ins	talled September 20-21, 2001	l, and retrieved Octo	ober 17, 2001—Cont	inued
79	GS11-079	WWD05-0300	300	281,599.4	826,440.1
80	GS11-080	WWD06-0050	50	281,563.7	826,593.8
81	GS11-081	WWD06-0125	125	281,564.2	826,570.9
82		WWD06-0210	210	281,564.8	826,545.0
83		WWD06-0250	250	281,565.1	826,532.8
84	GS11-084	WWD06-0300	300	281,565.5	826,517.6
85	GS11-085	WWD06-0350	350	281,565.8	826,502.4
86	GS11-086	WWD06-0400	400	281,566.2	826,487.1
87		WWD06-0450	450	281,566.5	826,471.9
88	GS11-088	WWD06-0500	500	281,566.9	826,456.7
89	GS11-089	WWD07-0050	50	281,518.7	826,546.8
90	GS11-090	WWD07-0100	100	281,519.3	826,531.6
91	GS11-091	WWD07-0175	175	281,520.1	826,508.8
92	GS11-092	WWD07-0250	250	281,520.9	826,485.9
93	GS11-093	WWD07-0325	325	281,521.8	826,463.1
94	GS11-094	WWD08-0050	50	281,470.9	826,542.5
95	GS11-095	WWD08-0100	100	281,470.4	826,527.2
96	GS11-096	WWD08-0175	175	281,469.7	826,504.4
97	GS11-097	WWD08-0250	250	281,469.0	826,481.5
98		WWD08-0325	325	281,468.2	826,458.7
22		WWD09-0050	50	281,697.0	826,750.4
23	GS11-023	WWD09-0125	125	281,696.5	826,727.6
24	GS11-024	WWD09-0200	200	281,696.1	826,704.7
25		WWD09-0275	275	281,695.6	826,681.9
99	GS11-099	WWD10-0012	13	281,635.8	826,804.8
100	GS11-100	WWD10-0025	25	281,635.8	826,800.9
26		WWD10-0050	50	281,635.9	826,793.6
27	GS11-027	WWD10-0100	100	281,636.1	826,778.3
28	GS11-028	WWD10-0150	150	281,636.3	826,763.1
29	GS11-029	WWD10-0225	225	281,636.6	826,740.2
30	GS11-030	WWD10-0300	300	281,636.9	826,717.4
31	GS11-031	WWD10-0375	375	281,637.2	826,694.5
32	GS11-032	WWD10-0450	450	281,637.5	826,671.7
33	GS11-033	WWD10-0525	525	281,637.8	826,648.8
34	GS11-034	WWD10-0600	600	281,638.0	826,625.9

Table 2. Locations, site identifiers, and installation and retrieval dates of diffusion samplers set in the bottom sediments of Snake Pond, Cape Cod, Massachusetts, August–October 2001—Continued

Site identifier (fig. 3)	STL control No.	USGS sample ID	Distance from shore (feet)	Easting (meters)	Northing (meters)
	Diffusion samplers i	nstalled September 20-21, 2001	1, and retrieved Octo	ober 17, 2001— <i>Cont</i>	inued
35	GS11-035	WWD10-0675	675	281,638.3	826,603.1
36	GS11-036	WWD10-0750	750	281,638.6	826,580.2
37	GS11-037	WWD10-0825	825	281,638.9	826,557.4
38	GS11-038	WWD10-0890	890	281,639.2	826,537.6
101	GS11-101	WWD11-0012	13	281,597.6	826,805.9
102	GS11-102	WWD11-0025	25	281,597.7	826,802.1
39	GS11-039	WWD11-0050	50	281,597.8	826,795.0
40	GS11-040	WWD11-0100	100	281,598.2	826,779.8
41	GS11-041	WWD11-0150	150	281,598.6	826,764.6
42	GS11-042	WWD11-0225	225	281,599.3	826,741.7
43	GS11-043	WWD11-0300	300	281,599.9	826,718.9
44	GS11-044	WWD11-0375	375	281,600.6	826,696.0
45	GS11-045	WWD11-0450	450	281,601.2	826,673.2
46	GS11-046	WWD11-0525	525	281,601.8	826,650.3
47	GS11-047	WWD11-0600	600	281,602.5	826,627.5
48	GS11-048	WWD11-0675	675	281,603.1	826,604.6
49	GS11-049	WWD11-0750	750	281,603.8	826,581.8
50		WWD11-0825	825	281,604.4	826,558.9
108	GS11-108	WWD11-0846	846	281,604.6	826,552.5
103	GS11-103	WWD12-0025	25	281,564.1	826,790.7
51	GS11-051	WWD12-0050	50	281,563.7	826,783.3
52	GS11-052	WWD12-0100	100	281,563.9	826,768.1
53		WWD12-0175	175	281,564.2	826,745.2
	GS11-109	Water blank from deionized	water used to fill diff	usion samplers	
	GS11-110	Trip blank			
	GS11-111	Snake Pond surface water		281,701.4	826,516.6

