ESTCP
Cost and Performance Report

(ER-200313)

Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Ground-Water Quality and Remediation Progress at DoD Site: Perchlorate and Ordnance Compounds

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ACRONYMS AND ABBREVIATIONS

APG	Aberdeen Proving Ground
ARTT	Alternative Restoration Technology Team
ASTM	American Society for Testing and Materials
BTEX	benzene, toluene, ethylbenzene, and xylenes
DoD	Department of Defense
DODEC	Department of Defense Environmental Conservation
ESTCP	Environmental Security Technology Certification Program
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
ITRC	Interstate Technology & Regulatory Council
LDPE	low-density polyethylene
MDL	minimum detection limit
NAVFAC ESC	Naval Facilities Engineering Command Engineering Service Center
NAWC	Naval Air Warfare Center
NJDEP	New Jersey Department of Environmental Protection
NTU	nephelometric turbidity units
PDB	polyethylene diffusion bag
PETN	pentaerythritol tetranitrate
PVC	polyvinyl chloride
RCDM	regenerated cellulose dialysis membrane
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RPM	Remedial Project Manager
TDS	total dissolved solids
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

This cost and performance report documents the demonstration and validation of regenerated cellulose dialysis membrane (RCDM) samplers for use in collecting groundwater samples for perchlorate and a suite of explosives compounds. This project, ER-200313, was funded by the Environmental Security Technology Certification Program (ESTCP).

1.2 OBJECTIVES OF THE DEMONSTRATION

The primary objectives of the project were (1) to determine the usefulness of RCDM samplers in collecting perchlorate and a suite of explosives compounds from groundwater, (2) to determine the optimum equilibration times for these constituents to diffuse into the RCDM sampler, (3) to compare water-quality results and sampling costs from samples collected with RCDM samplers to samples collected with a low-flow purging technique, and (4) to transfer the technology while gaining regulatory acceptance. Equilibration times were determined in bench-scale testing for perchlorate and 14 nitroaromatic and nitramine explosives compounds. Field comparisons were conducted at two Department of Defense (DoD) sites: Aberdeen Proving Ground (APG), MD and Picatinny Arsenal, NJ. Samples collected with the two sampling techniques were compared graphically and statistically to determine the significance of any differences found.

1.3 DEMONSTRATION RESULTS

Two bench-scale equilibration tests were conducted to evaluate perchlorate and 14 nitroaromatic and nitramine explosives compounds in groundwater from the two field sites. Greater than 95% equilibrium was reached in RCDM samplers within 1 day for perchlorate and within 3 to 7 days for all explosives compounds. Lower temperatures were found to have a small effect in that they lengthened equilibration times for several explosives constituents from 3 days to 7 days. No perchlorate or explosives compound concentrations were determined to desorb from the dialysis membrane in the bench-scale test blanks. Coefficients of variation for triplicate RCDM sampler analyses were less than 4% for perchlorate and less than 16% for all explosives compounds. Based on the results of the bench-scale testing, and by adding a safety factor, a 7-day equilibration time was chosen for RCDM samplers for perchlorate samples and a 14-day equilibration time was chosen for explosives compound samples.

The experimental design of the field demonstration was to sample groundwater from 8 to 11 wells per site at the two DoD sites with each of two sampling methods; the RCDM sampler and low-flow purging using a variable-speed peristaltic pump. Samples were collected at the same depth in each well using both sampling techniques. In all cases, the RCDM samplers were suspended in a well at the estimated depth of highest mass flux through the open interval and were allowed to equilibrate for at one to two weeks. After the RCDM samplers were retrieved and sampled, the pump intake was lowered to the same depth and the well was sampled using a low-flow purging procedure that included the monitoring of field parameters to stability prior to sample collection. All samples from a site were analyzed at the same laboratory for the same suite of constituents.

Results of the analyses for perchlorate showed excellent agreement between concentrations collected with RCDM samplers and low-flow purging. Statistical testing showed RCDM samplers recovered median concentrations that were not significantly different from median concentrations recovered by low-flow purging. Results of the analyses for four of six explosives compounds also showed excellent agreement between concentrations collected with RCDM samplers and low-flow purging. For four of six explosives compounds (hexahydro-1,3,5-trinitro-1,3,5-triazine [RDX], octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine [HMX], 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene), statistical testing showed RCDM samplers recovered median concentrations of explosives compounds that were not significantly different from median concentrations recovered by low-flow purging. For two of six explosives compounds (2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene), statistical testing showed RCDM samplers recovered median concentrations of explosives compounds that were significantly higher than median concentrations recovered by low-flow purging. For these latter two compounds it is recommended that RCDM samplers should only be used to qualitatively identify the presence/absence of these compounds in a well.

Sampling costs associated with the use of RCM samplers were found to be significantly less compared to the use of a low-flow purging procedure. Specifically, field sampling time (and hence field labor cost) was 84% less when RCDM samplers were used compared to low-flow purging (a reduction of more than six fold). Overall, sampling costs per sample were calculated to be 71% using an RCDM sampler compared to low-flow purging (a reduction of more than three fold). Such reductions in sampling costs are particularly significant when multiplied out over a typical 30-year long-term monitoring plan. Besides being able to collect samples more inexpensively for perchlorate and several explosives compounds in groundwater, in general, RCDM samplers were found to have additional advantages. They: (1) were easily constructed and deployed, (2) eliminated the production of essentially all purge water when sampling a well, (3) eliminated the need for field filtration of groundwater samples, and (4) eliminated cross-contamination between wells because they were disposable.

1.4 IMPLEMENTATION ISSUES

Regulatory agency acceptance is achieved on a case-by-case basis. The RCDM sampler is not currently manufactured commercially. An ESTCP Final Report (Imbrigiotta et al., 2007) and an ESTCP Protocol (Imbrigiotta et al., 2009) on construction and use of RCDM samplers are available on the ESTCP website at www.serdp-estcp.org. Additional information on the application, construction, and use of RCDM samplers is available in Interstate Technology & Regulatory Council (ITRC) Guidance Documents DSP-4 and DSP-5 (ITRC, 2005; ITRC, 2007).

2.0 INTRODUCTION

2.1 BACKGROUND

Collection of groundwater samples for long-term monitoring or to assess remedial progress at contaminated DoD sites is very costly in terms of manpower, time, and equipment requirements. Currently, the standard technique for groundwater collection is the U.S. Environmental Protection Agency's (USEPA) low-flow purging procedure using a variable-speed submersible pump with disposable discharge tubing (Puls and Barcelona, 1996). The low-flow procedure requires a monitoring well to be pumped at low-flow rates (500-1000 milliliters per minute [mL/min]) while field parameters are monitored to stability. Often this stabilization can take a long period of time (0.75 to 1.5 hours) prior to the time that samples can be collected. Following sample collection, time and effort must be spent decontaminating the pump and its components before it can be used in another well. Disposal of both contaminated purge water and wash water is also costly since they must be collected and transported offsite to treatment facilities for proper disposal. An additional problem in collecting groundwater samples with portable pumps or bailers is that the installation and removal of these sampling devices frequently results in increased turbidity in the groundwater brought to the surface. Low-flow purging requires that turbidity be monitored until it is less than 10 nephelometric turbidity units (NTU) or becomes stable prior to sample collection. If turbidity is stable but exceeds 5-10 NTU, serious bias can result for many contaminants that sorb readily onto suspended particulates (Gibs et al., 2000). This introduces uncertainty into the assessment of inorganic and organic contaminant concentrations in groundwater, which can result in incorrect conclusions concerning the water quality or remediation status of a site.

Diffusion sampler technology has been evolving over several decades and has shown promise as a way to reduce groundwater sampling field time, equipment decontamination costs, and purge-water treatment costs. It also is a way to avoid the potential problems caused by turbidity in wells. All diffusion membrane samplers developed to date involve suspending a container made of a semi-permeable membrane filled with high-purity water at a given depth in the water column of a well. The system operates on the principle that given the proper amount of time, diffusion of dissolved chemical species across a semi-permeable membrane will occur until concentrations inside the sampler are equivalent to those in the water outside the sampler. The diffusion membrane sampler is then brought to the surface and the enclosed water sample is transferred to sample bottles for analysis. Diffusion membrane samplers have sufficiently small membrane pores so that they do not allow the passage of suspended particulates into the sampler.

