

Toxic Substances Hydrology Program

Prepared in cooperation with the
U.S. Army Environmental Command

**Comparison of Pumped and Diffusion Sampling Methods
to Monitor Concentrations of Perchlorate and Explosive
Compounds in Ground Water, Camp Edwards, Cape Cod,
Massachusetts, 2004–05**



Scientific Investigations Report 2008–5109

Cover. Photograph shows tank used as a target for artillery practice in the Impact Area, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts. (Photograph by Darrin Smith, U.S. Army Corps of Engineers, September 2008)

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By Denis R. LeBlanc and Don A. Vroblesky

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**U.S. Department of the Interior
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Conversion Factors, Datums, and Abbreviations

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
inch (in.)	25,400	micrometer (µm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	0.4047	hectare (ha)
Volume		
gallon (gal)	3.785	liter (L)
quart (qt)	946.4	milliliter (mL)
Flow rate		
foot per day (ft/d)	0.3048	meter per day (m/d)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

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

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

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

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

ABBREVIATIONS

AFCEE	Air Force Center for Engineering and the Environment
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
IAGWSP	Impact Area Groundwater Study Program
IRP	Installation Restoration Program
MMR	Massachusetts Military Reservation
PCE	tetrachloroethene
PVC	polyvinyl chloride
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
TCE	trichloroethene
USAEC	U.S. Army Environmental Command
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound

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Comparison of Pumped and Diffusion Sampling Methods to Monitor Concentrations of Perchlorate and Explosive Compounds in Ground Water, Camp Edwards, Cape Cod, Massachusetts, 2004–05

By Denis R. LeBlanc and Don A. Vroblesky

Abstract

Laboratory and field tests were conducted at Camp Edwards on the Massachusetts Military Reservation on Cape Cod to examine the utility of passive diffusion sampling for long-term monitoring of concentrations of perchlorate and explosive compounds in ground water. The diffusion samplers were constructed of 1-inch-diameter rigid, porous polyethylene tubing. The results of laboratory tests in which diffusion samplers were submerged in containers filled with ground water containing perchlorate, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) indicate that concentrations inside the diffusion samplers equilibrated with concentrations in the containers within the 19-day-long test period. Field tests of the diffusion samplers were conducted in 15 wells constructed of 2- or 2.5-inch-diameter polyvinyl chloride pipe with 10-foot-long slotted screens. Concentrations of perchlorate, RDX, and HMX in the diffusion samplers placed in the wells for 42 to 52 days were compared to concentrations in samples collected by low-flow pumped sampling from 53 days before to 109 days after retrieval of the diffusion samples. The results of the field tests indicate generally good agreement between the pumped and diffusion samples for concentrations of perchlorate, RDX, and HMX. The concentration differences indicate no systematic bias related to contaminant type or concentration levels.

Introduction

Long-term monitoring of water quality is an important part of ground-water remediation. During most remediation projects, many monitoring wells are installed to determine the spatial distribution of contaminants and to obtain hydrogeologic information needed to design the remediation approach. Once the approach is implemented, monitoring changes in water quality may continue for many years. The

success of a monitoring program generally requires frequent sampling of many sites to discern temporal and spatial trends in contaminant concentrations and to obtain evidence of natural and enhanced attenuation of contaminant levels (National Research Council, 2000; Sara, 2006; Wiedemeier and others, 2006). Therefore, the cost of long-term monitoring can be a substantial part of the cost of a remediation program. Common methods for collecting water samples from monitoring wells include purging with a submersible pump that is set in the well and lifts the water to the surface, and purging with a suction pump that draws the water to the surface by suction through a sampling tube. These pumped sampling methods can involve the use of heavy or cumbersome pump reels, generators, and gas cylinders; require two or more people to operate the equipment safely; and necessitate disposal of water purged from the well prior to sample collection (U.S. Army Environmental Command, 2007a; Nielsen and Nielsen, 2006). Passive diffusion sampling is a low-cost alternative to pumped sampling in many situations (Vroblesky and Hyde, 1997; Interstate Technology & Regulatory Council, 2008). In the passive diffusion sampling method, a diffusion chamber filled with an appropriate fluid, usually water free of the contaminants of interest, is set in the well screen for a sufficient duration before retrieval to allow concentrations in the sampler and well screen to reach an equilibrium by diffusion across the membrane of the sampler (Vroblesky, 2001a). Installation and retrieval can commonly be done by one person using minimal equipment, and no purge water is produced.

The use of passive diffusion samplers to monitor concentrations of volatile organic compounds (VOCs) has been widely documented (Vroblesky and Hyde, 1997; Church, 2000; Savoie and others, 2000; Vroblesky, 2001b; Archfield and LeBlanc, 2005; Interstate Technology & Regulatory Council, 2008). The diffusion membranes of samplers used to monitor VOCs typically are made from low-density polyethylene bags or lay-flat tubing (Vroblesky, 2001a). Many contaminants of interest, such as inorganic species, cannot diffuse through the low-density polyethylene membrane, however, so other membranes have been proposed for use in

passive diffusion samplers, including regenerated-cellulose dialysis membranes (Vroblesky and others, 2002; LeBlanc, 2003; Ehlke and others, 2004); nylon mesh (Vroblesky and others, 2002; Vroblesky and others, 2003); rigid, porous polyethylene tubing (Parsons, 2005); and perforated tubing (Vroblesky and Casey, 2007).

Passive diffusion sampling is used at the Massachusetts Military Reservation (MMR) on Cape Cod to monitor concentrations of VOCs in a glacial sand and gravel aquifer (Archfield and LeBlanc, 2005; Air Force Center for Environmental Excellence, 2005). The VOCs are present in 12 contaminant plumes that extend as far as 3 mi from the reservation; originate from historical sources such as aircraft maintenance, fuel use, and fire-training areas; and are presently (2008) the focus of a major remediation effort (Air Force Center for Engineering and the Environment, 2007).

The sand and gravel aquifer also contains 11 plumes of perchlorate and explosive compounds from historical testing, use, and disposal of military munitions at Camp Edwards on the MMR (fig. 1). The plumes are present mostly in the northern part of the MMR in an area referred to as the Impact Area. These plumes also are the subject of a major remediation effort (U.S. Army Environmental Command, 2007b) that includes the drilling and regular sampling of many monitoring wells. There is a concern that the monitoring program, which involves repeated visits to wells with vehicles and equipment, detrimentally affects the restoration and preservation of ecological habitats in the northern 14,000 acres of the MMR, which are managed jointly as the Upper Cape Cod Groundwater Reserve by the Massachusetts National Guard and the state's environmental agencies (Massachusetts National Guard, 2008a). Therefore, there is an interest in whether passive diffusion sampling methods can be used for the long-term monitoring of concentrations of perchlorate and explosive compounds at Camp Edwards.

