

Toxic Substances Hydrology Program

# **Comparison of No-Purge and Pumped Sampling Methods for Monitoring Concentrations of Ordnance-Related Compounds in Groundwater, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010**



Scientific Investigations Report 2012–5084

**Cover.** View toward the northwest of the Impact Area at Camp Edwards on the Massachusetts Military Reservation, Cape Cod, Massachusetts. The pine-barren plant community in the foreground has an open canopy of pitch pine and a dense understory of scrub oak. The sand-colored areas near upper left of the photo are excavations associated with the removal of contaminated soil and unexploded ordnance. Cape Cod Bay is visible at the upper right of the photo. The photo was taken on April 20, 2012, by the Army National Guard.

# **Comparison of No-Purge and Pumped Sampling Methods for Monitoring Concentrations of Ordnance-Related Compounds in Groundwater, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010**

By Jennifer G. Savoie and Denis R. LeBlanc

Toxic Substances Hydrology Program

Prepared in cooperation with the Army National Guard

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**U.S. Department of the Interior**  
**U.S. Geological Survey**

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## Conversion Factors and Datums

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	0.4047	hectare (ha)
Volume		
ounce, fluid (fl. oz)	0.02957	liter (L)
ounce, fluid (fl. oz)	29.57	milliliter (mL)
gallon (gal)	3.785	liter (L)
Flow rate		
foot per second (ft/s)	0.3048	meter per second (m/s)
gallon per minute (gal/min)	3.785	liter per minute (L/min)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)
Hydraulic conductivity		
foot per second (ft/s)	0.3048	meter per second (m/s)
Hydraulic gradient		
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)

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

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S}/\text{cm}$  at 25°C).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g}/\text{L}$ ).

## Abbreviations

AFCEE	Air Force Center for Engineering and the Environment
ARNG	Army National Guard
$\text{ClO}_4^-$	perchlorate
EDTA	ethylenediaminetetraacetic acid
GRAB1L	1-liter polyethylene-film grab
GRAB2L	2-liter polyethylene-film grab
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
IAGWSP	Impact Area Groundwater Study Program
MMR	Massachusetts Military Reservation
MWCO	molecular weight cutoff
PVC	polyvinyl chloride
QA/QC	quality assurance and control
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RCELLM	regenerated-cellulose membrane
RPPOLY	rigid porous polyethylene
SPEIM	system performance and ecological impact monitoring
USAEC	U.S. Army Environmental Command
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound

# Comparison of No-Purge and Pumped Sampling Methods for Monitoring Concentrations of Ordnance-Related Compounds in Groundwater, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010

By Jennifer G. Savoie and Denis R. LeBlanc

## Abstract

Field tests were conducted near the Impact Area at Camp Edwards on the Massachusetts Military Reservation, Cape Cod, Massachusetts, to determine the utility of no-purge groundwater sampling for monitoring concentrations of ordnance-related explosive compounds and perchlorate in the sand and gravel aquifer. The no-purge methods included (1) a diffusion sampler constructed of rigid porous polyethylene, (2) a diffusion sampler constructed of regenerated-cellulose membrane, and (3) a tubular grab sampler (bailer) constructed of polyethylene film. In samples from 36 monitoring wells, concentrations of perchlorate ( $\text{ClO}_4^-$ ), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), the major contaminants of concern in the Impact Area, in the no-purge samples were compared to concentrations of these compounds in samples collected by low-flow pumped sampling with dedicated bladder pumps. The monitoring wells are constructed of 2- and 2.5-inch-diameter polyvinyl chloride pipe and have approximately 5- to 10-foot-long slotted screens. The no-purge samplers were left in place for 13–64 days to ensure that ambient groundwater flow had flushed the well screen and concentrations in the screen represented water in the adjacent formation.

The sampling methods were compared first in six monitoring wells. Concentrations of  $\text{ClO}_4^-$ , RDX, and HMX in water samples collected by the three no-purge sampling methods and low-flow pumped sampling were in close agreement for all six monitoring wells. There is no evidence of a systematic bias in the concentration differences among the methods on the basis of type of sampling device, type of contaminant, or order in which the no-purge samplers were tested. A subsequent examination of vertical variations in concentrations of  $\text{ClO}_4^-$  in the 10-foot-long screens of six wells by using rigid porous polyethylene diffusion samplers indicated that

concentrations in a given well varied by less than 15 percent and the small variations were unlikely to affect the utility of the various sampling methods.

The grab sampler was selected for additional tests in 29 of the 36 monitoring wells used during the study. Concentrations of  $\text{ClO}_4^-$ , RDX, HMX, and other minor explosive compounds in water samples collected by using a 1-liter grab sampler and low-flow pumped sampling were in close agreement in field tests in the 29 wells. A statistical analysis based on the sign test indicated that there was no bias in the concentration differences between the methods. There also was no evidence for a systematic bias in concentration differences between the methods related to location of the monitoring wells laterally or vertically in the groundwater-flow system. Field tests in five wells also demonstrated that sample collection by using a 2-liter grab sampler and sequential bailing with the 1-liter grab sampler were options for obtaining sufficient sample volume for replicate and spiked quality assurance and control samples.

The evidence from the field tests supports the conclusion that diffusion sampling with the rigid porous polyethylene and regenerated-cellulose membranes and grab sampling with the polyethylene-film samplers provide comparable data on the concentrations of ordnance-related compounds in groundwater at the MMR to that obtained by low-flow pumped sampling. These sampling methods are useful methods for monitoring these compounds at the MMR and in similar hydrogeologic environments.

## Introduction

Groundwater remediation often includes a long-term sampling program to monitor the success of the cleanup or the fate of contaminants that remain in the aquifer after remediation is completed. The sampling program typically consists of collection of groundwater samples from monitoring wells by

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using low-flow, or low-stress, sampling protocols (Puls and Barcelona, 1996; U.S. Environmental Protection Agency, 2010) and portable or dedicated sampling pumps. Low-flow sampling can be labor intensive, require expensive sampling equipment, and produce excess purge water that must be treated before disposal.

No-purge, or passive, sampling methods have been developed as a low-cost alternative to low-flow pumped sampling (Vroblesky and Hyde, 1997; Parsons, 2005; Interstate Technology & Regulatory Council, 2008). No-purge methods are based on the concept that natural flow through the well screen (Freeze and Cherry, 1979) results in chemical concentrations in the screen that are equal to concentrations in the surrounding formation. The no-purge methods use a diffusion or grab sampler to obtain a water sample from the screened interval without the need to purge the well before sampling. Diffusion samplers consist of a diffusion membrane filled with a sampling fluid, such as deionized and distilled water, that is suspended in the screened interval. After sufficient time has elapsed for concentrations of the chemicals of interest to equilibrate across the membrane, the sampler is retrieved without the need to pump water from the well. Grab samplers consist of a mechanical device that is lowered into the screened interval, triggered to capture the water in the screen, and retrieved without the need to pump the well. Grab samplers collect a sample of the groundwater passing through the screen, whereas diffusion samplers use a membrane that is permeable to the chemicals of interest so that the chemicals can pass into the sampling fluid in the sampler.

Diffusion samplers are being used for long-term monitoring at sites of groundwater contamination nationwide (Parsons, 2005; Interstate Technology & Regulatory Council, 2008). Most of these applications use a membrane composed of polyethylene film for monitoring volatile organic compounds (VOCs). However, the polyethylene film is not suitable for monitoring inorganic chemicals or organic compounds having higher molecular weights than the VOCs. Other membranes that are permeable to these chemicals, such as rigid porous polyethylene and regenerated-cellulose, have been used at sites where these contaminants are a concern (Vroblesky and others, 2002; Parson, 2005). Grab samplers are also being used at these sites because they capture the groundwater directly and do not rely on chemical diffusion through a permeable membrane.

Military munitions contain organic and inorganic chemicals, such as the high-energy explosive compounds hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and the oxidant perchlorate ( $\text{ClO}_4^-$ ). These chemicals, which have been detected at levels of concern in groundwater beneath active and former military ranges, do not pass through polyethylene diffusion membranes. Therefore, monitoring of these chemicals by using no-purge sampling methods would require the use of grab samplers or diffusion samplers with other types of membranes. Parker and Clark (2004), Parker and Mulherin (2007), LeBlanc and Vroblesky (2008), and Parker and others

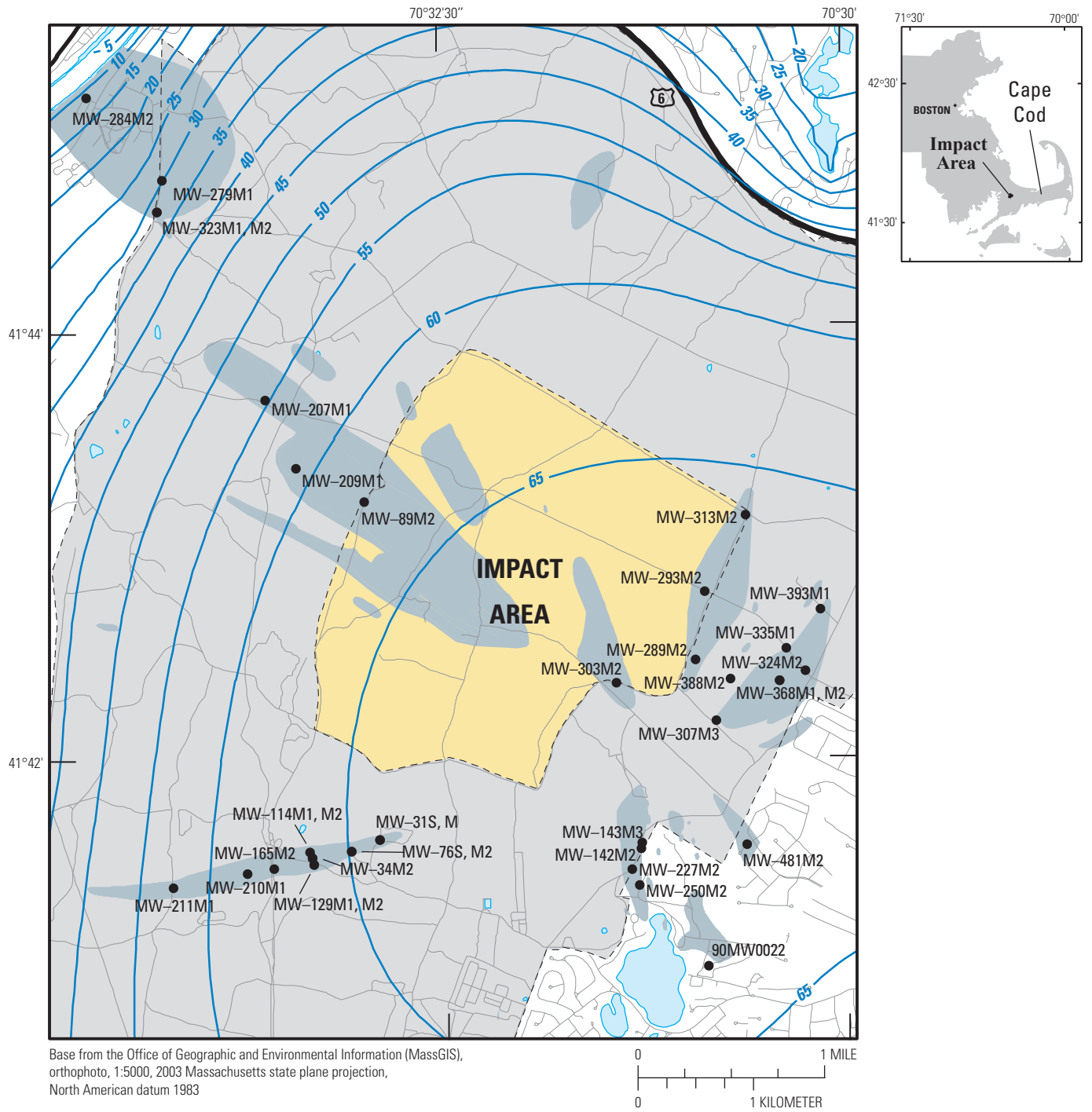
(2009) have demonstrated in field and laboratory studies that regenerated-cellulose and rigid porous polyethylene diffusion samplers and several types of grab samplers can be used to obtain groundwater samples from wells for analysis of explosive compounds and perchlorate.