The water samples were analyzed for the ordnance-related compounds shown in table 3, except for perchlorate, which was not analyzed for in any of the diffusion samples. A modification of USEPA method 8330 (U.S. Environmental Protection Agency, 1994) was used that targets various additional explosive compounds. The reporting limit for all but three of the explosive compounds in water was 0.25 µg/L for a 500-mL sample volume (table 3).

The samples from the diffusion samplers that were buried in the pond-bottom sediments exhibited numerous chromatographic peaks. However, an inspection of the

photo-diode-array (PDA) spectra showed that the peaks did not represent the target compounds. The inspections were done by comparing the sample spectra to the spectra of explosive compounds at known concentrations (Elizabeth Wessling, AMEC Earth & Environmental, Inc., written commun., 2002). The chromatographic peaks probably represent natural organic compounds in the pond-bottom sediments. The RDX control sample had detectable RDX; there were no detections in the distilled-water and water-blank control samples (table 4).

Table 3. Target chemical compounds included in analysis of diffusion and drive-point ground-water samples collected beneath Snake Pond, Cape Cod. Massachusetts

[Source of information: James Madison, Severn Trent Laboratories, Burlington, VT, 2001. HMX, Octahydro-1,3,5,7-tetranitro-1,3,5,7tetrazocine; MMR, Massachusetts Military Reservation; PETN, Pentaerythritol tetranitrate; RDX, Hexahydro-1,3,5-trinitro-1,3,5-triazine; USEPA, U.S. Environmental Protection Agency; µg/L, micrograms per

Method	Analyte	Reporting limit (µg/L)
USEPA 8330 explosives	НМХ	0.25
	RDX	.25
	1,3,5-Trinitrobenzene	.25
	1,3-Dinitrobenzene	.25
	Tetryl	.25
	Nitrobenzene	.25
	2,4,6-Trinitrotoluene	.25
	4-amino-2,6-Dinitrotoluene	.25
	2-amino-4,6-Dinitrotoluene	.25
	2,6-Dinitrotoluene	.25
	2,4-Dinitrotoluene	.25
	2-Nitrotoluene	.25
	3-Nitrotoluene	.25
	4-Nitrotoluene	.25
MMR-specific explosives	2,6-diamino-4-Nitrotoluene	.5
	2,4-diamino-6-Nitrotoluene	.25
	Picric acid	.25
	Nitroglycerin	5
	PETN	10
USEPA 314.0	Perchlorate ¹	1.5

¹Analyzed only for drive-point samples.

The results from the single transect of samplers demonstrated that the diffusion samplers could be installed and retrieved in Snake Pond. The analytical data did not indicate the presence of explosives at the sampling locations. The presence of RDX in the control sample, however, confirmed that RDX could diffuse through the cellulose membrane if it was present in the water surrounding the diffusion sampler.

The single transect of samplers was located along the flowpath simulated to pass through the monitoring wells on the peninsula in Snake Pond. This alignment was a reasonable choice for the first transect because

there were few other monitoring wells near the pond to delineate the width, thickness, and depth of the RDXcontaminated zone. However, ground water originating as recharge at the southeastern ranges could discharge at locations not crossed by the single transect.