Purpose and Scope

This report evaluates the results of laboratory and field tests of rigid, porous polyethylene diffusion samplers for monitoring concentrations of perchlorate and explosive compounds in ground water at Camp Edwards. The field tests were conducted near the Impact Area in 15 monitoring wells typical of the monitoring wells at the MMR known to contain various levels of these contaminants. Ground-water samples were collected from the 15 wells in 2005 by both pumped and diffusion sampling methods. The results presented in this report are intended for use in evaluating whether passive diffusion sampling is a useful alternative for long-term monitoring at the site. 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 U.S. Army Environmental Command (USAEC).

Site Description

The study was conducted in the shallow unconfined aquifer that underlies the western part of Cape Cod (fig. 1). The aquifer is composed of sand and gravel, with some silt and clay, which were deposited near the end of the Pleistocene Epoch, 15,000 to 16,000 years ago (Oldale, 1992; Walter and Masterson, 2003). In the study area, the sand and gravel aquifer is about 200 to 300 ft thick and overlies crystalline bedrock. The only source of water to the aquifer is about 27 in/yr of recharge from precipitation. The water table of western Cape Cod forms a mound with its highest point on the eastern side of the MMR (fig. 1). Ground water flows radially outward from the top of the mound at a rate of 1 to 2 ft/d toward discharge areas at streams, ponds, coastal wetlands, and the ocean (LeBlanc and others, 1986; Walter and Whealan, 2005).

The MMR has been used for military purposes since the early 1900s. The reservation was home to Camp Edwards during World War II and Otis Air Force Base during the Cold War. Since about 1973, the Massachusetts National Guard's Training Site Camp Edwards, Otis Air National Guard Base, and Coast Guard Air Station Cape Cod have been the major tenants on the MMR (Massachusetts National Guard, 2008b). Two environmental programs—the Installation Restoration Program (IRP) and the IAGWSP—are presently (2008) addressing ground-water contamination from the historical military activities at the MMR.

Study Design

The study included several rounds of field tests of the rigid, porous polyethylene diffusion samplers in wells near the Impact Area. The wells were installed by the IAGWSP during earlier investigations. The field tests included collection of water samples by pumped and diffusion sampling methods and laboratory analysis of the samples for concentrations of perchlorate and explosive compounds. The field tests were preceded by a laboratory test of the diffusion samplers in which the samplers were immersed in water collected from wells known to contain ordnance-related compounds.

Monitoring-Well Construction and Selection

The monitoring wells used in this study are sampled regularly by the IAGWSP. The selected wells (fig. 1 and table 1) are known from historical data to contain a range of concentrations of the contaminants of interest, primarily perchlorate, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). The wells were already scheduled for sampling by pumped methods during the time period of this study; thus, the cost of collecting and analyzing pumped samples solely for this study was obviated.

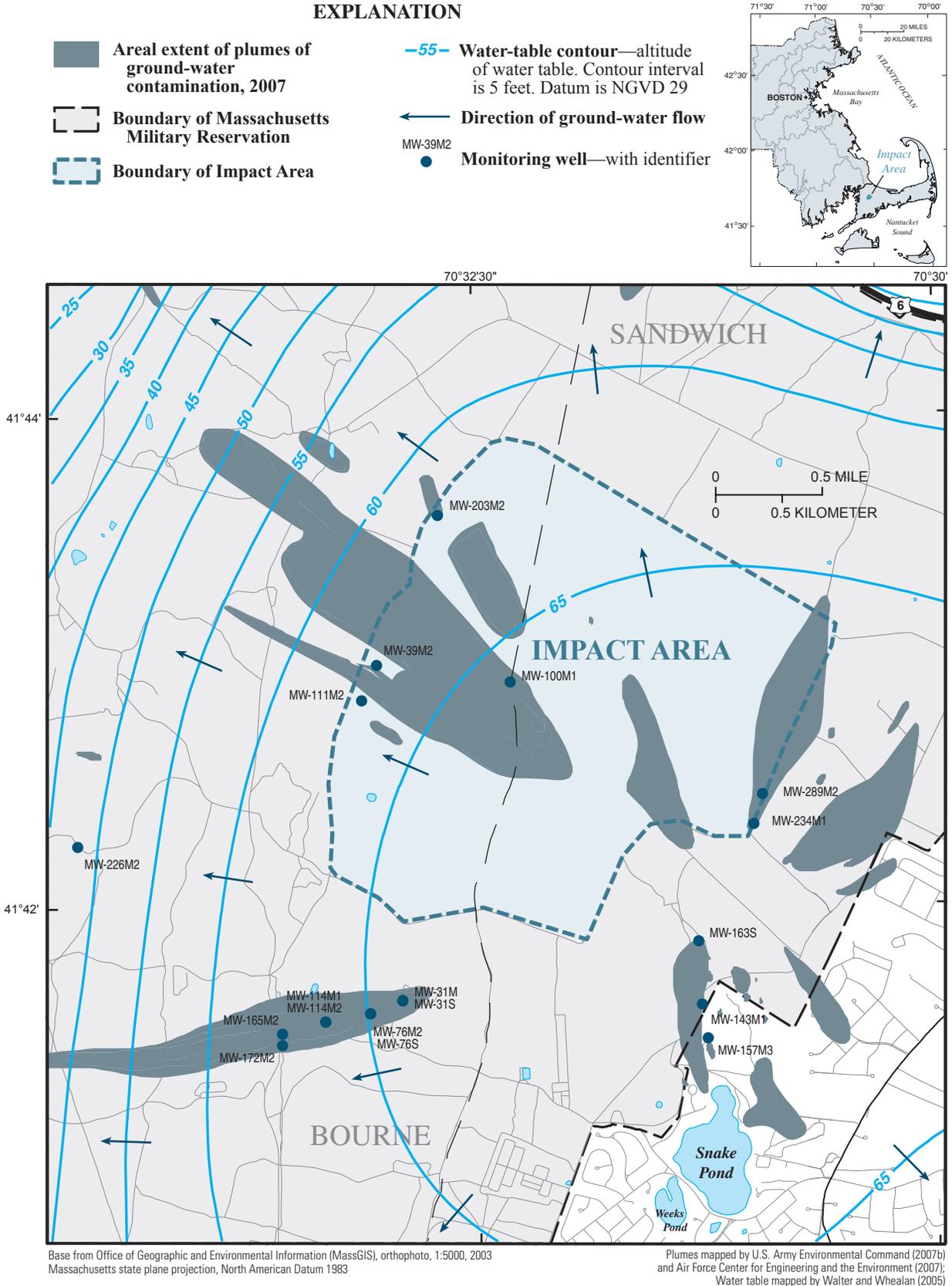


Figure 1. Location of monitoring wells, water table, plumes of ground-water contamination, and the Impact Area at Camp Edwards on the Massachusetts Military Reservation, Cape Cod, Massachusetts.