### Groundwater at the Massachusetts Military Reservation

Long-term monitoring of groundwater quality is a major component of groundwater remediation activities at the Massachusetts Military Reservation (MMR), a 22,000-acre multi-use military installation on western Cape Cod, Massachusetts, that includes Otis Air National Guard Base and Army National Guard Training Area Camp Edwards (fig. 1). The aquifer at the MMR consists of glacial deposits of sand and gravel that include layers of silt and clay and overlies crystalline bedrock. The aquifer is 150–400 feet (ft) thick, is unconfined, and is recharged solely by precipitation at an estimated average rate of 27 inches per year (in/yr) (Walter and Whealan, 2005). The water table on western Cape Cod forms a mound with a maximum altitude of about 70 ft near the eastern boundary of the MMR (fig. 1). Groundwater flows radially outward from the top of the mound toward discharge areas at lakes, streams, wetlands, and the coast (LeBlanc and others, 1986; Walter and Masterson, 2003; Walter and Whealan, 2005). Groundwater flow is predominantly in the horizontal direction, although substantial downward and upward flow occurs near the top of the water-table mound and near discharge areas.

Groundwater at the MMR is contaminated by a variety of chemicals related to military activities that date back to the mid-1900s. The contaminants of concern include VOCs, ethylene dibromide,  $\text{ClO}_4^-$ , RDX, and HMX. More than two dozen plumes of contaminants have been described in the aquifer, and several agencies of the Department of Defense are actively remediating contaminated soil and groundwater on and near the installation (Air Force Center for Engineering and the Environment and the U.S. Army Environmental Command, 2010). One area of concern, the Impact Area in Camp Edwards, encompasses about 2,200 acres in the northern area of the MMR (fig. 1). The contaminants in the Impact Area are related to the firing and disposal of military munitions and include the ordnance-related explosive compounds RDX and HMX and the oxidant  $\text{ClO}_4^-$  (U.S. Army Environmental Command, 2011). These contaminants occur in several plumes (fig. 1) that originate from various firing ranges, disposal sites, and artillery targets in and near the Impact Area.

Groundwater monitoring at MMR presently (2012) includes the quarterly to triennial collection of groundwater samples from more than 1,700 monitoring wells (Rose Forbes, Air Force Center for Engineering and the Environment (AFCEE), and Benjamin Gregson, Army National Guard Impact Area Groundwater Study Program (IAGWSP), written commun., 2012). Monitoring of plumes in the southern part of the installation, where VOCs are the main contaminants of concern, is done mostly by no-purge diffusion sampling using



Base from the Office of Geographic and Environmental Information (MassGIS), orthophoto, 1:5000, 2003 Massachusetts state plane projection, North American datum 1983

**Figure 1.** Location of Camp Edwards and the Impact Area at the Massachusetts Military Reservation, the plumes of ordnance-related contaminants, and the monitoring wells that were sampled for this study, as well as the altitude of the water table, western Cape Cod, Massachusetts.

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polyethylene-membrane samplers and, to a lesser extent, by pumped sampling using portable submersible pumps (Rose Forbes, AFCEE, written commun., 2012). Archfield and LeBlanc (2005) demonstrated that the two sampling methods provided similar VOC concentrations on the basis of samples collected from more than 50 monitoring wells near the MMR. Monitoring of plumes in and near the Impact Area in the northern part of the installation, where RDX, HMX, and  $\text{ClO}_4^-$  are the main contaminants of concern, is done primarily by pumped sampling using dedicated submersible pumps. In a field study at Camp Edwards in 2004–5, LeBlanc and Vroblesky (2008) compared concentrations of ordnance-related compounds in samples collected by using pumped and diffusion sampling methods. They concluded that no-purge diffusion sampling was a possible alternative to pumped sampling, although they noted that only 15 wells were sampled and only diffusion samplers constructed of rigid porous polyethylene were tested in their study. They also reported that there was poor agreement between concentrations in the diffusion and pumped samples for 4 of the 15 wells. Those four wells were resampled during this study.

### Purpose and Scope

This report evaluates the results of field tests of no-purge samplers for monitoring concentrations of  $\text{ClO}_4^-$  and explosive compounds in groundwater at Camp Edwards. The field tests were conducted in several phases in 2009–2010 in a total of 36 monitoring wells at Camp Edwards that were known to contain various levels of these contaminants. The wells are located in various hydrologic settings and have screens set at various depths below the water table. Groundwater samples were collected by both pumped and no-purge sampling methods, including two types of diffusion samplers and one type of grab sampler. The results presented in this report (1) compare several alternative methods for the no-purge sampling, (2) examine whether hydrologic setting and screen depth below the water table affect the degree of agreement between concentrations in no-purge and pumped samples, (3) present methods for obtaining sufficiently large volumes for quality assurance and control samples, and (4) confirm the conclusion presented in LeBlanc and Vroblesky (2008) that no-purge sampling may be a useful alternative to pumped sampling. This study was done cooperatively by the Toxic Substances Hydrology Program of the U.S. Geological Survey (USGS) and the Impact Area Groundwater Study Program (IAGWSP) of the Army National Guard.

### Design of Study

The study included four phases of field tests of the no-purge sampling methods in 36 monitoring wells near the Impact Area. The wells were installed by the IAGWSP in earlier investigations. The field tests included the collection

of water samples by pumped and no-purge sampling methods and laboratory analysis of the samples for concentrations of  $\text{ClO}_4^-$ , RDX, HMX, and other explosive compounds. The no-purge sampling methods included diffusion samplers with two different types of diffusion membranes and one type of grab sampler. The field tests also included the use of diffusion samplers to examine the vertical variations of  $\text{ClO}_4^-$  concentrations in six wells and the use of grab samplers to examine methods for obtaining sufficiently large volumes for quality assurance and control samples.

### Monitoring-Well Selection and Construction

The 36 monitoring wells used during this study are sampled annually or semiannually by the IAGWSP. The wells were chosen from this regularly sampled set to encompass the range of chemical and hydrologic conditions near the Impact Area. The selected wells are in the paths of various contaminant plumes and are known from historical chemical data to include a range of concentrations of  $\text{ClO}_4^-$ , RDX, and HMX (nondetectable to about 100, 37, and 10 micrograms per liter ( $\mu\text{g/L}$ ), respectively). The wells are located at various positions relative to the top of the water-table mound and, therefore, are in areas with gentle to steep horizontal hydraulic gradients. The depths of the wells range from about 18 to 191 ft below the water table and intercept shallow to deep groundwater-flow paths. Four wells (MW–31M, MW–76M2, MW–165M2, and MW–289M2) were included in the study in order to check the poor agreement between concentrations in pumped and diffusion samples from these wells, as reported by LeBlanc and Vroblesky (2008) in their study.

The wells are constructed of 2.0- and 2.5-in.-diameter polyvinyl chloride (PVC) well casings and slotted screens. The wells have about 10-ft-long screens, except for three wells that have about 5-ft-long screens (table 1). The wells were installed by hollow-stem-auger, dual-casing air-rotary, and sonic drilling methods according to the protocols described in U.S. Army Environmental Command (2007).

### Low-Flow Pumped Sampling Method

The pumped samples were collected by IAGWSP contractors and the USGS by using dedicated submersible bladder pumps and low-flow sampling methods according to the sampling protocols of the U.S. Environmental Protection Agency (2010). The average pumping rate was about 0.4 liters per minute (L/min), and field water-quality characteristics—specific conductance, pH, temperature, and dissolved oxygen concentration—were monitored for stabilization during the purging of each well (table 2). Approximately 3–5 gallons (gal) of water were pumped before stabilization was reached and samples were collected by the USGS and the IAGWSP contractors. This volume is equivalent to about 2–3 times the volume of water within the 10-ft-long screened interval of a 2-in.-diameter well.

**Table 1.** Location coordinates, land-surface and screened-interval altitudes, depths and altitudes of water levels, and well diameters for monitoring wells near the Impact Area, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts.

[Source of data: Impact Area Groundwater Study Program (IAGWSP). Locations shown in figure 1. Altitude in feet relative to National Geodetic Vertical Datum of 1929 (NGVD 29). Locations relative to the North American Datum of 1927 (NAD 27). no., number; ft, feet; mm/dd/yy, month/day/year; in., inch]

Well no.	Northing (NAD 27) (ft)	Easting (NAD 27) (ft)	Altitude of land surface (ft)	Altitude of top of screen (ft)	Altitude of bottom of screen (ft)	Water- level date (mm/dd/yy)	Depth to water below land surface (ft)	Altitude of water level (ft)	Diameter of well casing (in.)
90MW0022	254100.99	867113.01	105.10	-6.90	-11.90	10/06/09	34.18	70.92	2.5
MW-31M	254181.21	859727.31	153.59	40.59	30.59	10/26/09	85.47	68.12	2.5
MW-31S	254182.23	859727.32	153.59	55.59	50.59	10/26/09	85.48	68.11	2.0
MW-34M2	253831.69	857750.30	144.93	13.93	3.93	06/08/09	78.25	66.68	2.5
MW-76M2	253856.00	858929.99	136.06	31.06	21.06	11/16/09	68.33	67.73	2.5
MW-76S	253854.00	858930.01	136.06	51.06	41.06	11/16/09	68.31	67.75	2.0
MW-89M2	263731.01	859274.49	207.07	-6.93	-16.93	10/27/09	143.23	63.84	2.5
MW-114M1	253650.41	857818.91	146.73	-30.27	-40.27	06/09/09	79.97	66.76	2.5
MW-114M2	253648.40	857818.91	146.73	26.73	16.73	06/09/09	79.96	66.77	2.5
MW-129M1	253462.51	857861.09	136.25	0.25	-9.75	11/16/09	69.33	66.92	2.5
MW-129M2	253460.51	857861.11	136.25	20.25	10.25	11/16/09	69.32	66.93	2.5
MW-142M2	253946.61	867104.41	112.26	-27.74	-37.74	06/08/09	41.79	70.47	2.5
MW-143M3	254098.59	867130.91	101.83	-5.17	-10.17	10/06/09	30.94	70.89	2.5
MW-165M2	253351.69	856752.01	143.15	18.65	8.65	11/16/09	76.81	66.34	2.5
MW-207M1	266603.61	856491.41	197.74	-56.26	-66.26	10/27/09	140.97	56.77	2.5
MW-209M1	264652.71	857359.79	175.59	-64.41	-74.41	10/27/09	115.35	60.24	2.5
MW-210M1	253222.30	856000.89	161.54	-39.46	-49.46	06/08/09	96.22	65.32	2.5
MW-211M1	252822.49	853901.81	200.14	0.14	-9.86	11/03/09	138.01	62.13	2.5
MW-227M2	253351.09	866864.51	119.29	9.29	-0.71	06/08/09	48.89	70.40	2.5
MW-250M2	252903.00	867073.89	75.84	-69.16	-79.16	06/08/09	4.81	71.03	2.5
MW-279M1	272801.81	853562.53	102.68	6.58	-3.42	10/20/09	70.22	32.46	2.5
MW-284M2	275132.89	851430.84	28.40	-16.60	-26.60	11/03/09	22.62	5.78	2.5
MW-289M2	259281.08	868635.02	169.18	6.84	-3.16	10/06/09	98.51	70.67	2.5
MW-293M2	261216.15	868890.36	173.80	-23.12	-33.12	10/06/09	104.40	69.40	2.5
MW-303M2	258625.31	866413.09	180.79	-54.30	-64.31	10/20/09	109.83	70.96	2.5
MW-307M3	257560.60	869226.64	172.86	47.06	37.04	09/22/09	102.27	70.59	2.5
MW-313M2	263374.95	870040.63	186.42	-29.04	-39.07	10/14/09	119.29	67.13	2.5
MW-323M1	271899.40	853422.00	109.56	-85.44	-95.44	10/20/09	72.07	37.49	2.5
MW-323M2	271898.61	853421.99	109.56	-10.44	-20.44	10/20/09	72.05	37.51	2.5
MW-324M2	258966.00	871733.68	174.08	-29.66	-40.66	10/06/09	104.22	69.86	2.5
MW-335M1	259607.84	871192.56	177.52	-77.68	-87.68	09/22/09	107.70	69.82	2.5
MW-368M1	258680.41	871017.69	171.43	-64.57	-74.57	09/22/09	101.93	69.50	2.5
MW-368M2	258680.57	871017.69	171.43	-31.57	-41.57	09/22/09	101.72	69.71	2.5
MW-388M2	258727.57	869639.90	140.91	-3.84	-13.84	10/06/09	70.18	70.73	2.5
MW-393M1	260721.56	872166.01	156.51	-112.05	-122.05	09/21/09	87.99	68.52	2.5
MW-481M2	254052.88	870108.69	156.16	9.88	-0.12	10/27/09	85.24	70.92	2.5

## 6 Comparison of Sampling Methods for Monitoring Concentrations of Ordnance-Related Compounds in Groundwater

**Table 2.** Field water-quality analyses for water samples collected from monitoring wells near the Impact Area by low-flow pumped sampling, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010.