September-October 2001 Transects

On September 20–21, 2001, 12 transects of 108 diffusion samplers were set in Snake Pond to obtain samples from a larger area of the pond bottom (fig. 3) than previously sampled. The same methods used for the single transect were used to construct, install, and retrieve the samplers along the 12 transects. The transects extended southward from the northern shore of the cove, the southeastern shore of the peninsula, and a swimming beach at a youth summer camp. The transects set south of the peninsula extended to about 300 ft from shore (fig. 3) because ground-water discharge was less likely near the center of the pond in areas where the scuba divers had reported fine-grained, soft sediments. The diffusion samplers were placed at intervals of 12 to 75 ft along the transects (table 2).

The diffusion samplers were retrieved on October 17, 2001, about 27 days after they had been installed. These samplers were left in place about twice as long as the samplers in the initial transect to provide more time for equilibration between contaminant concentrations inside and outside of the diffusion samplers and for dissipation of the disturbance caused by the installation. The large sample volume (500 mL) and potentially low rates of ground-water flow through the fine-grained pond-bottom sediments at many of the sampled sites could possibly increase the equilibration time.

The longer time in the pond-bottom sediments described above, however, also resulted in increased biodegradation of the cellulose-based diffusion membrane (the polyethylene used in earlier studies was not affected by biodegradation). Many of the samplers were leaking when they were hauled into the boat, particularly the samplers that had been buried in the fine-grained, organically rich sediments in the center of the cove and in the main body of the pond farther than 200 ft from the peninsula. The membranes had become so fragile that a number of samplers burst and drained completely before the water could be decanted into the sample bottles. Other samplers leaked rapidly once out of the pond water, and less than 500 mL were obtained. Of the intended 108 diffusion samples, 12 were lost completely and 20 were partially lost because of the leaking membranes.

Table 4. Validated detections of ordnance-related compounds in diffusion and drive-point samples collected from the pond-bottom sediments of Snake Pond, Cape Cod, Massachusetts, August 2001-March 2002

[Analysis by Severn Trent Laboratories, Burlington, VT. Analyte: Photo diode array (PDA) confirmation by AMEC Earth & Environmental, Westford, MA. ID, identification number; No., number; RDX, Hexahydro-1,3,5-trinitro-1,3,5-triazine; STL, Severn Trent Laboratories; USGS, U.S. Geological Survey; μg/L, micrograms per liter; --, not applicable]

Site identifier (fig. 4)	STL control No.	USGS sample ID	Date	Sample type	Analyte	Concentration (µg/L)
	GS08-024	RDX control ¹	9-07-01	Diffusion	RDX	0.66
2	GS11-002	WWD03-0100	10-17-01	Diffusion	2,4-diamino-6- Nitrotoluene	.35
37	GS11-037	WWD10-0825	10-17-01	Diffusion	Nitroglycerin	16
64	GS11-064	WWD01-0050	10-17-01	Diffusion	2,4-diamino-6- Nitrotoluene	.37
71	GS11-071	WWD04-0200	10-17-01	Diffusion	2-Nitrotoluene	1.1
81	GS11-081	WWD06-0125	10-17-01	Diffusion	2,6-Dinitrotoluene	.62
DP5		DP0005	12-11-01	Drive point	Perchlorate	.89
DP9		DP0009	3-19-02	Drive point	Perchlorate	.86

¹Water collected from well MW34M1 by AMEC Earth & Environmental, Westford, MA.

To limit the rate of leakage, the samples were decanted from the diffusion samplers immediately upon being hauled into the boat. No time was taken to rinse off the mud and sediments on the outside of the samplers. Therefore, some of the water samples decanted into the sample bottles were turbid because they had entrained sediments that were clinging to the outside of the samplers.

The scuba divers reported that 11 samplers were completely or partially exposed on the pond bottom. Some samplers had been difficult to bury because of hard bottom sediments, and other samplers may have become exposed because of wave action near the shore. The length of time that these samplers were exposed could not be determined.

As a result of the lost and completely exposed diffusion samplers, water samples from only 88 of the 108 diffusion samplers were preserved and shipped to the laboratory for analysis. The 20 sampling sites that did not yield samples are indicated by dashes instead of STL control numbers in table 2. The sites that yielded useable samples provided good coverage of the sampled area (fig. 3).

Once again, three quality-control water samples were sent to the laboratory for analysis (table 2). The water blank was obtained directly from the deionized

water supply used to fill the diffusion samplers. The trip blank was also obtained directly from the deionized water supply, but it was decanted into a sample bottle prior to retrieval of the samples and was kept in the sample cooler on the boat on the retrieval day. The third sample was collected from the Snake Pond surface water near diffusion-sampler site 57 (fig. 3).