4 Pumped and Diffusion Sampling Methods to Monitor Perchlorate and Explosives, Camp Edwards, Massachusetts

Table 1. Characteristics of monitoring wells used for collection of pumped and diffusion samples at Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts. Well locations shown in figure 1.

[Source of data: Impact Area Groundwater Study Program (IAGWSP) Environmental Data Management System (EDMS). Altitude in feet relative to National Geodetic Vertical Datum of 1929 (NGVD 29). Location in meters relative to North American Datum of 1983 (NAD 83). m, meter; ft, foot; in., inch]

IAGWSP well name	X-coordinate east NAD 83 (m)	Y-coordinate north NAD 83 (m)	Altitude of land surface (ft)	Altitude of top of screen (ft)	Altitude of bottom of screen (ft)	Water-level date	Altitude of water level (ft)	Diameter of well casing (in.)
MW-100M1	280014.064	829891.049	200.92	21.92	11.92	6/27/2005	65.88	2.5
MW-111M2	278895.250	829748.877	198.07	16.07	6.07	6/27/2005	62.86	2.5
MW-114M1	278624.895	827326.319	146.73	-30.27	-40.27	4/26/2005	63.79	2.5
MW-114M2	278624.892	827325.708	146.73	26.73	16.73	4/26/2005	63.80	2.5
MW-143M1	281463.009	827463.085	101.83	-42.17	-52.17	6/27/2005	69.75	2.5
MW-157M3	281506.605	827207.673	81.80	11.80	1.80	6/27/2005	70.00	2.5
MW-163S	281435.757	827938.391	109.15	71.15	61.15	5/11/2004	68.66	2.5
MW-165M2	278299.704	827235.262	143.15	18.65	8.65	4/26/2005	62.77	2.0
MW-172M2	278298.909	827149.926	128.08	-40.92	-50.92	4/26/2005	62.72	2.0
MW-203M2	279468.281	831146.038	204.37	28.37	18.37	6/27/2005	60.34	2.5
MW-226M2	276758.007	828642.881	164.18	-10.82	-20.82	6/27/2005	53.82	2.0
MW-234M1	281851.990	828824.384	173.91	43.91	33.91	5/12/2004	68.19	2.5
MW-289M2	281917.110	829049.263	169.18	7.16	-2.84	6/27/2005	69.51	2.5
MW-31M	279206.575	827488.120	153.59	40.59	30.59	6/27/2005	66.60	2.5
MW-31S	279206.575	827488.430	153.59	55.59	50.59	5/11/2004	64.98	2.0
MW-39M2	279006.632	830016.878	201.63	26.63	16.63	6/27/2005	62.55	2.0
MW-76M2	278963.550	827388.991	136.06	31.06	21.06	4/26/2005	64.46	2.0
MW-76S	278963.558	827388.380	136.06	51.06	41.06	4/26/2005	64.47	2.0

The wells are constructed of 2.0- or 2.5-in.-diameter polyvinyl chloride (PVC) pipe and are finished with slotted PVC screens that are 10 ft long (with the exception of a 5-ft-long screen for well MW-31S, which was used only as a source of water for the laboratory test) (table 1). The length of the standing water columns in the wells used for the diffusion-sampler field tests ranged from about 23 to 122 ft. 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 (2007a).

Pumped Sampling Method

Water samples were collected from the monitoring wells by contractors for the IAGWSP by positive-displacement pumping methods according to sampling protocols in U.S.

Environmental Protection Agency (USEPA) (1996). The wells used for this study were fitted quasi-permanently with dedicated air-bladder pumps and Teflon-lined 3/8-in.-diameter polyethylene discharge tubing. The pump intakes generally were set near the middle of the screened interval. Approximately 6 to 8 gallons of water were pumped to waste prior to sample collection to ensure that field water-quality parameters had stabilized and formation water was sampled. The methods used to collect and preserve the water samples are described in U.S. Army Environmental Command (2007a).

The pumps had to be removed temporarily from the wells during the field tests of the diffusion samplers. Therefore, the pumped samples had to be collected before the diffusion samplers were set in the wells or after they were retrieved. The interval between collection of the pumped and diffusion samples ranged from 0 to 109 days.

Diffusion Sampling Method

The passive diffusion samplers used in this study were constructed of rigid, porous polyethylene tubing (fig. 2) similar to the aeration tubing used in fish aquariums. The tubing had an outside diameter of 1.5 in., was about 7 in. long, and had a pore size of 6 to 15 μm . Tubing sections longer than 7 in. could not be used because water would leak spontaneously through the tubing walls under pressure heads greater than those that could be counteracted by the capillary suction head in the pores. The ends of the tubing were sealed with polyethylene slip-on caps fitted with stopcock syringe valves with Luer connections. The entire assembly for each diffusion sampler was enclosed in a flexible open-mesh polyethylene sleeve (fig. 3) for protection and ease of deployment and retrieval.

The samplers were prepared in advance by capping one end, filling the tubing with distilled, deionized water, capping the other end, submerging the sampler in a container of the water, and forcing air from the pores of the tubing with a syringe attached to one of the valves. The samplers were stored submerged in the container until they were installed in the wells. Each sampler contained about 160 mL of distilled, deionized water.

The samplers were set in the wells by fastening them to braided polypropylene twine using plastic cable ties passed through the polyethylene mesh and loops tied in the twine at predetermined locations. The bottom end of the twine was tied to a 1-in.-diameter, 7-in.-long, stainless-steel weight to counteract the slight buoyancy of the twine and sampler materials. The top end of the twine was tied to a rubber stopper that fit tightly into the top of the well casing so that the samplers were suspended at the desired points within the screened interval of the wells.