[Source of data: U.S. Geological Survey. Locations shown in figure 1. no., number; --, not analyzed; mm/dd/yy, month/day/year; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter]

Well no.	Sample date (mm/dd/yy)	Temperature (°C)	Specific conductance (µS/cm)	pH (standard units)	Dissolved oxygen (mg/L)
90MW0022	10/06/09	11.6	78.4	5.83	2.9
MW-31M	11/18/09	11.1	84.3	5.77	11.5
MW-31S	11/18/09	10.7	120.7	5.49	9.8
MW-31S	09/01/10	14.2	99.5	5.41	8.4
MW-34M2	06/08/09	10.9	51.5	5.99	11.5
MW-34M2	07/20/09	11.6	52.7	5.92	11.4
MW-76M2	11/16/09	10.4	98.1	5.73	10.3
MW-76M2	09/01/10	11.4	81.5	5.62	10.7
MW-76S	11/16/09	10.6	55.3	5.97	11.8
MW-89M2	10/27/09	10.8	57.1	6.43	11.7
MW-89M2	09/01/10	14.3	43.3	6.28	11.0
MW-114M1	06/09/09	11.3	51.6	6.28	11.8
MW-114M1	07/21/09	13.1	51.2	6.25	12.2
MW-114M2	06/09/09	11.1	52.3	5.96	11.8
MW-114M2	07/21/09	11.4	52.5	5.97	11.9
MW-129M1	06/09/09	10.4	50.7	6.12	11.8
MW-129M1	06/23/09	10.6	50.9	--	11.9
MW-129M1	11/16/09	10.8	49.8	6.15	11.7
MW-129M2	06/09/09	10.4	52.0	5.98	11.9
MW-129M2	06/23/09	10.9	52.1	6.01	12.2
MW-129M2	11/16/09	10.4	51.1	6.06	11.6
MW-142M2	06/08/09	12.0	74.1	5.76	9.7
MW-142M2	06/23/09	11.3	74.5	5.78	10.3
MW-143M3	10/06/09	10.4	71.1	5.78	10.3
MW-165M2	11/16/09	10.1	53.2	6.07	11.6
MW-207M1	10/27/09	10.5	58.1	6.81	11.6
MW-209M1	10/27/09	10.4	49.3	6.51	11.7
MW-210M1	06/08/09	11.3	61.5	6.62	11.1
MW-210M1	07/20/09	12.4	64.4	6.62	11.3



**Table 2.** Field water-quality analyses for water samples collected from monitoring wells near the Impact Area by low-flow pumped sampling, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010.—Continued

Well no.	Sample date (mm/dd/yy)	Temperature (°C)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	pH (standard units)	Dissolved oxygen (mg/L)
MW–211M1	11/18/09	11.1	51.7	6.29	12.1
MW–211M1	09/02/10	16.9	51.2	6.49	11.5
MW–227M2	06/08/09	11.0	66.4	5.91	9.8
MW–227M2	07/20/09	11.8	64.3	5.92	11.3
MW–250M2	06/08/09	10.6	84.4	6.05	10.0
MW–250M2	07/20/09	11.8	83.1	6.07	9.8
MW–279M2	10/20/09	10.4	70.8	6.45	11.0
MW–284M2	11/03/09	11.3	103.1	6.03	10.2
MW–289M2	10/06/09	11.0	55.4	6.04	11.2
MW–293-M2	10/06/09	10.8	59.4	6.23	12.0
MW–303M2	10/21/09	12.0	53.0	6.08	6.9
MW–303M2	09/01/10	13.7	45.5	5.97	8.0
MW–307M3	09/22/09	13.0	47.2	5.87	12.2
MW–313M2	10/13/09	10.6	55.1	6.49	11.8
MW–323M1	10/20/09	11.3	68.8	6.10	7.9
MW–323M2	10/20/09	10.7	54.4	6.07	10.9
MW–323M2	09/02/10	14.4	53.5	6.04	11.6
MW–324M2	10/06/09	11.3	63.7	6.67	10.9
MW–335M1	09/22/09	11.3	56.9	6.55	8.6
MW–368M1	09/22/09	12.1	59.2	6.90	8.7
MW–368M1	09/02/10	14.7	60.0	6.96	8.8
MW–368M2	09/22/09	12.2	76.0	7.11	9.0
MW–368M2	09/02/10	13.5	80.1	7.06	10.0
MW–388M2	10/06/09	11.0	54.3	6.17	11.5
MW–393M1	10/13/09	9.7	68.6	7.22	12.0
MW–481M2	10/27/09	10.8	72.7	6.13	11.1

## No-Purge Sampling Methods

Three types of no-purge samplers were tested in this study: (1) diffusion samplers constructed of rigid porous polyethylene (RPPOLY) membranes, (2) diffusion samplers constructed of regenerated-cellulose (RCELLM) membranes, and (3) two sizes—1 liter (L) (GRAB1L) and 2 L (GRAB2L)—of disposable polyethylene-film grab samplers.

The RPPOLY samplers were constructed of rigid, porous polyethylene tubing as described in LeBlanc and Vroblesky (2008). RPPOLY samplers are available commercially (Columbia Analytical Services, 2012); for this study, however, the samplers from the 2004–5 study by LeBlanc and Vroblesky (2008) were reused after being soaked and rinsed thoroughly with deionized water. Each sampler holds about 160 milliliters (mL) of deionized water. Therefore, four RPPOLY samplers were used in each well to obtain the 625 mL of water required for chemical analysis. The samplers were suspended in the well on polypropylene line and spaced evenly along the length of the 10-ft-long well screen. After retrieval of the samplers, the water from all four samplers was decanted into a 1-L amber-colored glass bottle. About 125 mL was then decanted from the blended sample into a polyethylene bottle for analysis of  $\text{ClO}_4^-$ . The water remaining in the 1-L glass bottle was used for analysis of explosive compounds.

The RCELLM samplers were constructed of high-grade regenerated-cellulose tubular dialysis membrane. The membrane was 50 millimeters (mm) wide when lying flat and had a nominal molecular-weight cutoff (MWCO) of 8,000 daltons. The membrane is packed for shipping in a storage solution of ethanol, sodium benzoate, and ethylenediaminetetraacetic acid (EDTA) and must be rinsed thoroughly with deionized water before use. To construct the samplers, the membrane was cut to working lengths of about 40 in. and rinsed five times with deionized water. A knot was tied at one end of the tubular membrane, the tube was filled with about 480 mL of deionized water, and a knot was tied at the other end to close the tube. The water-filled tube, which was about 24 in. long, was then slid into a flexible nylon-mesh tube for protection. Two RCELLM samplers were suspended in the well on polypropylene line, with one sampler set directly above and the other set directly below the midpoint of the screened interval. After retrieval of the samplers, the water from the two samplers was decanted into a 1-L amber-colored glass bottle. About 125 mL was then decanted from the blended sample into a polyethylene bottle for analysis of  $\text{ClO}_4^-$ . The water remaining in the 1-L glass bottle was used for analysis of explosive compounds.

The grab samplers are tubular disposable bailers constructed of 4-mil-thick (4 thousandths of an inch) polyethylene film with a polyethylene check valve at the top of the sampler (GeoInsight, 2012a, b). Two sizes of grab samplers were used in the study. The smaller (HydraSleeve GRAB1L) samplers (model no. HS-2-1L) were 36 in. long and had a diameter of 1.6 in. and a volume of about 1 L when filled. The larger

(SuperSleeve GRAB2L) samplers (model no. HSSS-2L) were 60 in. long and had a diameter of 1.6 in. and a volume of about 2 L when filled. Only one sampler was needed per well to obtain sufficient volume for laboratory analysis.

The smaller GRAB1L samplers were deployed in wells with 10-ft-long screens by setting the check valve, attaching a stainless-steel weight to the bottom of the sampler, and lowering the sampler on a polypropylene line into the well until the weight rested on the bottom and, as a result, the top, open end of the sampler was about 3 ft below the midpoint of the screened interval. In wells with 5-ft-long screens, a stainless-steel weight was also attached to the top of the sampler. This upper weight caused the top of the sampler to rest near the bottom of the well and below the screened interval. To fill the sampler with water from the screened interval before retrieval from the wells with the 10-ft-long screens, the polypropylene line was pulled up in one continuous 5-ft-long stroke at a rate of about 1–2 feet per second (ft/s). In wells with 5-ft-long screens, two shorter strokes were used, and the sampler was allowed to settle to the bottom of the well between strokes. The filled sampler was raised to the surface at a steady rate of 1–2 ft/s.

The larger GRAB2L samplers were deployed only in wells with 10-ft-long screens. Stainless-steel weights were attached to the top and bottom of the sampler so that it rested on the bottom of the well when deployed. To fill the sampler with water from the screened interval, the polypropylene line was pulled up in two continuous 5-ft-long strokes at a rate of about 1–2 ft/s. The sampler was allowed to settle to the bottom of the well between the strokes, and it was raised to the surface at a rate of about 1–2 ft/s.

The water from the GRAB1L and GRAB2L samplers was decanted directly into either 500-mL or 1-L amber-glass bottles for analysis of explosive compounds and 125-mL polyethylene bottles for analysis of  $\text{ClO}_4^-$ . Blending of the sample in a 1-L bottle, as was done for the RPPOLY and RCELLM samples, was not necessary because one grab sample yielded sufficient water for the chemical analyses.

## Implementation of Field Tests

The field tests were conducted in four phases to (1) compare pumped sampling and several types of no-purge sampling in a smaller number of wells, (2) determine whether vertical variations in concentrations along the screened interval are present that could affect the sampling results, (3) compare pumped and one type of no-purge sampling in a larger number of wells, and (4) test several methods for obtaining larger sample volumes from the no-purge samplers for use in quality assurance and control evaluation. These phases are described in detail in the next section of this report.

Field tests during the first phase of the study began with the collection of water samples by using the dedicated sampling pumps, which were already in place in the wells. During all four phases of the study, the pumps were then

removed from the wells and stored in plastic bags, and the no-purge samplers were set in the wells as described above. The no-purge samplers, including the grab samplers, remained in the wells for 13–64 days before their retrieval to ensure that ambient flow through the well screen had flushed the screened interval after setting of the sampler and, therefore, that the water in the screen represented the water in the adjacent formation. The 13-day or longer time interval also allowed ample time for equilibration of contaminant concentrations between the groundwater in the screen and the deionized water inside the RPPOLY and RCELLM diffusion samplers (Vroblesky, 2001; LeBlanc, 2003). After collection of the no-purge samplers, the pumps were reinstalled in the wells and used to collect pumped samples about 2–24 hours later; this short time lag allowed sediment that had been resuspended into the water column during retrieval of the samplers and reinstallation of the pump to settle back to the bottom of the well.