As in the case of the single transect, the water samples from the diffusion samplers exhibited numerous chromatographic peaks. However, the PDA inspection of the spectra found the target compounds in only five cases (table 4). No detections were reported for the pond-water sample and the two quality-control samples composed of deionized water.

The five sites where target contaminant detections were confirmed by the PDA inspection are widely scattered and are not related to each other spatially (fig. 4). The pond-bottom sediments at the sites varied from sand to fine-grained, organically rich sediment. Only one compound was detected in each sample, and four different compounds were reported for the five sites. These compounds are not characteristic of contaminated groundwater samples collected from monitoring wells near the Camp Edwards ranges (AMEC, 2002a).

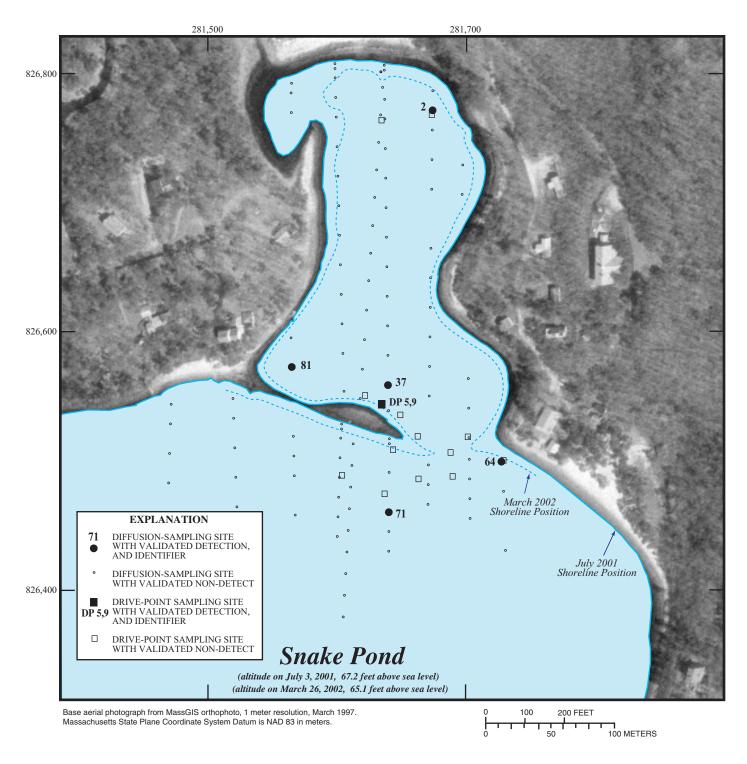


Figure 4. Locations of validated detections of ordnance-related compounds in diffusion and drive-point water samples collected from bottom sediments of Snake Pond, Cape Cod, MA, August 2001—March 2002. (Pond altitudes from Rose Forbes, Air Force Center for Environmental Excellence, written commun., 2003.)

Drive-Point Sampling of Ground Water

The results obtained from the diffusion samplers set in the pond-bottom sediments did not indicate an area of ground-water discharge containing RDX or other explosive compounds. However, the interferences in the chromatograms presumed to be caused by natural organic compounds resulted in uncertainty concerning this conclusion. In addition, the water samples from the diffusion samplers were not analyzed for perchlorate. This compound had been found in various wells upgradient of Snake Pond (AMEC, 2002a) and was known to be a propellant used in munitions.

Drive-point sampling was done in December 2001 and March 2002 to provide confirmation of the diffusionsampler results and to collect ground-water samples under the pond for analysis of perchlorate. A total of 21 samples were collected at 14 sites (fig. 5 and table 5). The sites were selected in areas where the pond bottom was sandy because the fine-grained sediments do not yield water readily. All but three of the sites were near the peninsula because four of the five confirmed detections of explosives were obtained from diffusion samplers in this general area.