One design developed for a diffusion membrane sampler consists of a series of short open-ended rigid polypropylene cylinders with hydrophilic cellulose acetate or polysulfone flat filter membranes covering each end (Ronen et al., 1987; Magaritz et al., 1989). This sampler has a restricted sample volume because the rigid cylinders must be less than the diameter of the well. Another diffusion membrane sampler design consists of a tubular-shaped bag made of flexible low-density polyethylene (LDPE) (Vroblesky, 2001a, 2001b). The LDPE tube is heat-sealed on one end, filled with high-purity water, heat-sealed at the top, and then suspended in a well to equilibrate for two weeks. This type of diffusion membrane sampler, unlike the short cylinder configurations, is inexpensive, can be made to any length to accommodate larger sample volume requirements, and can be constructed from small-diameter LDPE tubing that fits into small-

diameter wells. These polyethylene diffusion bag (PDB) samplers have been shown to be useful only for collection of volatile organic compounds (VOCs) (such as, chlorinated solvents and benzene, toluene, ethylbenzene, and xylenes [BTEX] compounds) because of the hydrophobic nature of the membrane material. The PDB sampler cannot be used for collection of inorganic contaminants (such as trace metals or other dissolved ionic species), inorganic parameters useful for monitored natural attenuation (such as nitrate, iron, sulfate, or alkalinity), highly soluble organic compounds (such as methyl tert-butyl ether or acetone), or most semi-volatile organic compounds (such as polychlorinated biphenyls and polycyclic aromatic hydrocarbons) (ITRC, 2004).

Because it is usually necessary to collect samples for both inorganic and organic constituents when monitoring water quality, another diffusion membrane sampler design has recently been developed by the U.S. Geological Survey (USGS) (Imbrigiotta et al., 2002; Ehlke et al., 2004; Vroblesky et al., 2002; Vroblesky and Pravecek, 2002; Vroblesky et al., 2003; Imbrigiotta et al., 2007). This type of diffusion membrane sampler is constructed from commercially available tubular RCDM. The dialysis membrane allows the passage of both dissolved inorganic and organic contaminants from groundwater into the sampler. The RCDM tubing can be purchased in a variety of diameters so the sampler may be configured to fit in both small- and large-diameter wells. The RCDM samplers can be made in various lengths to allow for the collection of a sufficient volume of water necessary for whatever analyses are of interest. The RCDM samplers are relatively low in cost, only slightly more expensive than PDB samplers, and are disposable after one use. RCDM samplers have been shown to effectively sample wells for major cations, anions, nutrients, most trace metals, all VOCs, dissolved organic carbon, and methane (Imbrigiotta et al., 2007). This project demonstrates the utility of RCDM samplers for sampling perchlorate and explosives compounds.

For the sake of brevity, throughout this report the RCDM diffusion sampler will be referred to simply as the RCDM sampler or the dialysis sampler.

2.2 OBJECTIVES OF DEMONSTRATION

The main goal of this project was to demonstrate and validate the usefulness of RCDM samplers for monitoring groundwater at DoD sites. Specific objectives of the project were as follows:

(1) To determine if the RCDM samplers will collect valid samples for perchlorate and explosives compounds, chemical constituents relevant to DoD for which there is no current RCDM testing information available,

(2) To determine the optimum equilibration period for these contaminants to diffuse into RCDM samplers,

(3) To compare the sampling efficiency and cost of the RCDM samplers to quantitatively recover these contaminants against the standard low-flow purging technique, and

(4) To transfer the RCDM sampler technology to DoD and private end-users and gain regulatory acceptance.

Objectives (1) and (2) were addressed during bench-scale testing at the USGS laboratory facility in West Trenton, NJ. Objectives (3) and (4) were addressed using the data generated during the field demonstrations conducted at two DoD field sites, APG, MD and Picatinny Arsenal, NJ.

2.3 REGULATORY DRIVERS

This demonstration responds to many DoD requirements, including: Navy 1.III.01.k Improved Field Analytical Sensors, Toxicity Assays, Methods, and Protocols to Supplement Traditional Sampling and Laboratory Analysis; Air Force 124 Plume Location and Source Identification; 131 Improved Remediation Monitoring Technologies; 1608 Find and Track Organic Contaminant Plumes; and 2705 Methods to Reduce the Cost of Long-Term Monitoring. Other pertinent requirements include: 1.III.02.n; 130; 145; 244; 246; 249; 254; 255; and 1701.

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3.0 TECHNOLOGY

3.1 TECHONOLOGY DESCRIPTION

Most of the diffusion membrane samplers developed to date involve suspending a container made of a semi-permeable membrane and filled with high-purity water in the water column of a well. These devices operate on the principle that given the proper amount of time, diffusion of dissolved chemical species across a semi-permeable membrane will occur until concentrations inside the sampler are equivalent to those in the groundwater. The ideal diffusion of chemicals through a membrane is described by Fick's Law of Diffusion and is dependent primarily on the concentration gradient across the membrane, the thickness of the membrane, and the diffusion coefficient for each chemical (Figure 1). Factors such as molecular size, membrane pore size, the hydrophobic/hydrophilic nature of the membrane, and water temperature can also affect the ability and speed of chemical diffusion across a membrane.

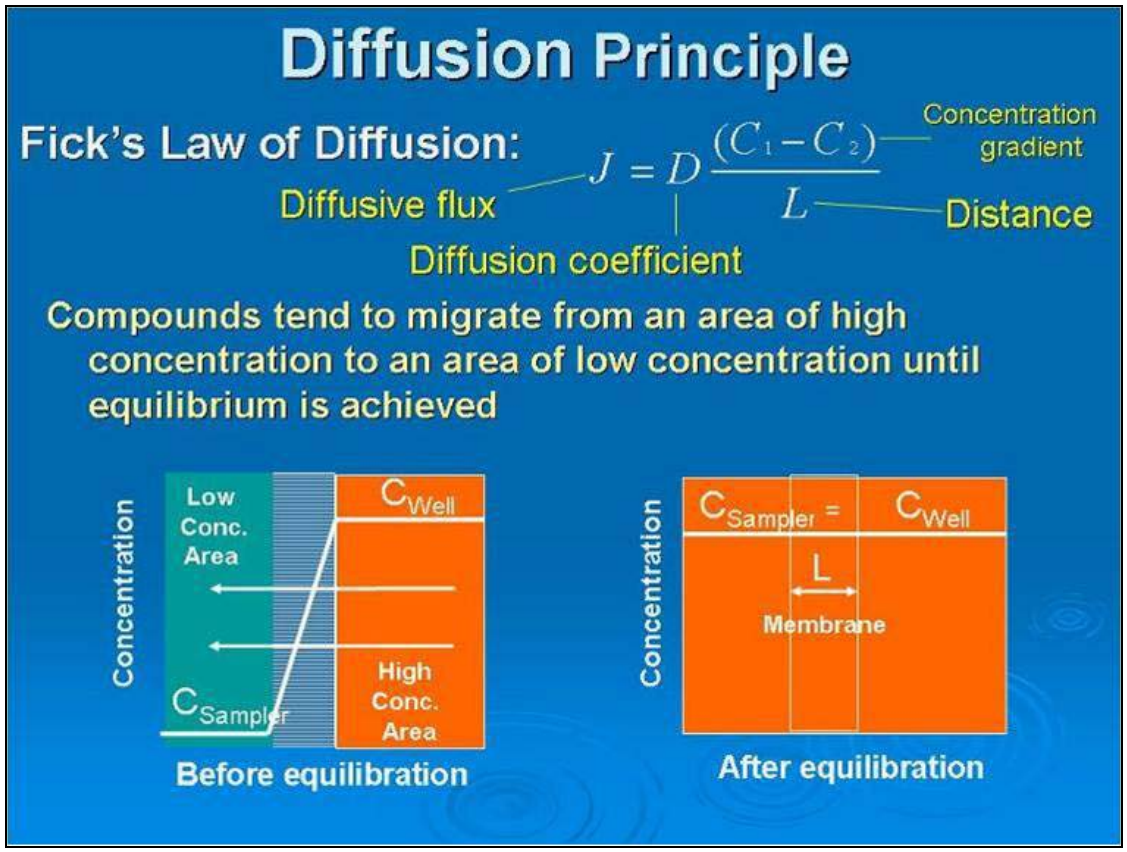

Figure 1. Diffusion across a membrane (Fick's Law of Diffusion)

Once the diffusion sampler has reached equilibrium, it is brought to the surface and the enclosed water sample is transferred to sample bottles for transport to and analysis at a laboratory. All diffusion samplers have sufficiently small membrane pores to prevent passage of suspended particulates into the sampler.

The RCDM samplers tested during this demonstration were constructed of regenerated cellulose. The membrane was obtained from Membrane Filtration Products, Inc., Seguin, Texas.[1] The membrane had a nominal molecular weight cut off of 8000 Daltons with a pore size of 18 Angstroms (Å). The 100-millimeter (mm) width membrane has a filled diameter of 63.7 mm, a volume of 31.8 milliliters per centimeter (mL/cm), and comes in rolls 5 meters (m) in length. The 50-mm width membrane has a filled diameter of 31.8 mm, a volume of 7.94 mL/cm, and comes in rolls 10 m in length. The membrane was pre-cleaned by the manufacturer to remove trace metals and sulfides. The membrane was cut into lengths appropriate for the volume needed for analyses at each well.