To obtain a detection limit sufficient for this study, about 500 mL and 100 mL of water sample were needed for the analysis of explosive compounds and perchlorate, respectively. To obtain this sample volume, four samplers were suspended in each well for periods of 42 to 52 days (fig. 3). Immediately upon retrieval, the samplers were extracted from the polyethylene mesh and wrapped tightly in polyethylene wrap to limit leakage through the tubing walls. Then, water from the four samplers was decanted into a 1-L amber glass bottle for explosive-compound analysis and mixed by gentle swirling. Finally, about 100 mL were decanted from the 1-L glass bottle into a 125-mL polyethylene bottle for perchlorate analysis.



Figure 2. Diffusion sampler showing rigid, porous polyethylene tubing and slip-on end caps with valves.



Figure 3. Vertical arrangement of diffusion samplers as they are retrieved from a well. Note flexible polyethylene mesh enclosing each diffusion sampler.

Sample Preservation and Laboratory Analysis Methods

Water samples for analysis of the explosive compounds were collected in 1-L amber glass bottles, chilled immediately, and stored chilled and in the dark until analysis. Samples for analysis of perchlorate were collected in 125-mL polyethylene bottles and stored in the dark at room temperature until analysis.

The samples were analyzed for 20 compounds (table 2). The explosive compounds were analyzed by a modification of USEPA method 8330 (U.S. Environmental Protection Agency, 1994). Perchlorate was analyzed by USEPA method 314.0 (U.S. Environmental Protection Agency, 1999). The pumped samples were analyzed by laboratories under contract to the

IAGWSP; the reporting limits ranged from 0.25 to 10 $\mu\text{g/L}$ (table 2). The diffusion samples were analyzed by Severn Trent Laboratories; the reporting limits for the diffusion samples were similar to those shown in table 2.

Laboratory Test of Diffusion Samplers

The diffusion-sampler design was tested in the laboratory prior to deployment of the diffusion samplers in the field to verify that diffusion of the perchlorate and explosive compounds through the rigid, porous polyethylene tubing would result in concentrations in the sampler that approximately

Table 2. Ordnance-related compounds analyzed in pumped and diffusion samples collected from monitoring wells at Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2004–05.

[Reporting limits are shown for the pumped samples. USEPA, U.S. Environmental Protection Agency; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; MMR, Massachusetts Military Reservation; PETN, Pentaerythritol tetranitrate; $\mu\text{g/L}$, microgram per liter]

Method	Analyte	Reporting limit ($\mu\text{g/L}$)
USEPA 314.0	Perchlorate	1.0
USEPA 8330 explosives	RDX	0.25
	HMX	0.25
	1,3,5-trinitrobenzene	0.25
	1,3-dinitrobenzene	0.25
	Tetryl	0.25
	Nitrobenzene	0.25
	2,4,6-trinitrotoluene	0.25
	4-amino-2,6-dinitrotoluene	0.25
	2-amino-4,6-dinitrotoluene	0.25
	2,6-dinitrotoluene	0.25
	2,4-dinitrotoluene	0.25
	2-nitrotoluene	0.25
	3-nitrotoluene	0.25
4-nitrotoluene	0.25	
MMR-specific explosives	2,6-diamino-4-nitrotoluene	0.5
	2,4-diamino-6-nitrotoluene	0.25
	Picric acid	0.25
	Nitroglycerin	5
	PETN	10

The close agreement indicated that the 19-day period was sufficiently long for concentrations inside the diffusion samplers to equilibrate with concentrations in the surrounding water. Except for the very low estimated concentration of perchlorate (0.0017 µg/L) in the diffusion sampler set in distilled, deionized water, there was no indication of contamination derived from the sampler materials. The diffusion-sampler concentrations were not compared to the concentrations in the original well water used to fill the carboys. The volumes of water varied among the carboys, and the concentrations in the original water were effectively diluted an unknown amount by the water in the samplers. Therefore, the valid comparison was between the water in the carboys and the water in the diffusion samplers at the end of the test.

Pumped and Diffusion Samples from the Monitoring Wells

The concentrations of perchlorate, RDX, HMX, and other minor explosive compounds in the diffusion and pumped samples collected from the monitoring wells during the field tests mostly were in close agreement (table 4). Only results for compounds detected in at least one sample are shown in table 4. The concentrations for the diffusion samples were compared to the concentrations for pumped samples collected on one or two pumped-sampling dates nearest the diffusion-sampling date. The diffusion samplers were left in the wells for an equilibration period of 42 to 52 days, which was substantially longer than the 19-day equilibration period for the laboratory tests.

The concentrations in the pumped and diffusion samples for the contaminants of greatest interest—perchlorate, RDX, and HMX—are compared graphically in figure 4. Concentrations below the reporting limit were plotted as values of 0.1 µg/L (zero values cannot be shown on a logarithmic scale). If the diffusion and pumped sampling methods produced samples with equal concentrations, all the points on the graphs would fall on the 1:1 lines. The finding that most of the points fell close to the lines indicated that the results from the diffusion samples were comparable to the results from the pumped samples. There is no evidence of a systematic bias in the concentration differences on the basis of type of contaminant or concentration level. This finding contrasts with the observation by Archfield and LeBlanc (2005) of a small systematic bias toward lower concentrations of trichloroethene (TCE) and tetrachloroethene (PCE) in diffusion samples compared to pumped samples.

The good agreement was observed at different concentration levels, as illustrated in figures 5A, C, and D for wells with low (MW-100M1), intermediate (MW-143M1), and high (MW-114M2) contaminant levels, respectively. The good agreement also was observed during two separate sampling events at wells MW-100M1 (figs. 5A and B) and MW-143M1 (table 4). This finding is similar to the observation by

Archfield and LeBlanc (2005) of a consistent degree of agreement between the methods for a given well.

For several wells, the agreement between concentrations for pumped and diffusion samples was poorer than the generally close agreement observed at most of the wells. The data for these wells plotted substantially off the 1:1 lines of exact agreement shown in figure 4. Wells characterized by poor agreement between the methods include MW-165M2, MW-289M2, MW-31M, and MW-76M2 (table 4). None of these wells was tested a second time, so it is unknown if the poor agreement was characteristic of the wells or was a one-time anomalous result.