The drive-point samples were collected by using a temporary well-point sampler (Macho Model, K-V Associates, Inc., Mashpee, MA). The sampler consists of threaded 0.63-in.-diameter steel tubing with a hardened conical drive point attached at the end. The bottom 10 in. of the sampler is slotted vertically to allow the entry of pore water. Water samples were collected through a 0.1875-in.-outside-diameter flexible polyethylene tube inserted inside the sampler opposite the slotted screen.

At each sampling site, the depth of the pond water was determined by using a folding rule or digital fathometer, and the horizontal location was determined by using a global positioning system (GPS). The drive point was manually driven 2–4 ft below the pond bottom by using a sliding hammer so that the point was set in hard bottom sediments that presumably were the permeable sands and gravels below the soft, poorly permeable

organically rich sediments. The polyethylene tubing was inserted into the sampler, and ground water was withdrawn from the tubing by using a peristaltic pump fitted with Norprene tubing.

About 1 L was pumped from the sampler prior to sample collection to purge the standing water and to ensure that representative pore water was being pumped from the bottom sediments. The specific conductance of the pumped water was measured during the purging and was compared to the specific conductance of the pond water at the site (table 5). The conductance values generally stabilized during the purging process. After purging was completed, a 250-mL sample was collected in a polyethylene bottle for analysis of perchlorate, and two to three 1-L samples were collected in amber glass bottles and chilled immediately for analysis of the explosive compounds. The sampler was then pulled from the sediments and was rinsed with 1-2 L of deionized water prior to use at the next sampling site.

The water samples were analyzed for the ordnancerelated compounds listed in table 3, including perchlorate. Perchlorate was analyzed by using USEPA method 314.0 (U.S. Environmental Protection Agency, 1999), which was modified to obtain a reporting limit of 1.5 µg/L. The explosives samples were analyzed by STL in Burlington, VT. Perchlorate was analyzed by Ceimic Corporation in Narragansett, RI.

No explosive compounds were detected in the ground-water samples collected from the drive points. Unlike the water samples obtained from the diffusion samplers, there were no chromatographic peaks presumed to be caused by natural organic compounds in the bottom sediments. The drive point was driven below the organically rich sediments and was used to sample ground water in the sand and gravel below the bottom sediments.

Perchlorate was detected at sub-ug/L levels (table 4) in two drive-point samples collected about 3 months apart at about the same location (sites DP5 and DP9, fig. 4). The pond water was less than 1 ft deep at this site on both sampling dates. The specific conductance of both samples was equal to the specific conductance of the pond water on the respective sampling dates (table 5).

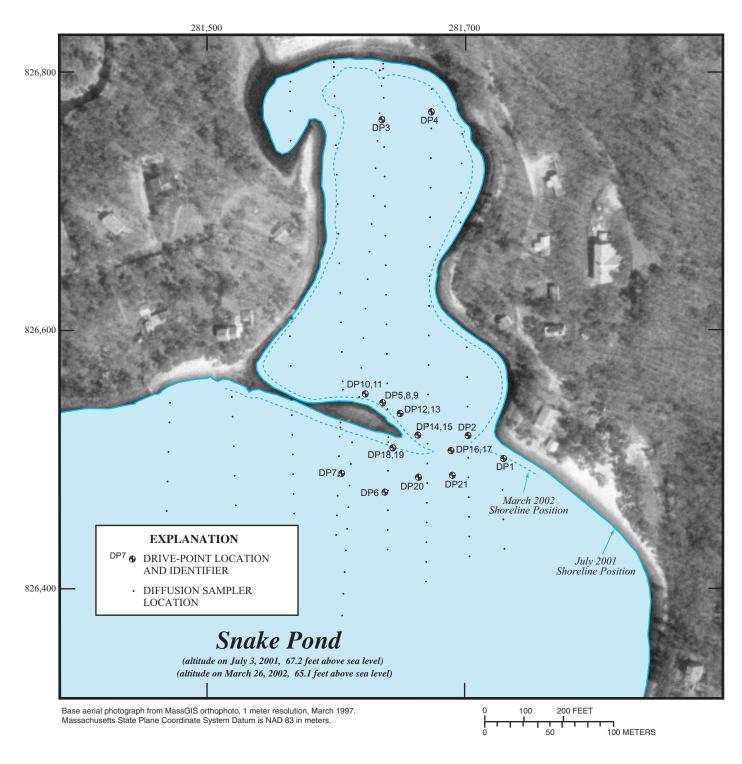


Figure 5. Locations of temporary drive points installed in the bottom sediments of Snake Pond, Cape Cod, Massachusetts, December 2001 and March 2002. (Pond altitudes from Rose Forbes, Air Force Center for Environmental Excellence, written commun., 2003.)