## Laboratory Analysis

Water samples for analysis of the explosive compounds were collected in 500-mL or 1-L amber-glass bottles, chilled immediately, and stored chilled until analysis. Samples for analysis of  $\text{ClO}_4^-$  were collected in 125-mL polyethylene bottles and stored in the dark at room temperature until analysis. The explosive compounds were analyzed by U.S. Environmental Protection Agency (USEPA) method 8830A (U.S. Environmental Protection Agency, 2008), and the  $\text{ClO}_4^-$  samples were analyzed by USEPA method 314.0 (U.S. Environmental Protection Agency, 1999). The samples were analyzed by laboratories under contract to the USGS. The reporting and detection limits vary with sample volume and magnitude of measured concentration; the reporting limits for  $\text{ClO}_4^-$ , RDX, and HMX were about 1.0, 0.2, and 0.4  $\mu\text{g}/\text{L}$ , respectively; the detection limits for  $\text{ClO}_4^-$ , RDX, and HMX were about 0.25, 0.06, and 0.10  $\mu\text{g}/\text{L}$ , respectively. Concentrations between the reporting and detection limits are considered estimated values. The compounds that are measured by USEPA method 8830A are shown in LeBlanc and Vroblesky (2008, table 2). Only compounds for which at least one sample had a concentration exceeding the detection limit of the compound are included in the tables in this report.

## Comparisons of Concentrations

The small sample sizes for most sets of comparisons between the no-purge and pumped sampling results precluded the use of formal statistical comparisons, except as part of the fourth phase of work, in which grab and pumped sampling methods were compared in 29 wells. For most comparisons, the degree of agreement between methods is assessed qualitatively by using bar graphs and scatter plots. Methods are described as showing a close agreement when, for example, the data points in a scatter plot are, by visual inspection, close to, and randomly scattered about, the line of

equal concentration. Other quantitative measures of the degree of agreement, such as percent differences or absolute differences between concentrations, can be misleading when applied over a large range of concentration values and, therefore, were not used in this study.

## Comparison of Pumped and No-Purge Sampling Methods

The comparison of pumped and no-purge sampling methods for monitoring ordnance-related compounds at the MMR was conducted in several phases in a total of 36 wells; several wells were used in more than one phase of the study. During the first phase, two types of diffusion samplers and one type of grab sampler were compared to low-flow pumped sampling in six monitoring wells. In the second phase, RPPOLY samplers were used in six monitoring wells to test whether vertical variations in chemical concentrations that could affect the performance of the no-purge sampling methods were present in the screened intervals of the wells. The grab-sampler no-purge sampling method was compared to low-flow pumped sampling in 29 wells in the third phase of the study to obtain sufficient data for a statistical as well as graphical comparison of the methods and to test whether well location and construction affected the degree of agreement between the two methods. During the fourth phase of the study, several grab sampling approaches for collecting sufficiently large volumes for quality control and assurance samples were tested in five wells.

The comparisons among the sampling methods focus on concentrations of ordnance-related compounds and especially those of most concern at the MMR— $\text{ClO}_4^-$ , RDX, and HMX. Water-quality measurements were made in the field during collection of the pumped samples (table 2). The groundwater at all the wells sampled during this study had a low dissolved solids content (specific conductance of 43.3–120.7 microsiemens per centimeter) and was aerobic (dissolved oxygen concentrations of 2.9–10.7 milligrams per liter) and generally mildly acid (pH of 5.41–7.22).

## Comparison of Diffusion and Grab Sampling to Pumped Sampling

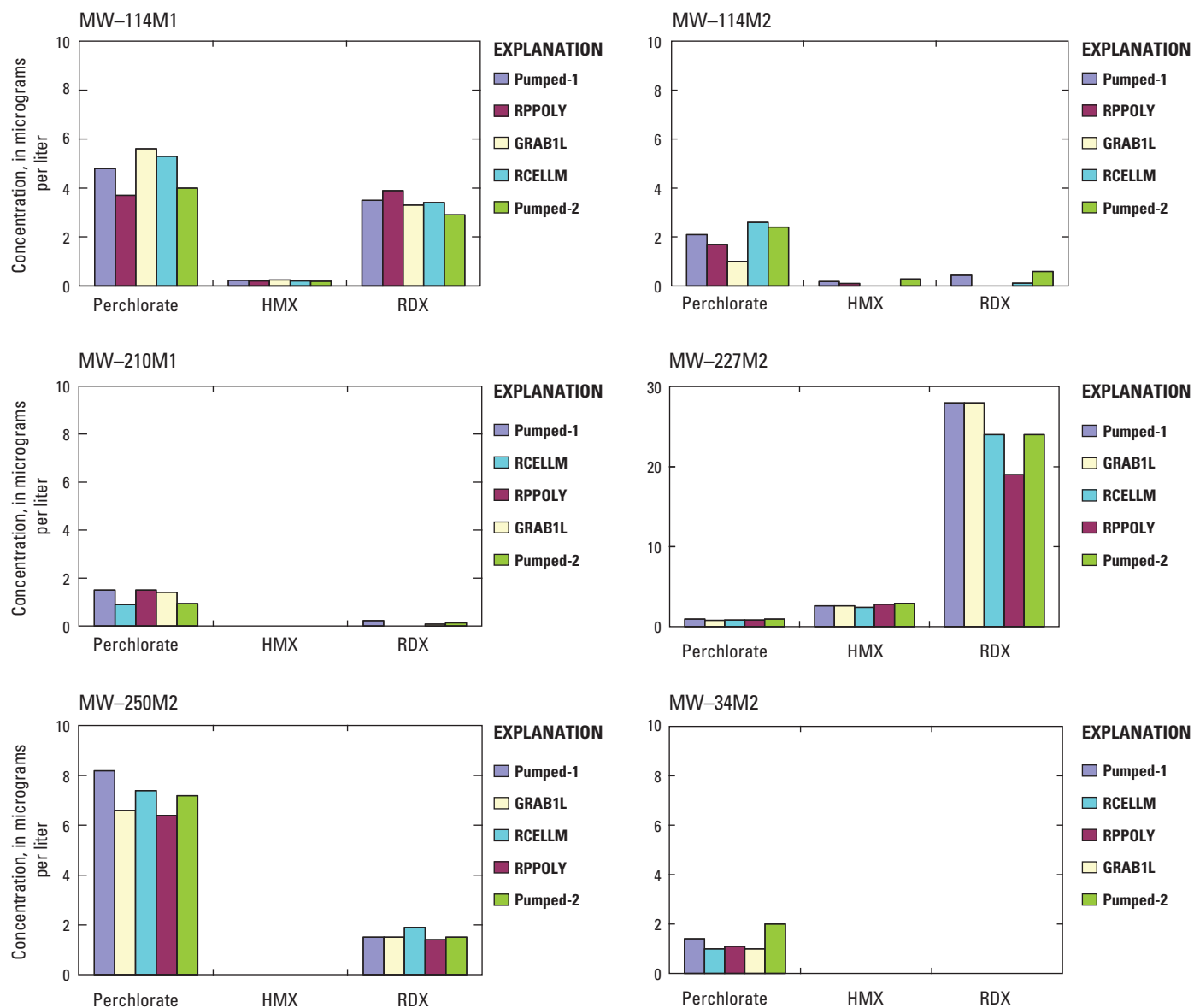
In the first phase of the study, concentrations of  $\text{ClO}_4^-$ , RDX, HMX, and other minor explosive compounds in water samples collected by using RPPOLY and RCELLM diffusion sampling and GRAB1L grab sampling were compared to concentrations of these compounds in samples collected by using low-flow pumped sampling in six wells (table 3). At each well, the no-purge samplers were set sequentially following collection of the initial pumped sample. Each type of diffusion and grab sampler was left in the well for 13–15 days. The final pumped sample was collected within 24 hours of retrieval of the last no-purge sampler. The order of testing of the no-purge

## 10 Comparison of Sampling Methods for Monitoring Concentrations of Ordnance-Related Compounds in Groundwater

**Table 3.** Concentrations of perchlorate and explosive compounds in water samples collected from monitoring wells near the Impact Area by using rigid porous polyethylene diffusion samplers, regenerated-cellulose membrane diffusion samplers, polyethylene-film grab samplers, and low-flow pumped sampling, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, June–July 2009.

[Samples analyzed by Test America, Arvada, Colo. Sample designation: Well number in tables 1–2 and suffix; PUMPED, low-flow pumped; RCELLM, regenerated-cellulose membrane; RPPOLY, rigid porous polyethylene; GRAB1L, 1-liter polyethylene-film grab. Locations shown in fig. 1. mm/dd/yy, month/day/year; µg/L, microgram per liter; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; WATERBLANK, deionized water used to fill RPPOLY and RCELLM samplers; <, less than value shown; E, estimated value]

Sample designation	Sample date (mm/dd/yy)	Perchlorate (µg/L)	HMX (µg/L)	RDX (µg/L)	4-Amino-2,6-dinitrotoluene (µg/L)
MW-34M2-PUMPED	06/08/09	1.4	<0.40	<0.20	<0.20
MW-34M2-RCELLM	06/22/09	1.0	<0.40	<0.20	<0.20
MW-34M2-RPPOLY	07/07/09	1.1	<0.40	<0.20	<0.20
MW-34M2-GRAB1L	07/20/09	1.0	<0.40	<0.20	<0.20
MW-34M2-PUMPED	07/20/09	2.0	<0.40	<0.20	<0.20
MW-114M1-PUMPED	06/09/09	4.8	E 0.23	3.5	<0.20
MW-114M1-RPPOLY	06/23/09	3.7	E 0.21	3.9	<0.20
MW-114M1-GRAB1L	07/07/09	5.6	E 0.25	3.3	<0.20
MW-114M1-RCELLM	07/20/09	5.3	E 0.21	3.4	<0.20
MW-114M1-PUMPED	07/21/09	4.0	E 0.19	2.9	<0.20
MW-114M2-PUMPED	06/09/09	2.1	E 0.18	0.44	<0.20
MW-114M2-RPPOLY	06/23/09	1.7	E 0.10	<0.20	<0.20
MW-114M2-GRAB1L	07/07/09	2.0	<0.40	<0.20	E 0.13
MW-114M2-RCELLM	07/20/09	2.6	<0.40	E 0.12	<0.20
MW-114M2-PUMPED	07/21/09	2.4	E 0.28	0.59	<0.20
MW-210M1-PUMPED	06/08/09	1.5	<0.40	0.22	<0.20
MW-210M1-RCELLM	06/22/09	E 0.90	<0.40	<0.20	<0.20
MW-210M1-RPPOLY	07/07/09	1.5	<0.40	<0.20	<0.20
MW-210M1-GRAB1L	07/20/09	1.4	<0.40	E 0.08	<0.20
MW-210M1-PUMPED	07/20/09	E 0.94	<0.40	E 0.14	<0.20
MW-227M2-PUMPED	06/08/09	E 0.94	2.6	28	<0.20
MW-227M2-GRAB1L	06/22/09	E 0.77	2.6	28	<0.20
MW-227M2-RCELLM	07/07/09	E 0.82	2.4	24	<0.20
MW-227M2-RPPOLY	07/20/09	E 0.82	2.8	19	<0.20
MW-227M2-PUMPED	07/20/09	E 0.96	2.9	24	<0.20
MW-250M2-PUMPED	06/08/09	8.2	<0.40	1.5	<0.20
MW-250M2-GRAB1L	06/23/09	6.6	<0.40	1.5	<0.20
MW-250M2-RCELLM	07/07/09	7.4	<0.40	1.9	<0.20
MW-250M2-RPPOLY	07/20/09	6.4	<0.40	1.4	<0.20
MW-250M2-PUMPED	07/20/09	7.2	<0.40	1.5	<0.20
WATERBLANK	06/08/09	<1.0	<0.40	<0.20	<0.20