Factors Affecting Agreement Between the Methods

The differences in concentrations observed for the pumped and diffusion samples for several wells (table 4) were partly explained by the time lag between collection of the pumped and diffusion samples, particularly for wells in which concentrations were changing rapidly with time. For example, pumped samples were collected from well MW-165M2 at 54 days before and 62 days after collection of the diffusion sample. During this time period, concentrations of perchlorate, RDX, and HMX were decreasing rapidly (fig. 6). As a result, concentrations in the diffusion sample were substantially lower than the concentrations in the first pumped sample (fig. 5E) and substantially higher than the concentrations in the second pumped sample (fig. 5F). Temporal changes in groundwater concentrations also may be factors in the generally poor agreement between sampling methods at wells MW-289M2 and MW-76M2.

Even for samples collected on or about the same day, concentrations that are changing with time could affect the degree of agreement between the methods. Concentrations in pumped samples, which are collected by using low-flow methods, represent concentrations near the well screen at the time of sampling. Concentrations in the diffusion samples, which rely on chemical diffusion through the sampler membrane, represent concentrations in the ground water passing through the well screen during the equilibration period. The diffusion-sample concentration is most strongly influenced by concentrations near the end of the equilibration period; therefore, the concentration differences between samples collected on or about the same day would potentially be greatest when ground-water concentrations are changing rapidly.

The concentrations in both types of samples also may be affected by various hydraulic and chemical factors at the wells, including well construction, chemical and geological heterogeneity near the well screen, and fluid circulation within the wellbore during and between sampling events. For example, concentrations can vary considerably over long screened intervals (Reilly and LeBlanc, 1998), and fluid can circulate vertically inside long screens during and between sampling events (Church and Granato, 1996; Vroblesky and

Table 4. Installation and collection specifications and concentrations of perchlorate, RDX, HMX, and other explosive compounds in diffusion and pumped samples collected from monitoring wells at Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, November 2004–August 2005.

[Analyses by Severn Trent Laboratories. Pumped samples collected by AMEC Earth & Environmental, Inc. RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; µg/L, microgram per liter; J, estimated value; <, value less than the reporting limit shown; --, no data]

Well name	Sample type	Date diffusion sampler set	Date diffusion or pumped sample collected	Days diffusion sampler in well	Days between collection of diffusion and pumped samples	Perchlorate (µg/L)	RDX (µg/L)	HMX (µg/L)	Tetryl (µg/L)	Nitro-glycerin (µg/L)	4-amino-2,6-dinitro-toluene (µg/L)	2,6-dinitro-toluene (µg/L)
MW-100M1	Diffusion	11/30/04	01/11/05	42	--	0.52J	2.1	0.34	2.0	5.7	<0.28	<0.28
	Pumped		01/11/05	--	0	0.53J	2.1	0.29	<0.25	<5	<0.25	<0.25
MW-100M1	Diffusion	06/27/05	08/18/05	52	--	0.50J	1.9	0.32	<0.26	<5.2	<0.26	<0.26
	Pumped		08/22/05	--	4	0.41J	2.2	0.33	<0.25	<5	<0.25	<0.25
MW-111M2	Diffusion	06/27/05	08/18/05	52	--	<1.0	<0.27	<0.27	<0.27	<5.4	<0.27	<0.27
	Pumped		08/19/05	--	1	0.47J	<0.25	<0.25	<0.25	<5	<0.25	<0.25
MW-114M1	Diffusion	04/26/05	06/07/05	42	--	2.0	0.46	<0.27	<0.27	<5.4	<0.27	<0.27
	Pumped		04/13/05	--	-55 ¹	1.7	--	--	--	--	--	--
	Pumped		06/21/05	--	13	--	0.26	<0.25	<0.25	<5	<0.25	<0.25
MW-114M2	Diffusion	04/26/05	06/07/05	42	--	55.5	130	27	<0.27	<5.4	2.0	<0.27
	Pumped		04/13/05	--	-55 ¹	54	140	27	<0.25	<5	1.9	<0.25
MW-143M1	Diffusion	11/30/04	01/11/05	42	--	5.0	0.73	5.2	<0.27	<5.5	<0.27	<0.27
	Pumped		01/12/05	--	1	4.0	0.80	6.7	<0.25	<5	<0.25	<0.25
MW-143M1	Diffusion	06/27/05	08/17/05	51	--	5.6	0.59	5.3	<0.32	<6.3	<0.32	<0.32
	Pumped		08/19/05	--	2	5.2	0.69	6.6	<0.25	<5	<0.25	<0.25
MW-157M3	Diffusion	06/27/05	08/17/05	51	--	0.45J	<0.28	1.4	<0.28	<5.6	<0.28	<0.28
	Pumped		06/03/05	--	-75 ¹	0.78J	<0.25	3.2	<0.25	<5	<0.25	<0.25
	Pumped		10/10/05	--	53	0.53J	<0.25	2.9	<0.25	<5	<0.25	<0.25
MW-165M2	Diffusion	04/26/05	06/07/05	42	--	4.7	4.6	0.76	<0.27	<5.5	<0.27	<0.27
	Pumped		04/14/05	--	-54 ¹	9.8	23	2.1	<0.25	<5	<0.25	<0.25
	Pumped		08/08/05	--	62	0.62J	0.56	<0.25	<0.25	<5	<0.25	<0.25

Table 4. Installation and collection specifications and concentrations of perchlorate, RDX, HMX, and other explosive compounds in diffusion and pumped samples collected from monitoring wells at Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, November 2004–August 2005.—Continued

[Analyses by Severn Trent Laboratories. Pumped samples collected by AMEC Earth & Environmental, Inc. RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; µg/L, microgram per liter; J, estimated value; <, value less than the reporting limit shown; --, no data]