Various components of the RCDM sampler are shown in Figures 2 through 5. Figure 2 shows the components of the sampler prior to assembly. Figure 3 shows the sampler partially constructed prior to being filled with deionized water. Figure 4 shows the completed sampler ready for deployment in a well. The polyvinyl chloride (PVC) sections are external to the membrane and are included to remove pressure from the ends of the membrane to prevent leakage. A second version of the RCDM sampler is pictured in Figure 5. This version has a perforated PVC tube inside the dialysis membrane to keep the membrane from collapsing in waters with high ionic strength. Both versions work on the same diffusion principle and sample the same chemical species.

In 2000, Ehlke et al. (2004) conducted laboratory studies using RCDM samplers and demonstrated that dialysis membranes could equilibrate with selected inorganics and VOCs in the laboratory. Imbrigiotta et al. (2002) used these RCDM samplers in actual field sampling at the Naval Air Warfare Center (NAWC), West Trenton, NJ site from 2000 to 2002 and found the results compared favorably with those of a low-flow purging technique and a modified conventional purging technique for several major cations and anions, chlorinated VOCs, and a few trace elements. Vroblesky et al. (2002) and Vroblesky and Pravecek (2002) developed a version of the RCDM sampler and tested it at several field sites and found that it compared well to low-flow purge samples for several aromatic VOCs.

Expected applications of RCDM samplers are to sample long-term monitoring wells at DoD sites: (1) where this method will save time and cost by not requiring the use of a pump to sample for a variety of dissolved organic and inorganic constituents, (2) where it would be difficult or impossible to bring in a pump and its power source (e.g., wells in remote wilderness areas, wells inside buildings), (3) to sample wells where normal sampling activities would be extremely hazardous or inconvenient (e.g., wells in high traffic areas, wells in airport runway areas, wells in residential areas near military bases), (4) where collection, transport, and treatment of purge water would be costly, difficult, or undesirable due to safety concerns (e.g., wells at all hazardous waste sites, wells at remote hazardous waste sites, wells in populated areas near military bases), and (5) where wells have water with high turbidity when purged due to their construction or the formation in which they are completed (e.g., incorrect screen size and filter pack).

[1] The use of brand names in this report is for identification purposes only and does not imply endorsement by the USGS or the U.S. Navy.

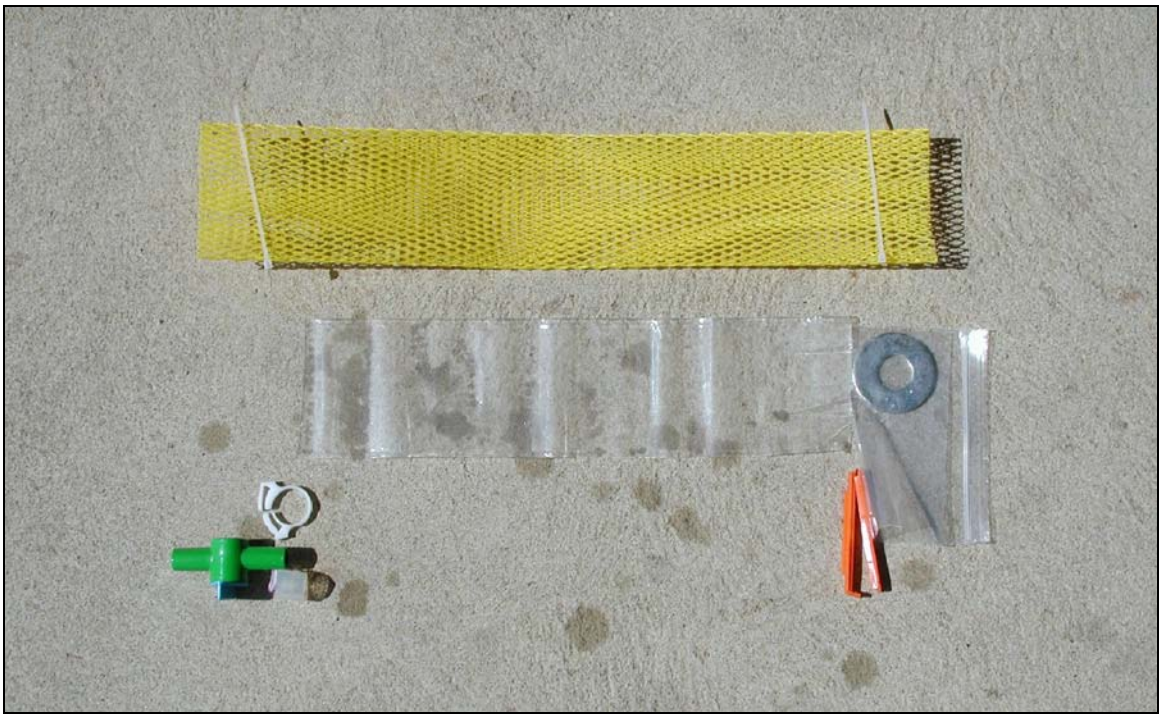

Figure 2. Disassembled regenerated cellulose dialysis membrane diffusion sampler, showing component parts.

Figure 3. Partially assembled regenerated cellulose dialysis membrane diffusion sampler, showing protective mesh and PVC pipe external to the membrane.

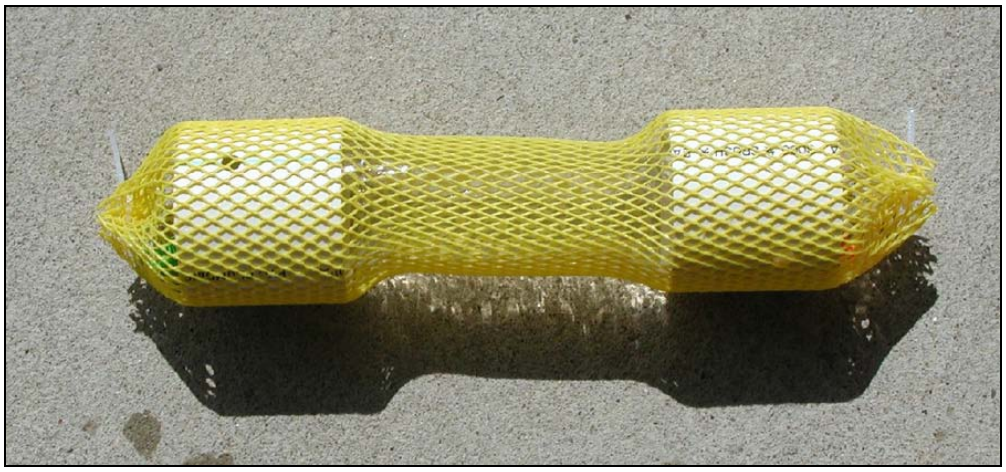

Figure 4. Assembled regenerated cellulose dialysis membrane diffusion sampler with PVC pipe sections external to the membrane.

Figure 5. Regenerated cellulose dialysis membrane diffusion sampler with perforated polyethylene support inside the membrane.

3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The advantages and limitations of the RCDM sampler and low-flow purging are compared in Table 1.

Table 1. Advantages and limitations of sampling technology.

Regenerated Cellulose Dialysis Membrane Diffusion (RCDM) Sampler	Low-Flow Purging
Advantages	
No purge water is produced to drum, transport, or treat.	Purge water is produced to drum, transport, and treat.
No particulates can pass through the membrane so no sample filtration is necessary.	Turbidity is minimized but not eliminated so sample filtration is still recommended.
Sampler is disposable so no decontamination is needed between wells.	Pump must be decontaminated between wells.
Time in field is minimized for field personnel.	Time in field can be 0.75 to 1.5 hours waiting for field parameters to stabilize.
Dialysis membrane is fairly inexpensive; slightly more expensive than LDPE, but still far less than the cost of a pump setup.	Initial investment in pump setup is expensive (pump, control box, generator, extension cords, and tubing).
Can be used to sample for both inorganic and organic dissolved chemical species.	Can be used to sample for both inorganic and organic dissolved chemical species.
Limitations	
Pre-cleaned dialysis membrane must be kept wet in preservative solution prior to use.	Pump must be cleaned prior to use.
RCDM samplers lose water with time due to the nature of the dialysis process.	Not applicable.
Dialysis membranes are subject to attack by bacteria and fungi.	Pumps are not affected by bacteria and fungi.
Sample volume is finite.	Sample volume is not limited.

The limitations of the RCDM sampler indicated in the table above with respect to the loss of water volume with time and the potential attack of the membrane by bacteria or fungi are not significant considerations when the equilibration time needed for the sampler is short (<2 weeks).