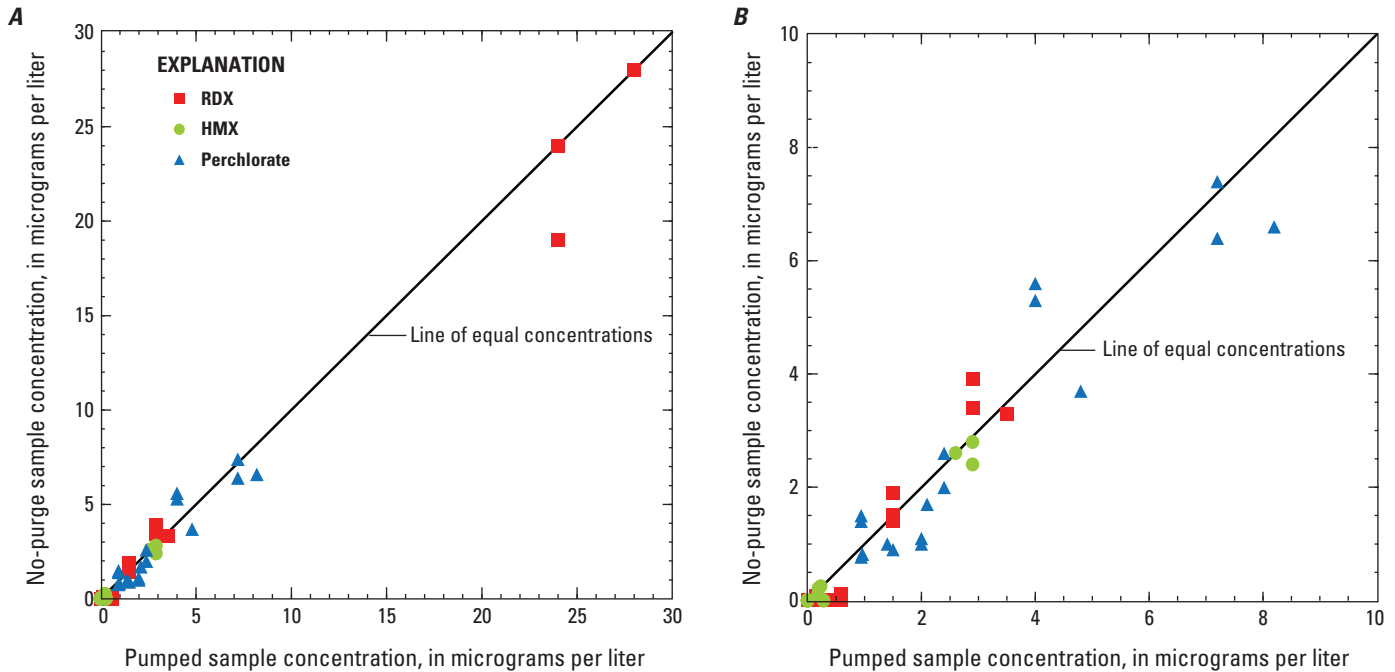
**Figure 2.** Comparison of perchlorate, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) concentrations for pumped, diffusion, and grab samples collected from six monitoring wells near the Impact Area on Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009. Concentrations include estimated values (identified in table 3) and are plotted as zero values where less than the detection limit. Pumped-1, initial low-flow pumped sample; RPPOLY, rigid porous polyethylene diffusion sample; RCELLM, regenerated-cellulose membrane diffusion sample; GRAB1L, 1-liter polyethylene-film grab sample; Pumped-2, final low-flow pumped sample.

samplers was varied among the wells to limit any potential bias owing to the sampling order.

The compounds of interest were not detected in a sample of the deionized water that was used to fill the RPPOLY and RCELLM samplers (water blank, table 3). In this study, blank samples were not collected from no-purge samplers set in chambers filled with water known to be free of the compounds of concern. Similar tests in earlier studies (LeBlanc, 2003; LeBlanc and Vroblecky, 2008) had not detected any contamination from the samplers themselves, including RPPOLY

samplers that had been reused after soaking and rinsing with deionized water.

The concentrations of  $\text{ClO}_4^-$ , RDX, and HMX in the no-purge and pumped samples collected from the six monitoring wells were in close agreement, as is evident qualitatively in bar graphs that compare the concentrations (fig. 2). There is no evidence of a systematic bias in the concentration differences on the basis of type of sampling device or type of contaminant. There is also no evidence of a systematic bias on the basis of the order in which the no-purge samplers were tested



**Figure 3.** Comparison of perchlorate, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) concentrations for pumped and no-purge samples collected from six monitoring wells near the Impact Area on Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009, for concentration ranges of *A*, 0–30 and *B*, 0–10 micrograms per liter. Concentrations include estimated values (identified in table 3) and are plotted as zero values where less than the detection limit.

(fig. 2, table 3). The concentrations are also in close agreement over the range of observed values for  $\text{ClO}_4^-$ , RDX, and HMX (fig. 3). RDX and HMX were detected at low concentrations (less than  $0.6 \mu\text{g/L}$ ) in more pumped than no-purge samples, but the concentrations are near the detection limits for the compounds.  $\text{ClO}_4^-$  was detected in all the pumped and no-purge samples.

### Vertical Variations of Perchlorate Concentrations in Monitoring-Well Screens

The second phase of the project examined whether vertical variations in contaminant concentrations were present in the well screens. The diffusion and grab sampling methods differ in the vertical position and number of devices set within the well screen. The diffusion samplers do not remove water from the screened interval, whereas the grab sampler scoops up water from the screened interval. The pumped sampling method draws water from the formation, but the contributions to the pumped sample from various intervals along the screen are unknown and thus may conceal vertical variations in concentrations and hydraulic properties along the screen.

Concentrations of contaminants can vary considerably over long screened intervals (Reilly and LeBlanc, 1998), and

fluid can circulate vertically inside long screens and even in the blank casing above the screen during and between sampling events (Church and Granato, 1996; Vroblesky and others, 2007). The degree of agreement between sampling methods, which differ in where and how the samples are collected, could be affected by these factors. The close agreement among concentrations of  $\text{ClO}_4^-$ , RDX, and HMX in the no-purge and pumped samples collected from the six monitoring wells in the first phase of the study, in which the three no-purge sampling methods were tested, suggests that variations in concentrations over the screened intervals were small, but these data were not sufficient to confirm this hypothesis or quantify the variability.

To examine whether the close agreement among concentrations could be due partly to uniform concentrations in the screened intervals, variations in concentrations of  $\text{ClO}_4^-$  were measured by using RPPOLY diffusion samplers in six wells. Only variations in  $\text{ClO}_4^-$  concentrations were examined because each RPPOLY sampler did not contain a sufficient sample volume for analysis of explosive compounds (500 mL). In three of the six wells, four RPPOLY samplers were placed at about 2, 4, 6, and 8 ft below the top of the 10-ft-long screen (table 4). Pumped samples were collected before and after collection of the RPPOLY samplers. In the other three wells, in addition to the four samplers in the

**Table 4.** Concentrations of perchlorate in water samples collected from six monitoring wells with 10-foot-long screens near the Impact Area by using low-flow pumped sampling and rigid porous polyethylene diffusion samplers, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010.

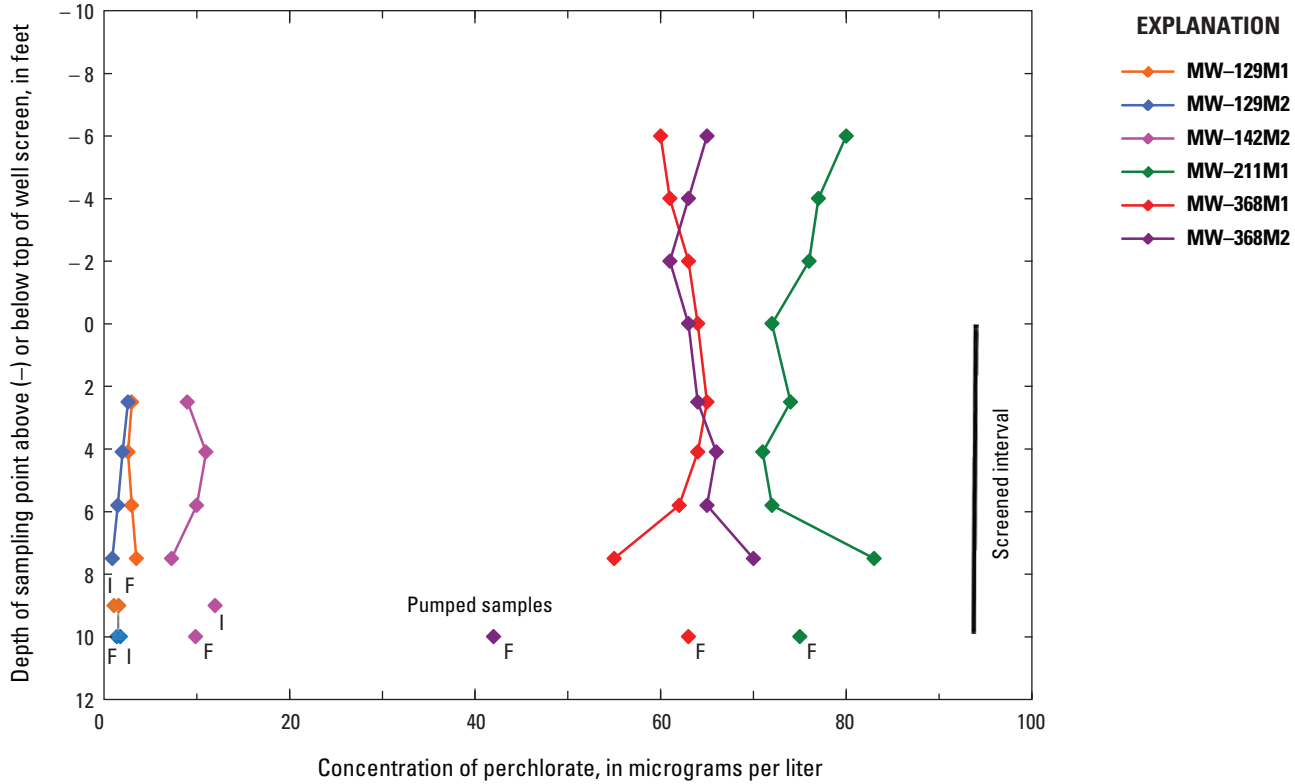
[Samples analyzed by Test America, Arvada, Colo. Locations shown in figure 1. Sample designation: Pumped, low-flow pumped sample; xx ft, depth below top of screen of rigid porous polyethelene sampler. no., number; mm/dd/yy, month/day/year; µg/L, microgram per liter; E, estimated value; ft, foot].

Well no.	Sample designation	Sample date (mm/dd/yy)	Perchlorate (µg/L)	Well no.	Sample designation	Sample date (mm/dd/yy)	Perchlorate (µg/L)
MW-129M1	Pumped	06/09/09	1.1	MW-211M1	2.5 ft	09/02/10	74
MW-129M1	2.5 ft	06/23/09	3.0	MW-211M1	4.1 ft	09/02/10	71
MW-129M1	4.1 ft	06/23/09	2.6	MW-211M1	5.8 ft	09/02/10	72
MW-129M1	5.8 ft	06/23/09	3.0	MW-211M1	7.5 ft	09/02/10	83
MW-129M1	7.5 ft	06/23/09	3.5	MW-211M1	Pumped	09/02/10	75
MW-129M1	Pumped	06/23/09	1.6	MW-368M1	-6.0 ft	09/02/10	60
MW-129M2	Pumped	06/09/09	1.8	MW-368M1	-4.0 ft	09/02/10	61
MW-129M2	2.5 ft	06/23/09	2.6	MW-368M1	-2.0 ft	09/02/10	63
MW-129M2	4.1 ft	06/23/09	2.0	MW-368M1	0 ft	09/02/10	64
MW-129M2	5.8 ft	06/23/09	1.5	MW-368M1	2.5 ft	09/02/10	65
MW-129M2	7.5 ft	06/23/09	E 0.91	MW-368M1	4.1 ft	09/02/10	64
MW-129M2	Pumped	06/23/09	1.4	MW-368M1	5.8 ft	09/02/10	62
MW-142M2	Pumped	06/08/09	12	MW-368M1	7.5 ft	09/02/10	55
MW-142M2	2.5 ft	06/23/09	9.0	MW-368M1	Pumped	09/02/10	63
MW-142M2	4.1 ft	06/23/09	11	MW-368M2	-6.0 ft	09/02/10	65
MW-142M2	5.8 ft	06/23/09	10	MW-368M2	-4.0 ft	09/02/10	63
MW-142M2	7.5 ft	06/23/09	7.3	MW-368M2	-2.0 ft	09/02/10	61
MW-142M2	Pumped	06/23/09	9.9	MW-368M2	0 ft	09/02/10	63
MW-211M1	-6.0 ft	09/02/10	80	MW-368M2	2.5 ft	09/02/10	64
MW-211M1	-4.0 ft	09/02/10	77	MW-368M2	4.1 ft	09/02/10	66
MW-211M1	-2.0 ft	09/02/10	76	MW-368M2	5.8 ft	09/02/10	65
MW-211M1	0 ft	09/02/10	72	MW-368M2	7.5 ft	09/02/10	70
				MW-368M2	Pumped	09/02/10	42

screened interval, RPPOLY samplers were placed in the blank casing above the well screen at about 0, 2, 4, and 6 ft above the top of the screen. Pumped samples were collected from these wells only after collection of the RPPOLY samplers.