Well name	Sample type	Date diffusion sampler set	Date diffusion or pumped sample collected	Days diffusion sampler in well	Days between collection of diffusion and pumped samples	Perchlorate rate (µg/L)	RDX (µg/L)	HMX (µg/L)	Tetryl (µg/L)	Nitro-glycerin (µg/L)	4-amino-2,6-dinitro-toluene (µg/L)	2,6-dinitro-toluene (µg/L)
MW-172M2	Diffusion	04/26/05	06/07/05	42	--	3.7	<0.29	<0.29	<0.29	<5.7	<0.29	<0.29
	Pumped		04/05/05	--	-63 ¹	2.1	<0.25	<0.25	<0.25	<5	<0.25	<0.25
MW-203M2	Diffusion	06/27/05	08/18/05	52	--	<1.0	1.9	<0.27	<0.28	<5.4	<0.27	<0.27
	Pumped		08/19/05	--	1	<1.0	1.7	<0.25	<0.25	<5	<0.25	<0.25
MW-226M2	Diffusion	06/27/05	08/17/05	51	--	0.52J	<0.27	<0.27	<0.27	<5.4	<0.27	<0.27
	Pumped		08/22/05	--	5	0.71J	--	--	--	--	--	--
MW-289M2	Diffusion	06/27/05	08/17/05	51	--	10.2	3.4	2.0	<0.31	11	<0.31	<0.31
	Pumped		08/22/05	--	5	14.8	2.8	1.7	<0.25	<5	<0.25	<0.25
MW-31M	Diffusion	06/27/05	08/17/05	51	--	2.3	97	66	<0.28	<5.7	<0.28	<0.28
	Pumped		04/30/05	--	-109 ¹	16	120	27	<0.25	<5	0.32	<0.25
MW-39M2	Diffusion	06/27/05	08/18/05	52	--	<1.0	<0.27	0.75	<0.27	<5.3	<0.27	<0.27
	Pumped		08/19/05	--	1	<1.0	<0.25	0.57	<0.25	<5	<0.25	<0.25
MW-76M2	Diffusion	04/26/05	06/07/05	42	--	10.1	28	11	<0.27	<5.3	0.74	<0.27
	Pumped		04/13/05	--	-55 ¹	25	62	27	<0.25	<5	0.88	0.30
MW-76S	Diffusion	04/26/05	06/07/05	42	--	3.8	6.6	1.1	<0.27	<5.5	<0.27	<0.27
	Pumped		04/13/05	--	-55 ¹	3.2	3.9	0.48	<0.25	<5	<0.25	<0.25

¹ Negative value in days indicates that diffusion sample was collected after pumped sample.

others, 2007). The concentration variations and vertical flow may complicate direct comparison between pumped and diffusion sampling methods. Archfield and LeBlanc (2005) report that the degree of agreement between the sampling methods for VOCs in wells at the MMR was better in wells with 2-ft-long screens than in wells with 5-ft-long screens. Huffman (2002), Church (2000), and Vroblesky (2001b) report, however, that VOC concentrations in diffusion samples collected from wells with screens longer than 5 ft agreed well with concentrations in pumped samples from the wells. In the present study, water from diffusion samplers set at four intervals along the 10-ft-long well screens was blended to provide sufficient volume for the chemical analyses, and at least one screen volume was purged to waste during pumped sampling prior to sample collection (John Ehret, U.S. Army Corps of Engineers, oral commun., 2008). The sampling methods may have effectively averaged concentration variations along the well screens and improved the comparability of the two types of samples.

During this study, concentrations of perchlorate and explosive compounds in samples collected from two monitoring wells by diffusion and pumped sampling methods agreed closely in two separate sampling events. Archfield and LeBlanc (2005) report that, on the basis of a larger number of wells with multiple sampling events, the degree of agreement of VOC concentrations in pumped and diffusion samples was repeatable for a given well, although they were unable to determine which well-construction or aquifer characteristics affected the degree of agreement. They recommend 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. A similar approach could be used to determine the applicability of the diffusion sampling method for long-term monitoring of perchlorate and explosive compounds near the Impact Area at the MMR.

Limitations of Study and Suggestions for Future Investigations

The concentrations of the ordnance-related compounds in the pumped and diffusion samples were compared qualitatively in this study because too few wells were sampled to enable comparison of concentrations by statistical methods. The comparison also was complicated by the large variation in time lags between collection of the pumped and diffusion samples. The small sample size and sampling time lags resulted from the limited scope of this initial assessment and the logistical considerations associated with working in a military training area. Future studies could include sample collection from a larger number of wells to allow data analysis by the statistical methods used by Archfield and LeBlanc (2005) to examine diffusion sampling at the MMR for VOCs. Shorter time lags between collection of the diffusion and pumped samples may aid in identifying wells appropriate for long-term monitoring of ordnance-related compounds at the MMR by diffusion sampling methods.