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4.0 PERFORMANCE OBJECTIVES

The overall performance objective of this demonstration project was to evaluate the performance of RCDM samplers versus low-flow purging and to compare their costs. The performance was evaluated by comparing the water-quality results from samples collected at the same depth using both sampling techniques in a series of wells at two test sites. The performance objectives, data requirements, success criteria, and results achieved are tabulated in Table 2 and are discussed in more detail in Section 6.

Table 2. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Qualitative Performance Objectives			
Determine if RCDM samplers equilibrate with perchlorate and explosives compounds in the laboratory.	List of chemical constituents that equilibrated in the RCDM samplers in bench-scale testing.	All compounds tested equilibrate through the dialysis membrane.	Criteria met.
Determine if RCDM samplers and low-flow purging collect the same chemical constituents in the same wells in the field.	List of chemical constituents recovered by both RCDM and low-flow purging in each well.	Detection of the same chemical constituents in field samples collected with both RCDM samplers low-flow purging.	Criteria met.
Determine if dialysis membrane integrity is maintained over the course of equilibration.	Observations of the RCDM samplers after removal from the well.	No perforations noted during the length of the test.	Criteria met.
Determine if RCDM samplers are easier to use than low-flow purging.	Observations of the field sampling personnel.	RCDM samplers should be as easy or easier to use than low-flow purging.	Criteria met.
Quantitative Performance Objectives			
Determine minimum equilibration times for RCDM samplers for perchlorate and explosives compounds.	Bench-scale test concentration data.	Minimum times to equilibration are determined. All compounds tested equilibrate in less than 4 weeks.	Criteria met.
Determine if RCDM samplers and low-flow purging recover similar concentrations of detected perchlorate and explosives compounds in field samples.	Concentrations of perchlorate and explosives compounds in samples collected by both RCDM samplers and low-flow purging.	No significant difference (at $p<0.05$) between chemical concentrations recovered by the RCDM sampler and low-flow purging.	Criteria met for perchlorate and four of six detected explosive compounds compared in field demonstration test wells.
Determine if RCDM samplers can collect low concentration samples.	Concentrations of perchlorate and explosives compounds in samples collected by both RCDM samplers and low-flow purging.	Concentrations within 2 to 5 times the reporting limit can be detected.	Criteria met.

Table 2. Performance objectives. (continued)

Performance Objective	Data Requirements	Success Criteria	Results
Determine reproducibility of RCDM and low-flow data.	Concentrations of perchlorate and explosives compounds collected by both RCDM samplers and low-flow purging.	Concentrations within +/-15% for perchlorate and +/-30% for explosives compounds.	Criteria met.
Determine if use of RCDM samplers reduces field sample collection time compared to low-flow purging.	Length of time to collect samples in the field with the RCDM sampler and with low-flow purging (including installation, sample collection, and equipment decontamination).	Length of field time required to sample with RCDM samplers should be at least 25% shorter than low-flow purging.	Criteria met.
Determine if use of RCDM samplers reduces field sample collection costs compared to low-flow purging.	Records of costs for equipment and supplies and record of personnel field time.	Cost savings using RCDM samplers should be at least 25% less than low-flow purging.	Criteria met.

RCDM = regenerated cellulose dialysis membrane
$p<0.05$ = 95 percent confidence level

5.0 SITE DESCRIPTION

5.1 SITE LOCATION

Field comparison demonstrations were done at two sites; APG, MD, and Picatinny Arsenal, NJ. These sites were chosen for the following reasons:

(1) The geology and hydrology of the sites were well characterized,

(2) The construction of wells installed at the sites were well documented and met recommended minimum standards (ITRC, 2004),

(3) The sites had existing water-quality analyses for perchlorate or the explosives compounds of interest to this project, and

(4) The groundwater at the sites had a range of concentrations of the compounds of interest.

APG is located on the Chesapeake Bay approximately 30 miles northeast of Baltimore, MD. Over the past 80 years, activities at this base have included research on nerve gas, explosives, munitions and their delivery systems. In one area near West Canal Creek, perchlorate was used in the manufacture and storage of mortar shells. Perchlorate was spilled and/or leaked in and around a number of buildings over the years and reached the shallow groundwater system. Figures 6 and 7 show the locations of the wells sampled for perchlorate in the field demonstration at APG, MD.

Picatinny Arsenal is located in north central New Jersey approximately 40 miles due west of New York City, NY. For more than a century, activities at this base have included research and production of munitions of all types. In one area near Picatinny Lake, explosives were tested and stored. Over the years, explosives compounds have been spilled or leaked around a few of the buildings and have entered the shallow groundwater system. Figure 8 shows the locations of wells sampled for explosives compounds in the field demonstration at Picatinny Arsenal, NJ.

5.2 SITE GEOLOGY/HYDROGEOLOGY

The wells sampled for the field demonstration at APG, are screened in a shallow unconsolidated sand-and-gravel aquifer in the coastal plain of Maryland (Figures 6 and 7). In the area of the wells shown on Figure 6, groundwater flows generally east to west toward a wetland area and Canal Creek within the base boundaries. In the area of the well shown on Figure 7, groundwater flows generally east toward Chesapeake Bay.

Picatinny Arsenal is located in the valley and ridge physiographic province of New Jersey. The base is located in a narrow elongated valley that extends from the northeast to the southwest. The wells sampled for the field demonstration at this site are screened in a shallow sand-and-gravel outwash aquifer surrounding Picatinny Lake (Figure 8). Groundwater generally flows from the west to east towards the lake in this area.

Figure 6. Wells sampled for perchlorate in the field demonstration at Aberdeen Proving Ground, MD.

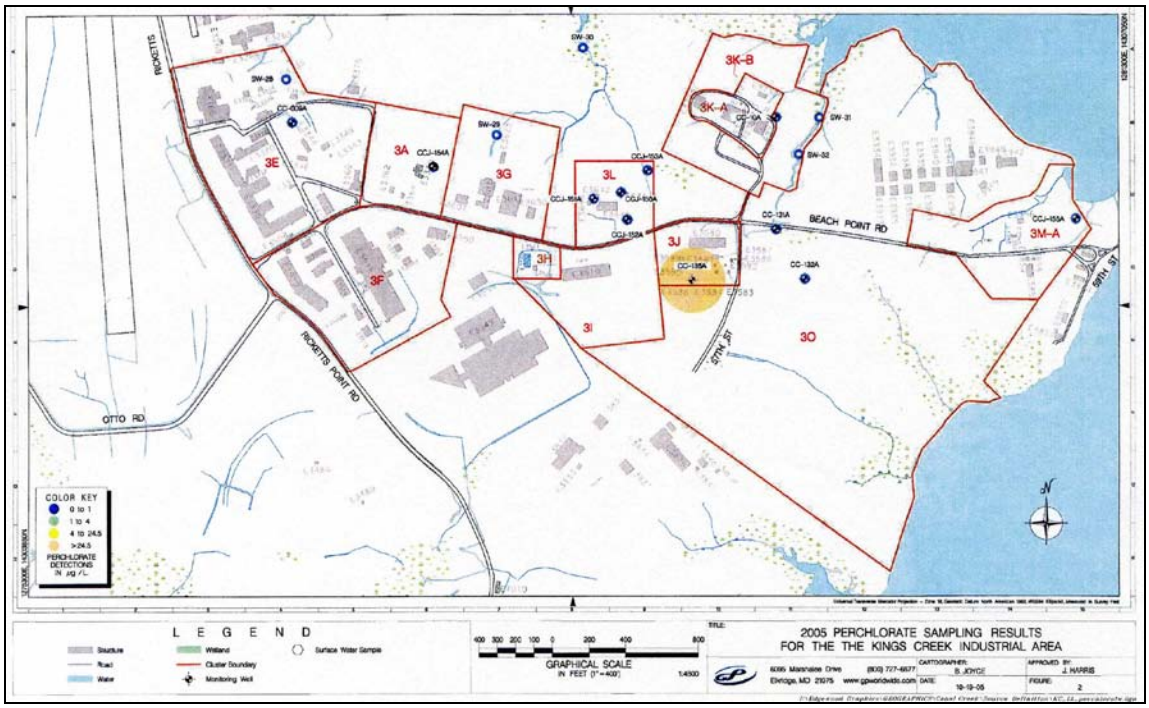

Figure 7. Additional well sampled for perchlorate as part of the field demonstration at Aberdeen Proving Ground, MD.

Figure 8. Wells sampled for explosives compounds as part of the field demonstration at Picatinny Arsenal, NJ.

5.3 CONTAMINANT DISTRIBUTIONS

The primary contaminants in the wells sampled at APG are perchlorate and chlorinated VOCs. The range of concentrations of these compounds is given in Table 3. The areal distribution of wells containing above detection concentrations of perchlorate from samples collected in 2005 are presented on Figures 6 and 7. The groundwater in these wells generally had detectable dissolved oxygen concentrations, pH's ranging from 4 to 6, and moderate to high ionic strength with total dissolved solids (TDS) concentrations ranging from 148 to 800 milligrams per liter (mg/L).