Small variations in concentrations of  $\text{ClO}_4^-$  over the sampled interval were measured in all six wells (table 4, fig. 4), but the individual sample concentrations in a given well generally differed by less than 15 percent from the average concentration of the four or eight samples in the well. For the 6 out of

36 samples with relative differences greater than 15 percent, the absolute differences were less than 2 µg/L. The largest deviations from the average concentration were in the bottom sample in the three wells with the highest average concentrations. The  $\text{ClO}_4^-$  concentrations in the pumped samples were in close agreement with the average concentrations in the RPPOLY samples, with the exception of the pumped sample from well MW-368M2. The cause for this anomalously large difference is not known.



**Figure 4.** Vertical profiles of perchlorate concentrations in samples collected by low-flow pumped and rigid porous polyethylene diffusion sampling methods in and above the 10-foot-long screened intervals of six monitoring wells near the Impact Area on Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010. Concentrations include estimated values (identified in table 4). I, initial pumped sample; F, final pumped sample.

### Comparison of Pumped and Grab Sampling Methods

The technical staff of the IAGWSP selected the GRAB1L grab sampler for field tests in 29 wells in order to provide sufficient data from the third phase of the study for a statistical comparison of the no-purge and pumped sampling methods and to determine if the degree of agreement between the methods was affected by location in the groundwater-flow system or the depth below the water table of the monitoring-well screens. The GRAB1L sampler was selected because of the close agreement of concentrations of ordnance-related compounds in water samples collected by the GRAB1L and pumped sampling methods in the first phase of the project and because of the ease of use of the method and commercial availability of the device. For this phase of the study, generally

only a final sample was collected by pumped sampling following retrieval of the GRAB1L sampler. The results of the field tests in the 29 wells are given in table 5.

The degree of agreement between concentrations of  $\text{ClO}_4^-$ , RDX, and HMX in the GRAB1L and pumped samples collected from the 29 monitoring wells is shown in figure 5. The concentrations were in close agreement over the range of concentrations measured in the samples, as indicated by the distribution of the points in close proximity to the lines of equal concentrations (fig. 5). The close agreement was also observed for minor, less frequently detected explosive compounds such as 3-nitrotoluene, 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 2,4-dinitrotoluene, and 2,4,6-trinitrotoluene (table 5). There is no evidence of a systematic bias in the concentration differences between the methods on the basis of type of compound or concentration level.



**Table 5.** Concentrations of perchlorate and explosive compounds in water samples collected from monitoring wells near the Impact Area by using low-flow pumped sampling and 1- and 2-liter polyethylene-film grab samplers, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010.

[Samples analyzed by Test America, Arvada, Colo. Sample designation: Well number in tables 1–2 and suffixes; PUMPED, low-flow pumped; GRAB1L, 1-liter polyethylene-film grab; GRAB2L, 2-liter polyethylene-film grab; Gx, sequence number of grab sample. Locations shown in figure 1. mm/dd/yy, month/day/year; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; <, less than value shown; --, no data; E, estimated value; µg/L, microgram per liter].

Sample designation	Sample date (mm/dd/yy)	Perchlorate (µg/L)	HMX (µg/L)	RDX (µg/L)	3-Nitrotoluene (µg/L)	2-Amino-4,6-dinitrotoluene (µg/L)	4-Amino-2,6-dinitrotoluene (µg/L)	2,4-Dinitrotoluene (µg/L)	2,4,6-Trinitrotoluene (µg/L)
MW-31S-GRAB1L	11/18/09	E 0.42	3.6	6.2	<0.40	1.3	0.82	E 0.15	2.1
MW-31S-PUMPED	11/18/09	<1.0	3.3	5.9	<0.40	1.4	0.65	E 0.21	2.5
MW-31S-GRAB1L-G1	09/01/10	<1.0	1.6	2.5	<0.42	0.99	<0.21	<0.42	1.1
MW-31S-GRAB1L-G2	09/01/10	1.6	1.4	2.2	<0.41	0.97	<0.21	<0.41	1.4
MW-31S-GRAB1L-G3	09/01/10	<1.0	1.8	2.2	<0.42	0.96	0.42	E 0.20	1.6
MW-31S-PUMPED	09/01/10	<1.0	2.3	2.8	<0.40	0.99	0.33	E 0.20	1.9
MW-31M-GRAB1L	11/18/09	<1.0	2.1	0.29	<0.40	0.29	0.59	<0.40	<0.40
MW-31M-PUMPED	11/18/09	<1.0	2.3	E 0.18	<0.40	0.31	0.35	<0.40	<0.40
MW-76S-GRAB1L	11/16/09	1.2	<0.40	0.69	<0.40	<0.20	<0.20	<0.40	<0.40
MW-76S-PUMPED	11/16/09	1.5	E 0.14	0.91	<0.40	<0.20	<0.20	<0.40	<0.40
MW-76M2-GRAB1L	11/16/09	1.8	8.6	17	<0.40	<0.20	<0.20	<0.40	<0.40
MW-76M2-PUMPED	11/16/09	1.4	7.3	12	<0.40	<0.20	0.57	<0.40	<0.40
MW-76M2-GRAB2L	09/01/10	1.2	6.2	13	<0.43	E 0.10	<0.22	<0.43	<0.43
MW-76M2-PUMPED	09/01/10	1.2	5.7	13	<0.42	<0.21	0.30	<0.42	<0.42
MW-89M2-GRAB1L	10/26/09	9.5	0.72	18	<0.40	<0.20	<0.20	<0.40	<0.40
MW-89M2-PUMPED	10/27/09	9.6	0.75	17	<0.40	<0.20	<0.20	<0.40	<0.40
MW-89M2-GRAB1L-G1	09/01/10	11	0.73	17	<0.42	<0.21	<0.21	<0.42	<0.42
MW-89M2-GRAB1L-G2	09/01/10	11	--	--	--	--	--	--	--
MW-89M2-GRAB1L-G3	09/01/10	11	0.65	19	<0.41	<0.20	<0.20	<0.41	<0.41
MW-89M2-PUMPED	09/01/10	11	0.74	17	<0.45	<0.23	<0.23	<0.45	<0.45
MW-129M1-GRAB1L	11/16/09	<1.0	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-129M1-PUMPED	11/16/09	<1.0	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-129M2-GRAB1L	11/16/09	E 0.98	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-129M2-PUMPED	11/16/09	E 0.62	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-143M3-GRAB1L	10/06/09	5.5	2.9	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-143M3-PUMPED	10/06/09	5.3	3.0	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-165M2-GRAB1L	11/16/09	1.2	<0.40	<0.20	<0.40	<0.20	E 0.11	<0.40	<0.40
MW-165M2-PUMPED	11/16/09	1.1	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40

**Table 5.** Concentrations of perchlorate, and explosive compounds in water samples collected from monitoring wells near the Impact Area by using low-flow pumped sampling and 1- and 2-liter polyethylene-film grab samplers, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010.—Continued

Sample designation	Sample date (mm/dd/yy)	Perchlorate (µg/L)	HMX (µg/L)	RDX (µg/L)	3-Nitrotoluene (µg/L)	2-Amino-4,6-dinitrotoluene (µg/L)	4-Amino-2,6-dinitrotoluene (µg/L)	2,4-Dinitrotoluene (µg/L)	2,4,6-Trinitrotoluene (µg/L)
MW-207M1-GRAB1L	10/26/09	<1.0	0.52	6.3	<0.40	<0.20	<0.20	<0.40	<0.40
MW-207M1-PUMPED	10/27/09	<1.0	0.61	7.6	<0.40	<0.20	<0.20	<0.40	<0.40
MW-209M1-GRAB1L	10/26/09	<1.0	0.60	7.8	<0.40	<0.20	<0.20	<0.40	<0.40
MW-209M1-PUMPED	10/27/09	<1.0	0.48	7.8	<0.40	<0.20	<0.20	<0.40	<0.40
MW-211M1-GRAB1L	11/18/09	100	E 0.26	14	<0.40	<0.20	<0.20	<0.40	<0.40
MW-211M1-PUMPED	11/18/09	98	E 0.23	12	<0.40	<0.20	<0.20	<0.40	<0.40
MW-279M2-GRAB1L	10/20/09	7.8	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-279M2-PUMPED	10/20/09	9.3	<0.40	<0.20	<0.40	E 0.078	<0.20	<0.40	<0.40
MW-284M2-GRAB1L	11/03/09	5.9	<0.40	E 0.14	<0.40	<0.20	<0.20	<0.40	<0.40
MW-284M2-PUMPED	11/03/09	5.8	<0.40	E 0.14	<0.40	<0.20	<0.20	<0.40	<0.40
MW-289M2-GRAB1L	10/05/09	1.6	4.7	2.1	<0.40	<0.20	<0.20	<0.40	<0.40
MW-289M2-PUMPED	10/06/09	2.5	4.0	2.4	<0.40	<0.20	<0.20	<0.40	<0.40
MW-293M2-GRAB1L	10/05/09	2.3	<0.40	0.22	<0.40	<0.20	<0.20	<0.40	<0.40
MW-293M2-PUMPED	10/06/09	2.2	<0.40	0.30	<0.40	<0.20	<0.20	<0.40	<0.40
MW-303M2-GRAB1L	10/20/09	2.1	1.9	11	<0.40	<0.20	<0.20	<0.40	<0.40
MW-303M2-PUMPED	10/21/09	3.1	2.2	15	<0.40	<0.20	<0.20	<0.40	<0.40
MW-303M2-GRAB2L	09/01/10	4.6	4.3	18	<0.41	<0.21	<0.21	<0.41	<0.41
MW-303M2-PUMPED	09/01/10	4.0	4.2	17	<0.41	<0.21	<0.21	<0.41	<0.41
MW-307M3-GRAB1L	09/22/09	2.3	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-307M3-PUMPED	09/22/09	4.4	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-313M2-GRAB1L	10/13/09	14	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-313M2-PUMPED	10/13/09	14	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-323M1-GRAB1L	10/20/09	<1.0	E 0.23	1.6	<0.40	<0.20	<0.20	<0.40	<0.40
MW-323M1-PUMPED	10/20/09	<1.0	E 0.13	1.5	<0.40	<0.20	<0.20	<0.40	<0.40
MW-323M2-GRAB1L	10/20/09	<1.0	0.69	13	<0.40	<0.20	<0.20	<0.40	<0.40
MW-323M2-PUMPED	10/20/09	<1.0	0.68	14	<0.40	<0.20	<0.20	<0.40	<0.40
MW-323M2-GRAB1L-G1	09/02/10	<1.0	E 0.28	3.3	<0.41	<0.21	<0.21	<0.41	<0.41
MW-323M2-GRAB1L-G2	09/02/10	<1.0	E 0.29	3.1	0.57	<0.21	<0.21	<0.43	<0.43
MW-323M2-GRAB1L-G3	09/02/10	<1.0	E 0.30	4.2	<0.47	<0.23	<0.23	<0.47	<0.47
MW-323M2-PUMPED	09/02/10	<1.0	E 0.32	3.8	E 0.15	<0.21	<0.21	<0.42	<0.42

**Table 5.** Concentrations of perchlorate, and explosive compounds in water samples collected from monitoring wells near the Impact Area by using low-flow pumped sampling and 1- and 2-liter polyethylene-film grab samplers, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010.—Continued