Table 5. Locations, site identifiers, sampling depths and dates, and specific conductance of water samples collected from a temporary well point driven into the bottom sediments of Snake Pond, Cape Cod, Massachusetts, December 2001 and March 2002

[USGS sample ID: Samples retrieved December 11, 2001, preceded by SNP/RDX/1201. Samples retrieved March 19, 2002, preceded by SNP/RDX/0302. State-plane coordinates given as easting and northing, NAD 83. ID, identification number; USGS, U.S. Geological Survey; μ S/cm, microsiemens per centimeter at 25°Celsius; --, not applicable]

Site identifier (fig. 5)	USGS sample ID	Easting (meters)	Northing (meters)	Water depth (feet)	Drive distance below bottom (feet)	Specific conductance (µS/cm)
		Samples	collected Decemb	er 11, 2001		
DP1	DP0001	281,728.1	826,499.9	1.4	2.6	61
DP2	DP0002	281,700.8	826,517.7	2.3	2.1	96
DP3	DP0003	281,634.4	826,761.3	3.2	2.0	58
DP4	DP0004	281,672.6	826,767.3	2.3	4.0	78
DP5	DP0005	281,635.6	826,542.1	.9	2.2	57
DP6	DP0006	281,636.7	826,474.1	7.8	3.5	61
DP7	DP0007	281,603.4	826,488.5	10.0	2.8	64
	Pond water					57
		Sampl	es collected March	19, 2002		
DP8	DP0008	281,636.0	826,542.3	0.2	2.0	58
DP9	DP0009	281,636.0	826,542.3	.2	4.0	56
DP10	DP0010	281,621.4	826,549.7	.9	2.0	56
DP11	DP0011	281,621.4	826,549.7	.9	2.0	56
DP12	DP0012	281,648.4	826,534.2	.7	2.0	61
DP13	DP0013	281,648.4	826,534.2	.7	2.0	62
DP14	DP0014	281,661.9	826,517.4	1.4	2.0	65
DP15	DP0015	281,661.9	826,517.4	1.3	2.0	66
DP16	DP0016	281,687.5	826,505.9	.3	2.0	111
DP17	DP0017	281,687.5	826,505.9	.3	2.0	107
DP18	DP0018	281,642.1	826,508.0	1.0	2.0	59
DP19	DP0019	281,642.1	826,508.0	.8	2.0	59
DP20	DP0020	281,662.7	826,484.8	3.3	3.0	60
DP21	DP0021	281,688.7	826,486.7	3.0	2.0	114
	Pond water					56

The similarity of the ground-water and pond-water values for specific conductance could indicate that pond water was being drawn down to the sampling point during pumping from the drive-point sampler. A similarity between ground-water and pond-water values was observed at 16 of the 21 drive-point sampling sites. However, the ground-water conductance was substantially greater than the pond-water conductance at various sites in the northern part of the cove and between the eastern tip of the peninsula and the summer-camp swimming beach (for example, sites DP16 and DP21, fig. 5 and table 5). The drive-point method has been used successfully to sample ground water at other sites near Camp Edwards (Savoie and others, 2000; McCobb and others, 2003) without indication of sample contamination by pond water. The similarity of the values could reflect seepage of pond water into the aguifer under natural conditions, or could result from a coincidental agreement of conductance values in pond water and discharging shallow ground water in the sampled areas.

ORDNANCE-RELATED COMPOUNDS IN SHALLOW GROUND WATER BENEATH **SNAKE POND**

The diffusion and drive-point sampling was performed to determine if ground water containing ordnance-related compounds from the southeastern ranges at Camp Edwards was discharging to Snake Pond. There was concern that discharge could be occurring in specific areas at levels that might require prompt action to protect human health. Data on the discharge locations could also be used to design additional studies of the path of contaminants from the ranges, particularly near and beneath Snake Pond. Diffusion sampling had been used successfully in other ponds near the MMR to locate the discharge areas of VOC plumes (Savoie and others, 2000), and the use of this method at Snake Pond had the potential to provide information on the discharge of ordnancerelated compounds quickly and inexpensively as compared to a drilling program on the pond. However, the materials used and the sample size were different than those of Savoie and others (2000) because the target compounds, RDX and other explosives, are not volatile compounds.