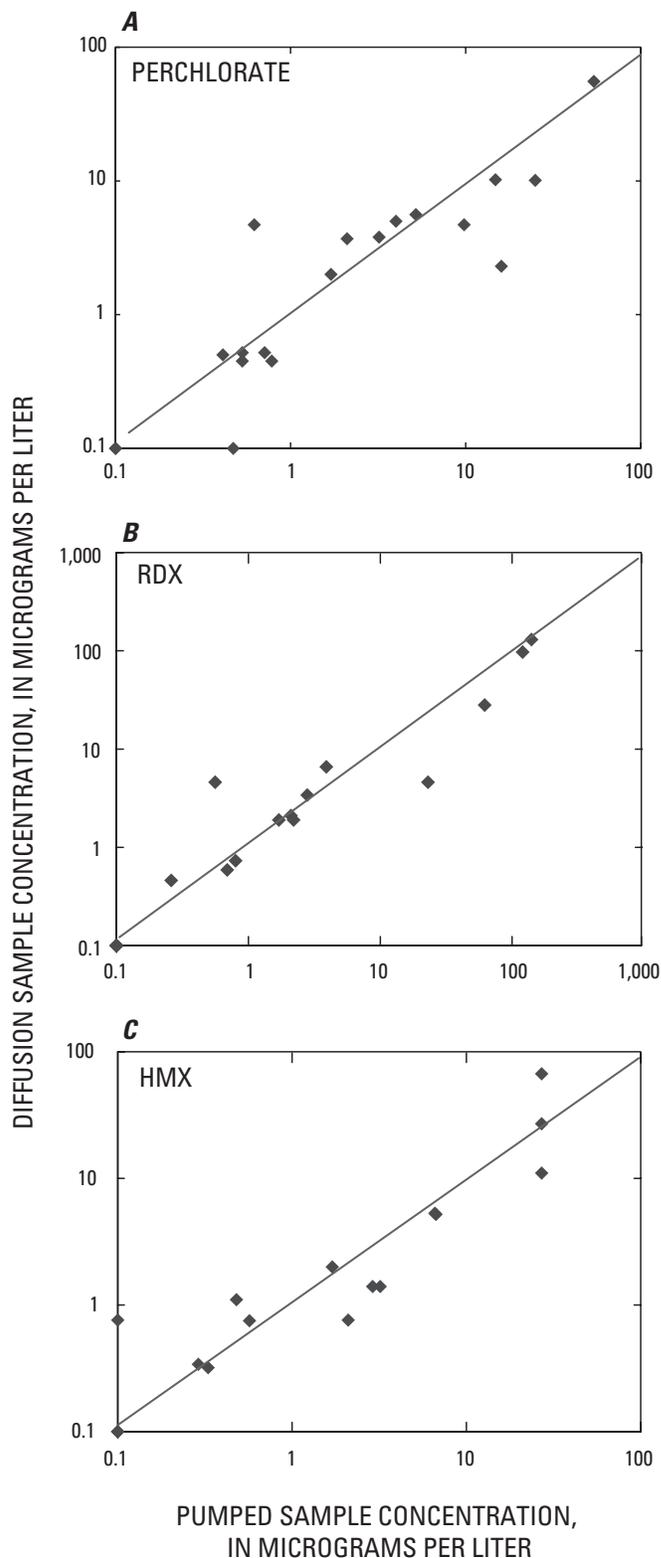


Figure 4. Comparison of (A) perchlorate, (B) RDX, and (C) HMX concentrations for pumped and diffusion samples collected from 15 wells, including two replicate samples, near the Impact Area at Camp Edwards on the Massachusetts Military Reservation, Cape Cod, Massachusetts, 2005.

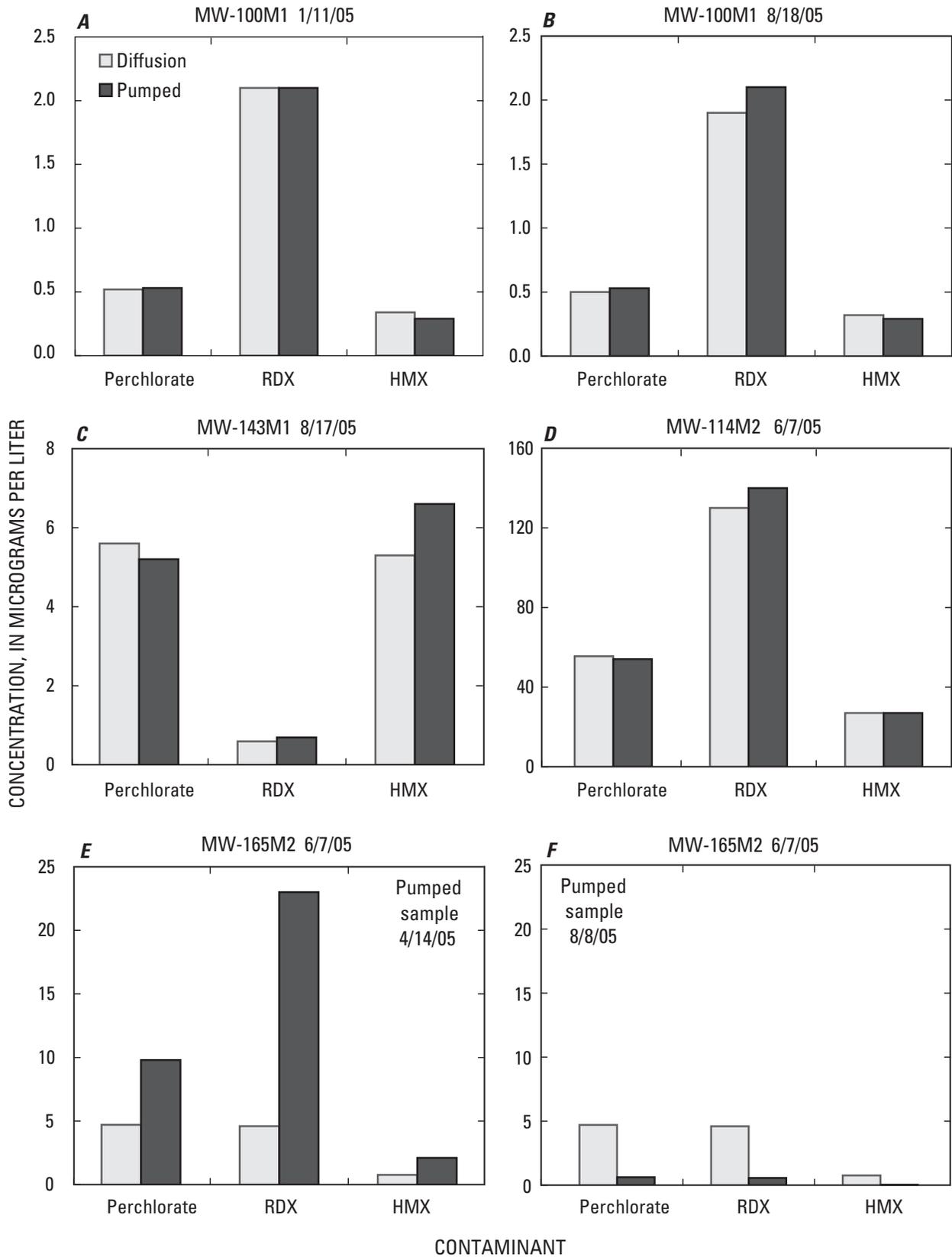


Figure 5. Comparison of perchlorate, RDX, and HMX concentrations for pumped and diffusion samples collected from selected wells near the Impact Area at Camp Edwards on the Massachusetts Military Reservation, Cape Cod, Massachusetts, 2005. (Note different Y-axis concentration scales.)