Table 3. List of sampled sites, chemical contaminants, and concentration ranges

Site	Chemical Contaminants	Concentration Ranges
Aberdeen Proving Ground, MD	Perchlorate, VOCs	Perchlorate <1-350 μg/L VOCs <1 – 1000 μg/L
Picatinny Arsenal, NJ	Explosives compounds	Explosives <1-1500 μg/L

μg/L = micrograms per liter

The main contaminants present in the wells sampled at Picatinny Arsenal are explosives compounds, primarily RDX and HMX. The range of concentrations of these compounds is also given in Table 3. The areal distribution of wells containing above detection concentrations of RDX is shown on Figure 9. The groundwater at the Picatinny Arsenal site generally had detectable dissolved oxygen concentrations, slightly acidic pH's ranging from 5 to 6, and moderate ionic strength with TDS concentrations ranging from 100 to 500 mg/L.

Figure 9. Areal and vertical extent of RDX contamination at Picatinny Arsenal, NJ.

6.0 TEST DESIGN

6.1 CONCEPTUAL EXPERIMENTAL DESIGN

The general conceptual design of these field demonstrations was as follows:

(1) RCDM samplers were constructed and deployed in 8 to 10 wells per site and allowed to equilibrate for at least the length of time necessary for equilibration in the bench-scale tests.

(2) Once equilibrated, the RCDM samplers were removed and samples were collected from them.

(3) A variable-speed low-flow pump was used to sample from the same depth as where the RCDM samplers had be positioned.

(4) Samples collected with both techniques were analyzed at the same laboratory for the appropriate compounds.

(5) Analytical results were compared graphically (using 1:1 correspondence plots) and statistically (using non-parametric analysis of variance testing) to determine if the two sampling techniques were significantly different in their ability to recover perchlorate or any of the explosives compounds present in the groundwater.

6.2 BASELINE CHARACTERIZATION

At APG the most recent perchlorate contamination data was collected two years prior to the sampling done on this project (General Physics Corporation, 2005). Eleven wells were sampled prior to the actual field demonstration to determine the current groundwater concentrations of perchlorate. Selected wells were also sampled to determine current VOC concentrations and background groundwater chemistry. A background well was pumped to collect the large volume sample used in the bench-scale testing for perchlorate.

At Picatinny Arsenal the latest explosives compounds data was collected less than six months prior to the sampling done on this project by another ESTCP funded project (ER-1425) (Paul Hatzinger, Shaw Environmental, Inc. written communication, 2008). Several other wells had been sampled less than four years prior to the sampling done on this project (Ted Gabel, Picatinny Arsenal, written communication, 2008). A background well was sampled to collect the large volume sample used in the bench-scale testing for explosives compounds.

6.3 LABORATORY BENCH-SCALE STUDY RESULTS

A significant portion of this project involved pre-demonstration testing to determine which chemical constituents would diffuse through the dialysis membrane and how long these chemicals would take to attain equilibrium with the groundwater. Additionally, the bench-scale work involved testing the effect of different water temperatures on equilibration times.

During the pre-demonstration portion of this project, background water samples from the chosen field sites were collected and brought back to the laboratory to conduct bench-scale equilibration

tests. Bench-scale equilibration tests were conducted to evaluate perchlorate and 14 explosives compounds (Table 4). During the bench-scale testing, RCDM samplers filled with deoxygenated deionized water were placed into containers of groundwater test solutions (background field samples that had been spiked with known concentrations of the chemicals being tested). Groundwater test solutions were stirred once per day for the duration of the testing to minimize any concentration stratification in the containers. After specified times (0, 1, 3, 7, 14, 21, or 28 days of equilibration), an RCDM sampler was removed and sampled. A sample of the groundwater test solution was also collected at the same time. Concentrations of chemicals inside the sampler were compared to concentrations of chemicals outside the sampler at each time step. Time to equilibrium was defined as the time needed for the concentration inside the RCDM sampler to be at least 95% of the concentration in the groundwater test solution outside the sampler. All tests were run at room temperature (21 EC) and at 10 EC in an incubator. This was done in an effort to approximately bracket groundwater temperatures across the continental United States. The equilibration times determined for the chemical constituents in the bench-scale tests were used to guide the time needed for the RCDM samplers to equilibrate in the wells during the field demonstration.

Table 4. Chemical constituents tested in bench-scale tests.

Bench-Scale Test 8 (9 mg/L; 21 °C and 10 °C)	
Perchlorate	
Bench-Scale Test 9 (20 μg/L; 21 °C and 10 °C)	
1,3,5-trinitrobenzene (TNB)	2,4,6-trinitrotoluene (TNT)
1,3-Dinitrobenzene	2,4-Dinitrotoluene
2-Amino-4,6-dinitrotoluene	2,6-Dinitrotoluene
4-Amino-2,6-dinitrotoluene	2-Nitrotoluene
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	3-Nitrotoluene
1,3,5-trinitroperhydro-1,3,5-triazine (RDX)	4-Nitrotoluene
N-methyl-*N*,2,4,6-tetranitroaniline (Tetryl)	Nitrobenzene

μg/L = micrograms per liter
mg/L = milligrams per liter
EC = degrees Celsius

Equilibrium was reached in all RCDM samplers within:

- 1 day for perchlorate at both the 10 EC and 21 EC temperatures.

Perchlorate was not detected in any of the blanks, indicating that there was no desorption of this anion from the dialysis membrane material. Coefficients of variation for triplicate perchlorate analyses of water from the RCDM sampler and the test solutions were <4%. Thus, perchlorate is an excellent candidate chemical to be sampled using RCDM samplers.

Equilibrium was reached in RCDM samplers within:

- 3 to 7 days for the 14 explosives compounds tested.

Twelve of the 14 explosives compound equilibrated within 3 days at both 10 EC and 21 EC. HMX and 4-Nitrotoluene took 7 days to equilibrate at the colder temperature versus the warmer

temperature. Trace concentrations of RDX and HMX were found in a few of the blanks. The authors believe that these trace concentrations were not the result of desorption from the dialysis membrane material, but instead most likely due to contamination of the equipment used to sample the test solutions in the bench-scale testing. Coefficients of variation of triplicate analyses from the RCDM samplers and test solutions for all 14 explosives compounds ranged between 5 and 16%. Based on the bench-scale results, all 14 explosives compounds tested were considered favorable candidate chemicals to be sampled using RCDM samplers. The findings of all bench-scale testing are summarized in Table 5.

Table 5. Summary of all bench-scale testing results: Suitability and equilibration times of all chemicals tested.

Favorable Bench-Scale Equilibration Testing Results	
Anions (1 day equilibration times at 21EC and 10EC)	
Perchlorate	
Explosives compounds (3-7 day equilibration times at 21EC and 10EC)	
1,3,5-trinitrobenzene	2,4,6-trinitrotoluene
1,3-Dinitrobenzene	2,4-Dinitrotoluene
2-Amino-4,6-dinitrotoluene	2,6-Dinitrotoluene
4-Amino-2,6-dinitrotoluene	2-Nitrotoluene
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	3-Nitrotoluene
1,3,5-trinitroperhydro-1,3,5-triazine	4-Nitrotoluene
N-methyl-*N*,2,4,6-tetranitroaniline	Nitrobenzene

6.4 FIELD TESTING

6.4.1 Field Demonstration Preparation and Mobilization

Access to and integrity of the wells to be sampled at each field demonstration site was checked one month prior to the start of the field comparison test at each site. RCDM samplers were constructed one week prior to the start of each field test. Low-flow purge pumps were cleaned and equipment blanks were collected prior to their use in the field tests. All other equipment needed to carry out the field demonstration at each site was assembled and checked out the week prior to each field comparison test. The site manager was contacted in advance of field tests to obtain drums and make arrangements for transport and treatment of any contaminated purge water collected.

6.4.2 Field Demonstration Sampling Events

Sampling periods at the two full demonstration sites are given in Table 6 below. The RCDM samplers were deployed in the test wells for about one week at the perchlorate field test site and for approximately two weeks at the explosives compounds field test site prior to the collection of samples. On the sample collection date, the RCDM samplers were removed from the test wells and sampled prior to the collection of samples by low-flow purging.

Table 6. Sampling periods at field demonstration sites.

Demonstration Site	RCDM Sampler Deployment Dates	RCDM Sample Collection Dates
Aberdeen Proving Ground, MD	April 15, 2008	April 22-24, 2008
Picatinny Arsenal, NJ	August 15, 2008	September 3-4, 2008

6.4.3 Field Demonstration Wells

The wells sampled during the field demonstrations are shown in Figures 6 through 9. Table 7 provides details about the wells sampled in the field demonstrations. Field sites, dates of sampling, well names, details of the well construction, water levels, and depths at which each sampler was used are given in this table.