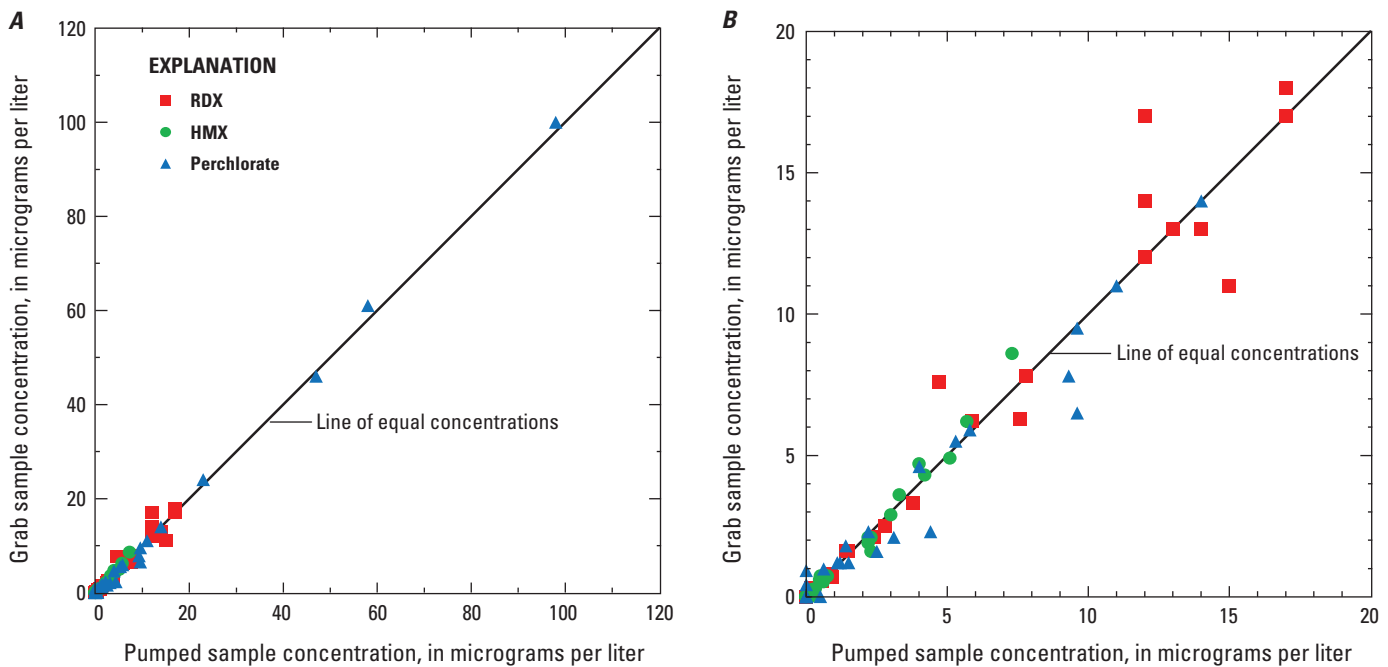
Sample designation	Sample date (mm/dd/yy)	Perchlorate (µg/L)	HMX (µg/L)	RDX (µg/L)	3-Nitrotoluene (µg/L)	2-Amino-4,6-dinitrotoluene (µg/L)	4-Amino-2,6-dinitrotoluene (µg/L)	2,4-Dinitrotoluene (µg/L)	2,4,6-Trinitrotoluene (µg/L)
MW-324M2-GRAB1L	10/05/09	<1.0	2.1	0.56	<0.40	<0.20	<0.20	<0.40	<0.40
MW-324M2-PUMPED	10/06/09	<1.0	2.2	0.55	<0.40	<0.20	<0.20	<0.40	<0.40
MW-335M1-GRAB1L	09/22/09	24	<0.40	0.80	<0.40	<0.20	<0.20	<0.40	<0.40
MW-335M1-PUMPED	09/22/09	23	<0.40	0.90	<0.40	<0.20	<0.20	<0.40	<0.40
MW-368M1-GRAB1L	09/22/09	46	<0.40	1.6	<0.40	<0.20	<0.20	<0.40	<0.40
MW-368M1-PUMPED	09/22/09	47	<0.40	1.4	<0.40	<0.20	<0.20	<0.40	<0.40
MW-368M2-GRAB1L	09/22/09	61	E 0.13	12	<0.40	<0.20	<0.20	<0.40	<0.40
MW-368M2-PUMPED	09/22/09	58	E 0.18	12	<0.40	<0.20	<0.20	<0.40	<0.40
MW-388M2-GRAB1L	10/05/09	<1.0	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-388M2-PUMPED	10/06/09	E 0.50	E 0.16	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-393M1-GRAB1L	10/13/09	E 0.92	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-393M1-PUMPED	10/13/09	<1.0	<0.40	<0.20	<0.40	<0.20	<0.20	<0.40	<0.40
MW-481M2-GRAB1L	10/26/09	<1.0	0.73	7.6	<0.40	<0.20	<0.20	<0.40	<0.40
MW-481M2-PUMPED	10/27/09	<1.0	0.51	4.7	<0.40	<0.20	<0.20	<0.40	<0.40
90MW0022-GRAB1L	10/06/09	6.5	4.9	E 0.16	<0.40	<0.20	<0.20	<0.40	<0.40
90MW0022-PUMPED	10/06/09	9.6	5.1	0.21	<0.40	<0.20	<0.20	<0.40	<0.40

The sign test (Helsel and Hirsch, 2002) was used to determine statistically whether the concentrations in samples collected by the GRABIL method were generally larger or smaller than the concentrations in samples collected by the low-flow pumped method. The paired data for  $\text{ClO}_4^-$ , RDX, and HMX were analyzed separately, and only data pairs in which the concentrations were above the detection limit (nonzero values) were included in the analysis. The sign tests indicate that there is no bias in the concentration differences at a Type I risk level of  $\alpha=0.01$  (number of paired values and computed p-values were 20 and 1.000 for  $\text{ClO}_4^-$ , 19 and 0.815 for RDX, and 21 and 0.824 for HMX, respectively).

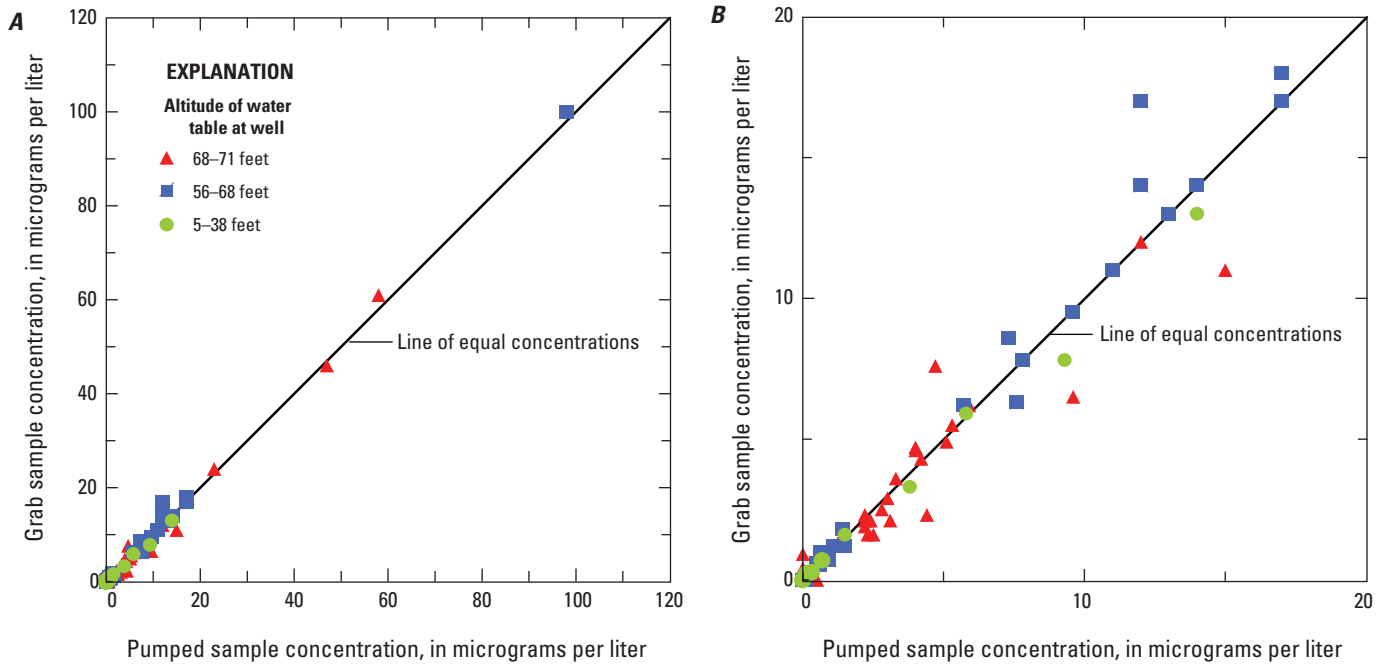
To determine if the degree of agreement between the methods was affected by the location of the monitoring well in the groundwater-flow system, the monitoring wells were divided into groups based on water-table altitude. The selected ranges in water-table altitudes of 68–71, 56–68, and 5–38 ft correspond to locations with gentle, intermediate, and steep horizontal hydraulic gradients, respectively (fig. 1). Near the top of the water-table mound (water-table altitude of 68–71 ft), the horizontal component of groundwater flow generally is small, and downward flow may be substantial (Walter and Masterson, 2003; Walter and LeBlanc, 2008). In contrast, near the coast (water-table altitude of 5–38 ft) the horizontal

component of groundwater flow generally is large, and upward flow also may be substantial. These patterns of flow may affect the rate of ambient flow laterally through and vertically within the wells screens and, therefore, affect the comparability of the samples obtained by the various no-purge sampling methods. There is no evidence from the field tests, however, of a systematic bias in concentration differences between the methods on the basis of location of the monitoring wells relative to the top of the water-table mound (fig. 6).

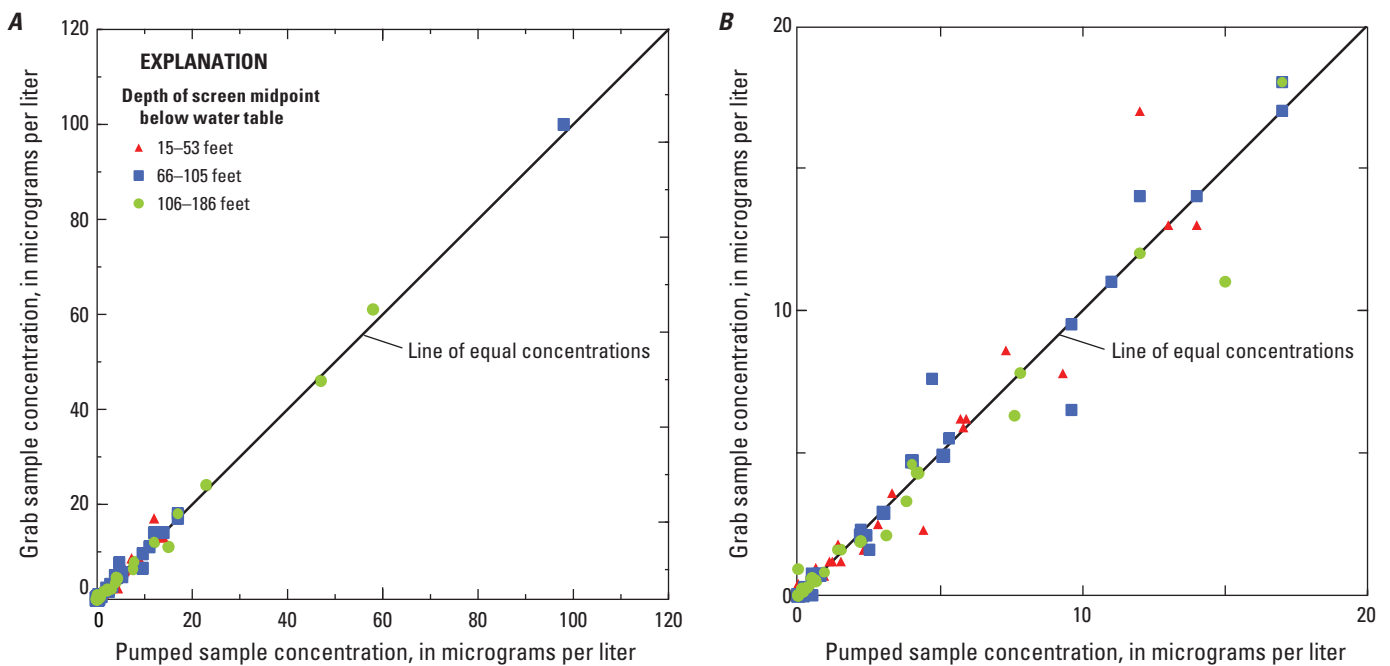
To determine if the degree of agreement between the methods was affected by the depth of the well screens below the water table, the monitoring wells were divided into groups having shallow (15–53 ft), intermediate (66–105 ft), and deep (106–186 ft) screen depths. The aquifer sediments generally become finer grained with depth (Walter and Masterson, 2003), and groundwater-flow rates therefore may be slower with increasing depth. Wells with screens set deep below the water table have longer water columns above the screens than wells with screens set near the water table. The longer water columns could affect natural circulation within the wells and, although not likely, the integrity of the no-purge samples owing to the long retrieval distances. There is no evidence from the field tests, however, for a systematic bias in concentration differences between the methods on the basis of the depth of the well screen below the water table (fig. 7).