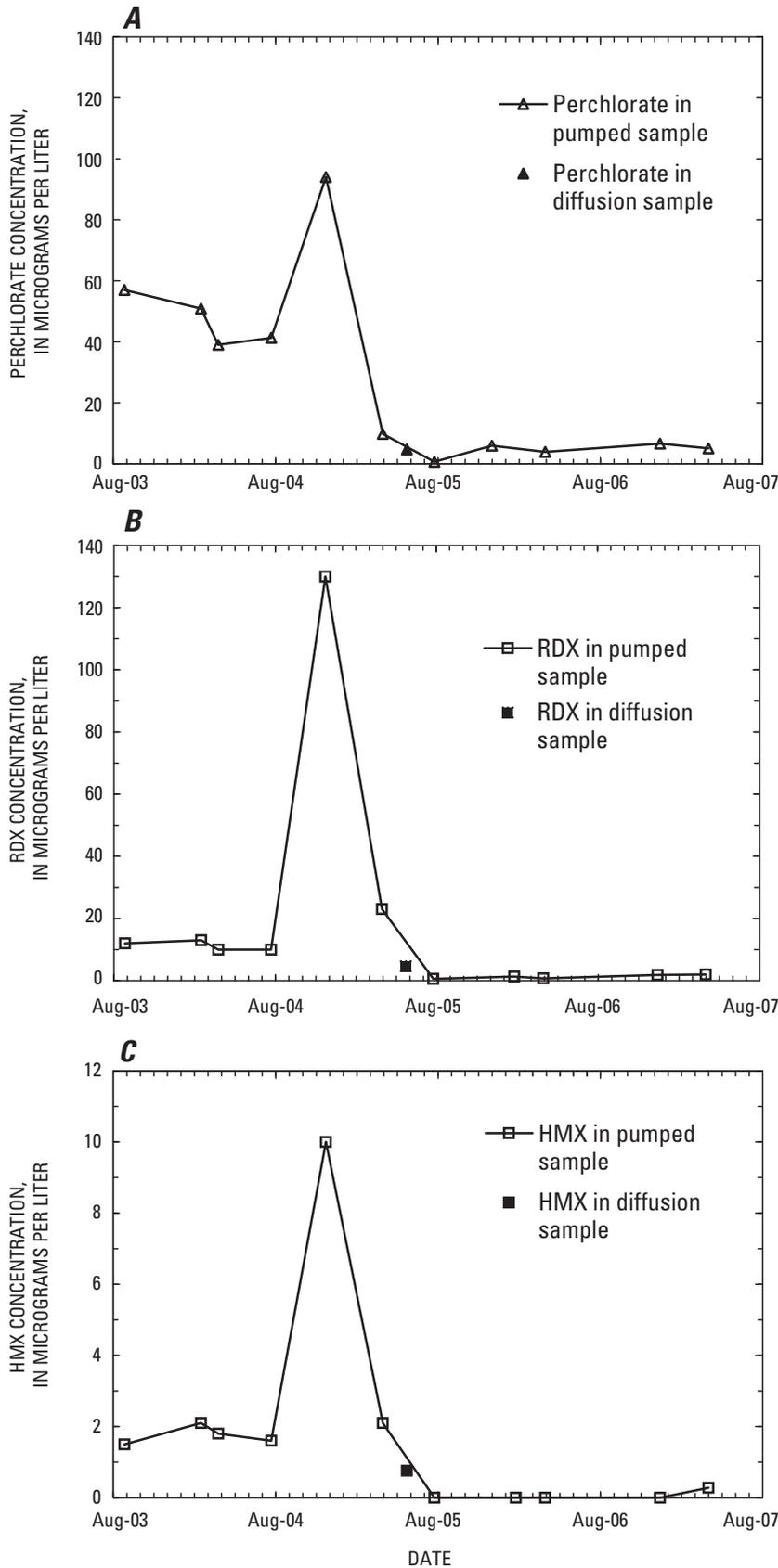


Figure 6. Time history of (A) perchlorate, (B) RDX, and (C) HMX concentrations for pumped and diffusion samples collected from monitoring well MW-165M2 at Camp Edwards on the Massachusetts Military Reservation, Cape Cod, Massachusetts, August 2003 to August 2007.

Summary

Long-term monitoring of water quality is an important part of ground-water remediation efforts. Most monitoring programs include regular collection by pumped sampling methods of ground-water samples from a network of monitoring wells. The costs of monitoring can be substantial. In addition, the monitoring process can require disposal of contaminated water produced during well purging prior to sample collection and can cause damage to the local environment by repeated visits to the well sites by field crews and their equipment and vehicles. Passive diffusion sampling is an alternative to pumped sampling that may offer the advantages of lower cost, no production of purge water, and lessened adverse impacts at well sites.

In this study, laboratory and field tests were done to determine the utility of the passive diffusion sampling method for monitoring concentrations of perchlorate and explosive compounds in wells near the Impact Area at Camp Edwards on the Massachusetts Military Reservation on Cape Cod. The sand and gravel aquifer at this site has been contaminated by historical use, testing, and disposal of military ordnance. The contaminant plumes emanating from the site are presently (2008) being remediated by the Impact Area Groundwater Study Program of the U.S. Army Environmental Command, the cooperating agency for this study.

The diffusion samplers tested during this study were constructed of 1-in.-diameter, 7-in.-long sections of rigid, porous polyethylene tubing (6- to 15- μ m pore size) filled with distilled, deionized water. Laboratory tests of the diffusion samplers were conducted by submerging the samplers in test chambers that were filled with ground water collected from monitoring wells containing various concentrations of perchlorate, RDX, and HMX. The results of the laboratory tests indicate that concentrations of perchlorate and explosive compounds in the water inside the diffusion samplers had equilibrated with concentrations in the water surrounding the samplers in the test chambers by the end of the 19-day-long test period.

Field tests of the diffusion sampling method were conducted in 15 wells near the Impact Area. Four diffusion samplers were set in each well screen for equilibration periods of 42 to 52 days. The wells were constructed of 2- or 2.5-in.-diameter PVC and had 10-ft-long screens. The water from the four diffusion samplers was blended together to produce sufficient volumes for laboratory analysis. For comparison, water samples were collected from the wells by low-flow pumped sampling methods either before or after the diffusion-sampler tests. Most wells had close agreement between concentrations of perchlorate, RDX, and HMX in samples collected by diffusion and pumped sampling methods. There was no apparent systematic bias in the concentration differences between the methods related to contaminant type or concentration levels. For several wells, substantial differences between concentrations for the pumped and diffusion samples

were related to changing concentrations in the ground water coupled with time lags from 0 to 109 days between collection of the pumped and diffusion samples. Earlier studies report that the degree of agreement between the methods may be a consistent characteristic of the individual monitoring wells, although too few wells were sampled during this study to examine this hypothesis for the ordnance-related compounds.

The results of the laboratory and field tests indicate that passive diffusion sampling may be a useful method for long-term monitoring of concentrations of perchlorate and explosive compounds in wells at the MMR and in similar hydrogeologic settings. One-time well-by-well comparisons between pumped and diffusion sampling results could be used to determine which wells are good candidates for the use of the diffusion sampling method.

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