Table 7. Wells sampled during the field demonstrations.

Site and Date	Well Name	Well Diameter (inches)	Casing Material	Total Depth (ft blse)	Open Interval Depth (ft blse)	Water Level (ft blse)	Sampling Technique	Sample Depth (ft blse)
Aberdeen Proving Ground, MD April 2008 Sampling for Perchlorate (Wells in Figures 6 and 7)	CC-016A	4	PVC	23	18-23	9.85	RCDM [a] Low-Flow	19.5-21.5 20.5
	CCJ-016B	4	PVC	37.5	32.5-37.5	9.09	RCDM RCDM-Dup Low Flow Low-Flow-Dup	34-36 34-36 35 35
	CCJ-017A	4	PVC	24.5	19.5-24.5	7.56	RCDM Low-Flow	21-23 22
	CC-017B	4	PVC	35	30-35	6.98	RCDM Low-Flow	31.5-33.5 32.5
	CC-018A	4	PVC	52	47-52	13.32	RCDM Low-Flow	48.5-50.5 49.5
	CC-021A	4	PVC	35	30-35	11.06	RCDM Low-Flow	31.5-33.5 32.5
	CCJ-030A	4	PVC	40	35-40	18.31	RCDM Low-Flow	36.5-38.5 37.5
	CCJ-110A	4	PVC	50	45-50	19.90	RCDM Low-Flow	46.5-48.5 47.5
	CCJ-111B	4	PVC	32.5	27.5-32.5	13.30	RCDM Low-Flow	29-31 30
	CC-118B	4	PVC	56	51-56	8.81	RCDM Low-Flow	52.5-54.5 53.5
	CC-135A	4	PVC	19	14-19	10.34	RCDM Low-Flow	15.5-17.5 16.5

Table 7. Wells sampled during the field demonstrations. (continued)

Site and Date	Well Name	Well Diameter (inches)	Casing Material	Total Depth (ft blse)	Open Interval Depth (ft blse)	Water Level (ft blse)	Sampling Technique	Sample Depth (ft blse)
Picatinny Arsenal, NJ September 2008 Explosives Compounds Sampled (Wells in Figures 8 and 9)	40MW1	4	PVC	36	24-34	11.00	RCDM [b] RCDM-Dup Low-Flow Low-Flow-Dup	27-29 29-31 28 30
	40MW2	4	PVC	36.2	25-35	11.07	RCDM RCDM-Dup Low-Flow Low-Flow-Dup	29-31 31-33 30 32
	40MW3	4	PVC	36.2	26.5-36.5	2.56	RCDM Low-Flow	30-32 31
	40MW6	2	PVC	33.6	24-34	12.62	RCDM[c] Low-Flow	27-33 30
	157MW1	4	PVC	35.7	24-34	6.98	RCDM Low-Flow	30-32 31
	157MW2	4	PVC	35.1	25.8-35.8	6.09	RCDM Low-Flow	29-31 30
	157MW3	4	PVC	35.7	26.5-36.5	6.40	RCDM RCDM-Dup Low-Flow Low-Flow-Dup	29-31 31-33 30 32
	157MW8D	2	PVC	50.9	35-50	5.04	RCDM Low-Flow	38-43 41

[a] One 2-ft long 1.75-inch diameter RCDM sampler was equilibrated per 4-inch diameter well to sample for perchlorate. If a duplicate sample is indicated, two RCDM samplers were suspended side-by-side.
[b] One 2-ft long 3.5-inch diameter RCDM sampler was equilibrated per 4-inch diameter well to sample for explosives compounds. If a duplicate sample is indicated two RCDM samplers were suspended vertically as close as possible.
[c] Two 2-ft long 1.75-inch diameter RCDM samplers were stacked vertically to collect a sufficient volume of water for the explosives analysis in 2-inch diameter wells.

ft blse = feet below land surface elevation
PVC = polyvinyl chloride
RCDM = regenerated cellulose dialysis membrane diffusion sampler
Low-Flow = low-flow purging
Dup = duplicate

6.4.4 Residuals Handling

Essentially all of the water contained in the RCDM samplers was captured in filling sample containers and sent to the laboratory for analysis. The only residual wastewater produced during RCDM sampling was the few milliliters of water used to rinse each sample container. The empty RCDM samplers were properly disposed of at each site.

Low-flow pumping did produce purge water that had to be drummed and disposed of properly at each site. The volume of purge water collected varied from well to well but was on average about 10 gallons per well. All procedures for proper disposal of purge water were followed.

6.5 SAMPLING METHODS

6.5.1 Sampler Deployment

RCDM samplers were deployed in the open interval of wells at depths of highest mass flux of the primary chemicals of concern at each site. Depths were chosen based on knowledge of the well construction, and water-chemistry results from previous sampling at each site and the pre-demonstration plan sampling. Duplicate samplers were deployed side by side where the diameter of the well allowed (1.75-inch samplers in 4-inch APG wells). Where the diameter of the well did not allow this, duplicate samplers were deployed as close as possible to one another vertically (3.5-inch samplers in 4-inch Picatinny Arsenal wells or 1.75-inch samplers in 2-inch Picatinny Arsenal wells). The variable-speed low-flow purge pump intake was positioned at a depth that corresponded with approximately the center of the RCDM sampler in each well to try and sample the same zone in the well.

6.5.2 Sample Frequency

Comparison field samples were collected once from wells at the APG site and once from the wells at the Picatinny Arsenal site during the course of the field demonstrations. The dates each site was sampled are given in Table 6.

6.5.3 Tested Chemical Constituents

Comparison field samples were collected from each well at the APG site and analyzed for perchlorate only. Comparison field samples were collected from each well at the Picatinny Arsenal site and analyzed for the list of explosives compounds shown in Table 8. Basically this was the same list of nitroamines and nitroaromatics analyzed in the bench-scale testing, with the addition of pentaerythritol tetranitrate (PETN) and nitroglycerin. The latter two chemical constituents were not tested for equilibration times in the bench-scale tests, but were measured in the field samples because they were on the same analytical scan as all the other explosives compounds. The complete list of sampled chemical constituents and their minimum detection limits is given in Table 8.

Table 8. Chemical constituents analyzed in samples from the field demonstrations.

Anions (MDL=0.009 μg/L)	
Perchlorate	
Explosives compounds (MDLs=0.05-0.92 μg/L)	
1,3,5-trinitrobenzene	2,4,6-trinitrotoluene
1,3-Dinitrobenzene	2,4-Dinitrotoluene
2-Amino-4,6-dinitrotoluene	2,6-Dinitrotoluene
4-Amino-2,6-dinitrotoluene	2-Nitrotoluene
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	3-Nitrotoluene
1,3,5-trinitroperhydro-1,3,5-triazine	4-Nitrotoluene
N-methyl-*N*,2,4,6-tetranitroaniline	Nitrobenzene
Pentaerythritol tetranitrate	Nitroglycerin

MDL = minimum detection limit
μg/L = micrograms per liter
mg/L = milligrams per liter

6.5.4 Sample Collection

The RCDM samplers were allowed to equilibrate for at least one week when collecting samples for perchlorate. The RCDM samplers were allowed to equilibrate for at least two weeks when collecting samples for explosives compounds. These equilibration times were actually longer than those determined during the bench-scale testing, partially as a safety factor to make sure that chemical equilibrium was reached and partially to allow the well enough time to re-establish hydraulic equilibrium with the aquifer.

After the equilibration period, field comparison sampling was conducted at each site. All necessary equipment was assembled at the field site. A dry run was conducted to insure that all equipment and supplies were present and performing as expected before proceeding with the demonstration.

After initial water levels were taken, the RCDM sampler was retrieved from each well and samples were collected immediately in appropriate containers (Figure 10). All samples were collected and preserved according to standard sampling protocols. All sample bottles were placed in a cooler on ice for transport back to the office.

Figure 10. Removal of diffusion sampler from a well prior to sampling.

Following removal of the RDCM sampler, low-flow purging was initiated. Teflon-lined polyethylene intake tubing attached to a variable-speed low-flow peristaltic pump was lowered into the well and centered at the depth at which the RCDM sampler was suspended during its equilibration. Low-flow purging at 500 to 1000 mL/min was conducted as per the USEPA and USGS protocols (Puls and Barcelona, 1996; Wilde et al., 1998) and field parameters (temperature, pH, specific conductance, dissolved oxygen, and turbidity) were monitored until stability was reached using a multi-parameter instrument (YSI 6920) in a flow-through cell at the surface (Figure 11). Field parameters were considered stabilized when three successive readings

taken five minutes apart were within +/-0.1 EC for temperature, +/-0.1 units for pH, +/-5% for conductance in micro-Siemens per centimeter (µS/cm), <10 NTU or +/-5 NTU if above 10 NTU for turbidity, and +/-0.1 mg/L for dissolved oxygen. After reaching stabilization of field parameters, samples were collected from the discharge line of the low-flow peristaltic pump. All samples were collected in appropriate sample containers and preserved according to standard sampling protocols. Samples were placed in a cooler on ice for transport back to the office.