**Figure 5.** Comparison of concentrations of perchlorate, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) for concentration ranges of A, 0–120 and B, 0–20 micrograms per liter for pumped and grab samples collected from 29 monitoring wells near the Impact Area on Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010. Concentrations include estimated values (identified in table 5) and are plotted as zero values where less than the detection limit.



**Figure 6.** Comparison of concentrations of three ordnance-related compounds for concentration ranges of A, 0–120 and B, 0–20 micrograms per liter, for pumped and grab samples collected from wells grouped by location relative to the altitude of the water table near the Impact Area on Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010. Concentration data are for perchlorate, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (not identified by compound on the graphs). Concentrations include estimated values (identified in table 5) and are plotted as zero values where less than the detection limit.



**Figure 7.** Comparison of concentrations of three ordnance-related compounds for concentration ranges of A, 0–120 and B, 0–20 micrograms per liter, for pumped and grab samples collected from wells grouped by depth of screened interval below the water table near the Impact Area on Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010. Concentrations shown are for perchlorate, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (not identified by compound on the graphs). Concentrations include estimated values (identified in table 5) and are plotted as zero values where less than the detection limit.

## Collection of Replicate and Large-Volume Samples

The no-purge sampling devices used in this study may not provide a sufficient volume of water to collect replicate and spiked samples for quality assurance and control (QA/QC) purposes. Groundwater-monitoring programs often require QA/QC data for legal and regulatory reasons. During the fourth phase of the study, an approach for collection of replicate samples that is similar to traditional bailing was tested in three wells. A GRAB1L sampler was set in the well, left in place for 63–64 days, and then retrieved as described above. The sample obtained from this sampler is designated GRAB1L-G1 in table 5. A second sampler (GRAB1L-G2) was then set in the well and retrieved immediately, followed by a third sampler (GRAB1L-G3). A pumped sample was collected following retrieval of sample GRAB1L-G3. Although the second and third GRAB1L samples were turbid because of surging during the sample-collection sequence, the concentrations of  $\text{ClO}_4^-$ , RDX, and HMX in the three GRAB1L samples and the corresponding low-flow pumped sample were in close agreement for all three wells (table 5).

A second approach for collecting replicate samples with a GRAB2L grab sampler was tested in two wells. The volume of one GRAB2L sampler (about 2 L) was sufficient to obtain as many as three sets of samples for analysis of  $\text{ClO}_4^-$  and explosive compounds, although in this study only one set of samples was sent to the laboratory for chemical analysis. The concentrations of these compounds in the GRAB2L sample and the corresponding low-flow pumped sample were in close agreement for both wells (table 5).

## Implications of the Choice of Sampling Methods

Concentrations of  $\text{ClO}_4^-$ , RDX, HMX, and other less frequently detected explosive compounds in the no-purge and low-flow pumped samples were mostly all in close agreement. This field evidence supports the conclusion that diffusion sampling with rigid porous polyethylene (RPPOLY) and regenerated-cellulose (RCELLM) membranes, and grab sampling with the tubular polyethylene-film samplers, are useful methods for monitoring concentrations of ordnance-related compounds at the MMR and in similar hydrogeologic environments. LeBlanc and Vroblesky (2008) reached a similar conclusion from their field tests in 15 monitoring wells of the RPPOLY samplers. They reported that there was poor agreement between concentrations in RPPOLY and pumped samples in 4 of the 15 wells (MW-31M, MW-76M2, MW165M2, and MW-289M2), but they hypothesized that the poor agreement was due to a long time interval between collection of the two types of samples and changing concentrations in the aquifer during that time. The close agreement between concentrations in GRAB1L and pumped samples in the same wells in the present study (table 5) supports their hypothesis.

The close agreement among concentrations in samples collected by all the sampling methods indicates that ambient groundwater flow through the monitoring-well screens is sufficiently rapid that the residence time of water in the screens is small compared to the 2-week and longer equilibration period used in this study. The combination of high hydraulic conductivity in the sand and gravel aquifer and substantial hydraulic gradients in most areas contribute to the high flushing rate, although direct measurement of these rates was beyond the scope of this study. The close agreement may also be due to the chemical properties of the explosive compounds and  $\text{ClO}_4^-$ , which, unlike VOCs or reactive metals, are not subject to loss by volatilization or rapid chemical transformations during sample collection. The extrapolation of these results to other hydrogeologic settings or to monitoring wells that are constructed differently from those tested in this study should be done with caution. Archfield and LeBlanc (2005) recommended that a one-time well-by-well comparison between pumped and diffusion sample results could determine which wells are good candidates for the use of diffusion samplers for monitoring concentrations of VOCs at the MMR. A similar approach could be used to determine the utility of the no-purge sampling method for monitoring explosive compounds and  $\text{ClO}_4^-$  near the Impact Area at the MMR. In a long-term monitoring program that relies on no-purge sampling, confirmation of the no-purge results by comparison to pumped-sample results also could be warranted when large or unexpected changes in concentrations are observed.

A quantitative comparison of the costs and effort required for the various no-purge sampling methods was beyond the scope of this study. Several observations may be useful, however, when evaluating which sampling method is best suited to a particular monitoring program. One person can implement all three methods in the field, although the handling of the four RPPOLY samplers is more difficult than the handling of the two RCELLM and one GRAB1L sampler. The installation and retrieval of the GRAB1L sampler is especially easy because the single sampler is suspended at one point at the end of the polypropylene line, whereas the RCELLM and RPPOLY samplers are suspended at several points along the weighted line, and 2–4 samplers must be processed upon retrieval. An additional advantage of the grab samplers is the option to obtain QA/QC samples by using the large-volume GRAB2L sampler or multiple grabs with the low-volume GRAB1L sampler.

The three no-purge methods differ most in the effort associated with preparation of the sampling devices for installation in the field. The GRAB1L, GRAB2L, and RCELLM samplers are used only once and are then discarded, whereas the RPPOLY samplers can be cleaned and reused multiple times. The GRAB1L and GRAB2L samplers require almost no advanced preparation other than attachment of the weights. In contrast, the RPPOLY samplers must be filled with deionized water and stored and transported in water so that the internal fluid does not drain inadvertently before deployment in the wells. The membranes of the RCELLM samplers must

be rinsed thoroughly before construction of the samplers, and the samplers also must be filled and transported in deionized water. The relative importance of these factors should be considered when evaluating which device best fits a proposed monitoring program.

## Summary

A long-term sampling program is an important part of most groundwater-remediation efforts. The sampling program typically consists of collection of groundwater samples from monitoring wells by using low-flow pumped sampling methods and involves considerable cost and effort. No-purge, or passive, sampling methods have been developed as a useful alternative to pumped sampling. The no-purge methods are based on the concept that natural flow through the well screen results in the same chemical concentrations in the screen and adjacent formation. The no-purge methods include diffusion sampling, in which the sampling device consists of a diffusion membrane that is filled with a sampling fluid such as deionized water, and grab samplers that consist of a device that is lowered into the well screen to capture the groundwater in the screen.

Diffusion samplers that are constructed with polyethylene diffusion membranes are used at the Massachusetts Military Reservation (MMR) to monitor concentrations of volatile organic compounds in Cape Cod's sand and gravel aquifer. This study examined the utility of diffusion samplers that are constructed of rigid porous polyethylene (RPPOLY) and regenerated-cellulose (RCELLM) membranes and two sizes (1 L and 2 L) of polyethylene-film grab samplers to monitor concentrations of ordnance-related compounds near the Impact Area of Camp Edwards at the MMR. The study extends the findings from a 2008 investigations report by LeBlanc and Vroblesky, which demonstrated that RPPOLY diffusion sampling was a useful alternative to pumped sampling for monitoring  $\text{ClO}_4^-$ , RDX, HMX, and other minor explosive compounds in the contaminant plumes near the Impact Area. The study was conducted in a total of 36 monitoring wells constructed of 2- or 2.5-in.-diameter PVC casing and approximately 5- to 10-ft-long slotted PVC screens.

In the first phase of the study, RPPOLY and RCELLM no-purge samplers and 1-L grab samplers were compared to pumped sampling in six wells. At each well, no-purge samplers were set sequentially following the collection of an initial pumped sample, and a final pumped sample was collected within 24 hours of retrieval of the last no-purge sampler. In all six wells, the concentrations of  $\text{ClO}_4^-$ , RDX, and HMX in the no-purge and pumped samples were in close agreement. There was no evidence of a systematic bias in concentration differences among the methods on the basis of the type of sampling device, the type of contaminant, or the order in which the no-purge samplers were deployed in the well.

The second phase of the study examined whether vertical variations in concentrations along the screened interval are present that could affect the sampling results, given that the sampling methods differ in where and how the samples are obtained. Samples were collected for  $\text{ClO}_4^-$  analysis by using 4–8 RPPOLY samplers set at 2-ft intervals along and as much as 6 ft above the top of the 10-ft-long screens of six wells. Small variations in concentrations of  $\text{ClO}_4^-$  were measured in all six wells, but the variations generally were less than 15 percent of the average concentration for the RPPOLY samplers in a given well. In five of the six wells, the average concentrations for the RPPOLY samplers also agreed closely with the concentrations in the pumped samples. The cause for the anomalous result in the sixth well is unknown.

Grab sampling with the 1-L sampler (GRAB1L) was compared to pumped sampling in 29 wells during the third phase of the study. Concentrations of  $\text{ClO}_4^-$ , RDX, HMX, and other less frequently detected explosive compounds in water samples collected by grab and pumped sampling were in close agreement for all the wells. A sign test was used to determine if there was a statistically significant bias in the concentration differences between the methods. There was no evidence of a bias at the Type I risk level of  $\alpha=0.01$ . There was also no evidence for a systematic bias in concentration differences on the basis of the location of the monitoring well relative to the top of the water-table mound or the depth of the well screen below the water table. Groundwater-flow rates that affect the ambient flow through the well screen, which in turn could affect the utility of no-purge sampling methods, are likely to be related to these two factors.

In the final phase of the study, two methods to obtain the larger sample volumes that may be needed for quality assurance and control (QA/QC) samples were field-tested in five wells. The tests demonstrated that sample collection by using a larger volume 2-L grab sampler and sequential bailing with a smaller volume 1-L grab sampler were possible options for obtaining sufficient volumes for replicate and spiked QA/QC samples.

The evidence from the field tests supports the conclusion that diffusion sampling with RPPOLY and RCELLM membranes and grab sampling with the two sizes of polyethylene-film grab samplers (1 L and 2 L) are methods for monitoring concentrations of ordnance-related compounds at the MMR and in similar hydrogeologic environments that provide comparable data to that obtained by low-flow pumped sampling. The high groundwater-flow velocities and the chemical properties of the explosive compounds and  $\text{ClO}_4^-$ , which are not subject to loss by volatilization or rapid chemical transformations during sample collection, are factors favoring the utility of the no-purge sampling methods at the MMR. The applicability of no-purge sampling for monitoring concentrations of ordnance-related compounds in other hydrogeologic settings or different monitoring-well designs should be confirmed by site-specific comparisons similar to those conducted in this study.

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