The results from the diffusion and drive-point sampling do not indicate an area of ground-water discharge with concentrations of ordnance-related compounds and perchlorate that are sufficiently elevated to be detected by the sampling methods. The discharge may occur in areas that were not sampled. Alternatively, the contaminant levels may be too low, either because of dispersion in the aquifer or attenuation by dilution, sorption, or degradation in the bottom sediments, to be detected by the sampling methods. It is also possible that the ground water containing the RDX and perchlorate detected in monitoring wells north of the pond and on the peninsula separating the northern cove from the main body of Snake Pond may be deep enough below the water table to pass beneath the pond.

Perchlorate was detected in drive-point samples on two sampling dates at about the same location on the northern shore of the peninsula, but in water with the same specific conductance as the pond water. The concentrations were less than 1 µg/L. Perchlorate has been detected upgradient of Snake Pond, but not in the monitoring wells located on the peninsula near the drive-point site (AMEC, 2002a). The perchlorate in the drive-point samples cannot be linked to perchlorate contamination at Camp Edwards with presently (2003) available information.

The diffusion and drive-point sampling data cannot be interpreted further without additional information concerning the pattern of ground-water flow at Snake Pond and the distributions of RDX, HMX, and perchlorate in the aquifer near the pond. The irregular shape and bathymetry of the pond in the simulated area of ground-water discharge, including the peninsula that becomes smaller or larger or is completely submerged depending on the water level, complicate efforts to understand the flow directions. Walter and others (2002) demonstrated with a ground-water-flow model that discharge occurs to the pond in the study area, but the rate and location of discharge are affected by the pond-bottom characteristics and pumping associated with a nearby ground-water-treatment system. Additional model simulations could improve the understanding of groundwater flow near Snake Pond and provide a better hydrologic framework in which to evaluate water-quality data obtained from ground-water sampling by use of diffusion samplers, drive points, and monitoring wells.

Additional data delineating the spatial distribution of ordnance-related compounds north of Snake Pond and beneath the peninsula and shoreline of the pond would also help provide a framework for determining where and how deep below the pond bottom the contaminants might be found. Determining possible discharge locations from detections deep in the aquifer and far from the pond is highly uncertain, especially if the width and thickness of the actual contamination zone upgradient of the pond is small. Projecting flowpaths hundreds or thousands of feet downgradient from monitoring wells with detections to guide the selection of pond-bottom sampling sites is a challenging task even when the contaminant plume upgradient of the pond is large and reportedly well characterized (Savoie and others, 2000).

SUMMARY

Diffusion and drive-point sampling was used by the USGS, in cooperation with the Army National Guard Bureau, in 2001–02 to determine if ground water containing ordnance-related compounds from various military ranges at Camp Edwards on the Massachusetts Military Reservation was discharging to Snake Pond. The diffusion samplers were constructed with cellulose membranes that allow diffusion of RDX, HMX, and other explosive compounds into the samplers. The 130 diffusion samplers were buried into the pond-bottom sediments by scuba divers along 13 transects and allowed to equilibrate with shallow ground water beneath the pond for 13-27 days before retrieval. Ground-water samples were collected from temporary well points driven into the pond bottom at 21 sites and analyzed for explosives and perchlorate.

Four explosive compounds were detected in diffusion samplers at five widely spaced sites, but the detected compounds did not include RDX or MHX and generally are not found in the ground water near the ranges. Perchlorate was detected at less than 1 µg/L in two drive-point samples collected at the same site about 3 months apart. The results from the diffusion and drive-point sampling do not indicate an area of ground-water discharge with concentrations of ordnance-related compounds that are sufficiently elevated to be detected by these methods. Additional information from ground-

water modeling and sampling on the pattern of groundwater flow at Snake Pond and the distributions of RDX, HMX, and perchlorate in ground water in the aquifer near the pond would help provide a framework for evaluating further the water-quality data obtained from the diffusion samplers and drive points.

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