Eleven wells were sampled during the field demonstration for perchlorate. All 11 wells contained detectable concentrations of perchlorate. Eight wells were sampled during the field demonstration for explosives compounds. However, because detectable and quantifiable concentrations of most explosives compounds were not present in all wells sampled, fewer comparisons of these constituents could be made overall. All wells sampled in this study are noted in Table 7.

Figure 11. Low-flow purging set up for a 4-inch diameter well.
(A peristaltic pump is being used to purge, a multiparameter field sonde is being used to monitor the stability of field parameters in a flow cell, and an electric tape is being used to monitor drawdown.)

6.5.5 Sample Preservation

For perchlorate and explosives compounds analyses, all low-flow samples were filtered through 0.45 micron (µm) pore-diameter polyethersulfone in-line capsule filters and chilled to 4 EC for preservation. RCDM samples were not filtered through 0.45 µm filters because dialysis membranes are in and of themselves filters that have 18 Å pores. All RCDM samples were chilled to 4 EC for preservation.

6.5.6 Summary of Samples Collected

A summary of the total number and types of samples collected during both the pre-demonstration phase and the field demonstration phase of this project is given in Table 9.

Table 9. Total number and types of samples collected during project.

Component	Matrix	Number of Samples	Analytes	Location
Pre-demonstration sampling	Groundwater	12	Perchlorate, field parameters[1]	11 wells at Aberdeen Proving Ground, MD
	Groundwater	1	Explosives compounds[2], field parameters	1 well at Picatinny Arsenal, NJ
Technology performance sampling	Groundwater	11	Perchlorate, field parameters	10 wells at Aberdeen Proving Ground, MD
	Groundwater	11	Explosives compounds, field parameters	8 wells at Picatinny Arsenal, NJ

[1] Field parameters include temperature, specific conductance, dissolved oxygen, pH, and turbidity.
[2] Explosives compounds include all compounds listed in Table 8.

6.5.7 Demobilization

At each field comparison site, demobilization involved collecting the field equipment (i.e., pumps, multi-parameter meter, sonde, batteries, etc.), and returning it to the USGS office in West Trenton, NJ. Field equipment was checked and repairs were made as needed.

6.5.8 Additional Sampling Methods Information

Information on the calibration of analytical instrumentation, quality assurance/quality control sampling, field equipment decontamination procedures, and sample documentation procedures used in the field demonstrations are given in Appendix A.

6.6 SAMPLING RESULTS

6.6.1 Perchlorate Sampling Results from Field Demonstration at Aberdeen Proving Ground, MD

Table 10 provides a comparison of perchlorate sampling results from RCDM samplers and low-flow purging used during the APG field demonstration.

Table 10. Results from perchlorate field demonstration sampling

Well	Sample Date	Sample Time	Perchlorate (μg/L)
CC016A-RCDM	4/22/08	1535	<0.009
CC016A-LF	4/22/08	1635	<0.009
CCJ016B-RCDM	4/22/10	1700	23.0
CCJ016B-LF	4/22/08	1800	27.0
CCJ016B-RCDM-DUP	4/22/10	1705	22.0
CCJ016B-LF-DUP	4/22/08	1805	25.0
CCJ017A-RCDM	4/22/08	1330	7.3
CCJ017A-LF	4/22/08	1415	8.2
CC017B-RCDM	4/22/08	1430	2.9
CC017B-LF	4/22/08	1510	2.9
CC018A-RCDM	4/23/08	1320	2.6
CC018A-LF	4/23/08	1410	2.6
CC021A-RCDM	4/22/08	1825	41.0
CC021A-LF	4/22/08	1910	41.0
CCJ030A-RCDM	4/23/08	1635	9.2
CCJ030A-LF	4/23/08	1725	9.2
CCJ110A-RCDM	4/23/08	1540	24.0
CCJ110A-LF	4/23/08	1620	24.0
CCJ111B-RCDM	4/22/08	1045	16.0
CCJ111B-LF	4/22/08	1230	15.0
CC118B-RCDM	4/23/08	1435	20.0
CC118B-LF	4/23/08	1510	19.0
CC135A-RCDM	4/23/08	1215	170.0
CC135A-LF	4/23/08	1255	170.0
FLDBLK-RCDM	4/23/08	2200	<0.009
FLDBLK-LF	4/23/08	2245	<0.009

RCDM = regenerated cellulose dialysis membrane
LF = low-flow purging
FLDBLK = field equipment wash blank
μg/L = micrograms per liter

Perchlorate was detected in 10 of 11 wells sampled at the APG site. The concentrations ranged over approximately four orders of magnitude, from <0.009 to 170 μg/L.

6.6.2 Explosives Compounds Sampling Results from Field Demonstration at Picatinny Arsenal, NJ

Table 11 provides a comparison of RCDM samplers and low-flow purging used during the Picatinny Arsenal field demonstration.

Table 11. Results from explosives compounds field demonstration sampling.

Well	Sample Date	Sample Time	2-Amino-4,6-dinitro toluene (µg/L)	4-Amino-2,6-dinitro toluene (µg/L)	1,3-Dinitro benzene (µg/L)	2,4-Dinitro toluene (µg/L)
40MW1-RCDM	9/4/08	1120	4.95	7.40	<0.089	<0.084
40MW1-LF	9/4/08	1205	0.47	0.97	<0.089	<0.084
40MW1-RCDM-DUP	9/4/08	1125	4.95	7.40	<0.089	<0.084
40MW1-LF-DUP	9/4/08	1235	0.53	1.10	<0.089	<0.084
40MW2-RCDM	9/4/08	1345	35.00	33.50	<0.440	<0.420
40MW2-LF	9/4/08	1425	8.75	9.85	<0.440	<0.420
40MW2-RCDM-DUP	9/4/08	1350	33.00	33.50	<0.440	<0.420
40MW2-LF-DUP	9/4/08	1455	7.00	8.40	<0.440	<0.420
40MW3-RCDM	9/4/08	1515	4.50	8.55	<0.089	<0.084
40MW3-LF	9/4/08	1600	0.62	1.45	<0.089	<0.084
40MW6-RCDM	9/4/08	1230	4.00	4.55	<0.089	<0.084
40MW6-LF	9/4/08	1315	0.13	<0.058	<0.089	<0.084
157MW1-RCDM	9/3/08	1715	2.50	3.00	0.19 J COL	0.12 J COL
157MW1-LF	9/3/08	1810	0.079 J	0.071 J	<0.089	<0.084
157MW2-RCDM	9/4/08	1000	0.89	2.00	<0.180	<0.170
157MW2-LF	9/4/08	1050	<0.051	1.01	<0.089	<0.084
157MW3-RCDM	9/3/08	1535	14.00	11.00	<0.440	0.6 J COL
157MW3-LF	9/3/08	1630	0.63	<0.058	<0.089	<0.084
157MW3-RCDM-DUP	9/3/08	1540	15.00	11.00	<0.440	0.63 J COL
157MW3-LF-DUP	9/3/08	1700	0.54	<0.058	<0.089	<0.084
157MW8D-RCDM	9/3/08	1420	20.00	20.00	0.57	1.20
157MW8D-LF	9/3/08	1510	1.40	1.70	<0.180	<0.170
FLDBLK-RCDM	9/5/08	1045	<0.051	<0.058	<0.089	<0.084
FLDBLK-LF	9/5/08	1100	<0.051	0.080 J	<0.089	<0.084

RCDM = regenerated cellulose dialysis membrane
LF = low-flow purging
FLDBLK = field equipment blank
µg/L = micrograms per liter
J = above detection but below reporting limit
COL = more than 40% difference between primary and confirmation detector results with the lower of the two results reported

Table 11. Results from explosives compounds field demonstration sampling. (continued)

Well	Sample Date	Sample Time	2,6-Dinitro toluene (μg/L)	HMX (μg/L)	Nitro benzene (μg/L)	Nitro glycerin (μg/L)
40MW1-RCDM	9/4/08	1120	<0.064	2.85	<0.091	<0.92
40MW1-LF	9/4/08	1205	<0.064	5.90	<0.091	<0.92
40MW1-RCDM-DUP	9/4/08	1125	<0.064	2.90	<0.091	<0.92
40MW1-LF-DUP	9/4/08	1235	<0.064	8.55	<0.091	<0.92
40MW2-RCDM	9/4/08	1345	<0.320	14.00	<0.460	<4.60
40MW2-LF	9/4/08	1425	<0.320	11.50	<0.460	<4.60
40MW2-RCDM-DUP	9/4/08	1350	<0.320	14.00	<0.460	<4.60
40MW2-LF-DUP	9/4/08	1455	<0.320	11.50	<0.460	<4.60
40MW3-RCDM	9/4/08	1515	0.43	3.70	<0.091	<0.92
40MW3-LF	9/4/08	1600	0.19	2.45	<0.091	<0.92
40MW6-RCDM	9/4/08	1230	<0.064	4.95	<0.091	<0.92
40MW6-LF	9/4/08	1315	<0.064	4.90	<0.091	<0.92
157MW1-RCDM	9/3/08	1715	<0.064	8.00	<0.091	<0.92
157MW1-LF	9/3/08	1810	<0.064	4.20	<0.091	<0.92
157MW2-RCDM	9/4/08	1000	<0.130	2.35	<0.180	<1.80
157MW2-LF	9/4/08	1050	<0.064	1.15	<0.091	<0.92
157MW3-RCDM	9/3/08	1535	<0.320	4.70	<0.460	<4.60
157MW3-LF	9/3/08	1630	<0.064	1.90	<0.091	<0.92
157MW3-RCDM-DUP	9/3/08	1540	<0.320	4.60	<0.460	<4.60
157MW3-LF-DUP	9/3/08	1700	<0.064	1.90	<0.091	<0.92
157MW8D-RCDM	9/3/08	1420	<0.130	29.00	<0.180	<1.80
157MW8D-LF	9/3/08	1510	<0.130	20.00	<0.180	<1.80
FLDBLK-RCDM	9/5/08	1045	<0.064	<0.088	<0.091	<0.92
FLDBLK-LF	9/5/08	1100	<0.064	0.167 J COL	0.091	<0.92

RCDM = regenerated cellulose dialysis membrane
LF = low-flow purging
FLDBLK = field equipment blank
μg/L = micrograms per liter
J = above detection but below reporting limit
COL = more than 40% difference between primary and confirmation detector results with the lower of the two results reported

Table 11. Results from explosives compounds field demonstration sampling. (continued)

Well	Sample Date	Sample Time	2-Nitro toluene (μg/L)	3-Nitro toluene (μg/L)	4-Nitro toluene (μg/L)	PETN (μg/L)
40MW1-RCDM	9/4/08	1120	<0.086	<0.083	<0.20	<0.42
40MW1-LF	9/4/08	1205	<0.086	<0.083	<0.20	<0.42
40MW1-RCDM-DUP	9/4/08	1125	<0.086	<0.083	<0.20	<0.42
40MW1-LF-DUP	9/4/08	1235	<0.086	<0.083	<0.20	<0.42
40MW2-RCDM	9/4/08	1345	<0.430	<0.420	<1.00	<2.10
40MW2-LF	9/4/08	1425	<0.430	<0.420	<1.00	<2.10
40MW2-RCDM-DUP	9/4/08	1350	<0.430	<0.420	<1.00	<2.10
40MW2-LF-DUP	9/4/08	1455	<0.430	<0.420	<1.00	<2.10
40MW3-RCDM	9/4/08	1515	<0.086	<0.083	<0.20	<0.42
40MW3-LF	9/4/08	1600	<0.086	<0.083	<0.20	<0.42
40MW6-RCDM	9/4/08	1230	<0.086	<0.083	<0.20	<0.42
40MW6-LF	9/4/08	1315	<0.086	<0.083	<0.20	<0.42
157MW1-RCDM	9/3/08	1715	<0.086	<0.083	<0.20	<0.42
157MW1-LF	9/3/08	1810	<0.086	<0.083	<0.20	<0.42
157MW2-RCDM	9/4/08	1000	<0.170	<0.170	<0.40	<0.83
157MW2-LF	9/4/08	1050	<0.086	<0.083	<0.20	<0.42
157MW3-RCDM	9/3/08	1535	<0.430	<0.420	<1.00	<2.10
157MW3-LF	9/3/08	1630	<0.086	<0.420	<0.20	<0.42
157MW3-RCDM-DUP	9/3/08	1540	<0.430	<0.083	<1.00	<2.10
157MW3-LF-DUP	9/3/08	1700	<0.086	<0.170	<0.20	<0.42
157MW8D-RCDM	9/3/08	1420	<0.170	<0.170	<0.40	<0.83
157MW8D-LF	9/3/08	1510	<0.170	<0.083	<0.40	<0.83
FLDBLK-RCDM	9/5/08	1045	<0.086	<0.083	<0.20	<0.42
FLDBLK-LF	9/5/08	1100	<0.086	<0.420	<0.20	<0.42

RCDM = regenerated cellulose dialysis membrane
LF = low-flow purging
FLDBLK = field equipment blank
μg/L = micrograms per liter
J = above detection but below reporting limit
COL = more than 40% difference between primary and confirmation detector results with the lower of the two results reported

Table 11. Results from explosives compounds field demonstration sampling. (continued)

Well	Sample Date	Sample Time	RDX (μg/L)	Tetryl (μg/L)	1,3,5-Trinitro benzene (μg/L)	2,4,6-Trinitro toluene (μg/L)
40MW1-RCDM	9/4/08	1120	3.10	<0.079	<0.20	1.30
40MW1-LF	9/4/08	1205	8.10	<0.079	0.83 J	1.80
40MW1-RCDM-DUP	9/4/08	1125	3.20	<0.079	<0.20	1.20
40MW1-LF-DUP	9/4/08	1235	17.50	<0.079	1.00	2.20
40MW2-RCDM	9/4/08	1345	41.50	<0.400	4.35 J	62.00
40MW2-LF	9/4/08	1425	48.00	<0.400	4.80 J	46.00
40MW2-RCDM-DUP	9/4/08	1350	44.50	<0.400	3.15 J	54.50
40MW2-LF-DUP	9/4/08	1455	55.00	<0.400	4.35 J	40.00
40MW3-RCDM	9/4/08	1515	11.50	<0.079	<0.20	12.50
40MW3-LF	9/4/08	1600	11.00	<0.079	0.35 J	9.65
40MW6-RCDM	9/4/08	1230	3.90	<0.079	0.34 J	1.75
40MW6-LF	9/4/08	1315	11.00	<0.079	1.00	1.00
157MW1-RCDM	9/3/08	1715	24.00	<0.079	1.10	<0.072
157MW1-LF	9/3/08	1810	21.00	<0.079	4.20	<0.072
157MW2-RCDM	9/4/08	1000	29.50	<0.160	<0.40	<0.140
157MW2-LF	9/4/08	1050	25.50	<0.079	<0.20	<0.072
157MW3-RCDM	9/3/08	1535	5.60	<0.400	5.20	47.00
157MW3-LF	9/3/08	1630	5.00	<0.079	4.40	21.00
157MW3-RCDM-DUP	9/3/08	1540	6.20	<0.400	4.80 J	49.00
157MW3-LF-DUP	9/3/08	1700	4.90	<0.079	4.30	18.00
157MW8D-RCDM	9/3/08	1420	31.00	<0.160	38.00	12.00
157MW8D-LF	9/3/08	1510	23.00	<0.160	42.00	4.10
FLDBLK-RCDM	9/5/08	1045	0.57 COL	<0.079	<0.20	<0.072
FLDBLK-LF	9/5/08	1100	0.84	<0.079	<0.20	<0.072

RCDM = regenerated cellulose dialysis membrane
LF = low-flow purging
FLDBLK = field equipment blank
μg/L = micrograms per liter
J = above detection but below reporting limit
COL = more than 40% difference between primary and confirmation detector results with the lower of the two results reported

Explosives compounds were detected in all eight of the wells sampled at the Picatinny Arsenal site. While detection limits varied from compound to compound, concentrations typically ranged over two to three orders of magnitude, from <0.05 to 55 μg/L.

6.6.3 Quality Assurance/Quality Control Sample Results

Equipment Wash Blanks

During the field demonstration at APG, one wash blank was collected from the low-flow peristaltic purge pump and one was collected from an RCDM sampler. Both were submitted for analysis of perchlorate. Perchlorate concentrations were found to be below detection (<0.009 μg/L) in both samples (Table 10).

During the field demonstration at Picatinny Arsenal one wash blank was collected from the low-flow peristaltic pump and one was collected from an RCDM sampler. Both were submitted for

analysis of the 16 explosives compounds. No explosives compounds were detected in the RCDM blank except trace amounts of RDX (<0.6 μg/L) (Table 11). The reason for this is not clear. It is possible that the deionized water used to fill the dialysis membranes was slightly contaminated in the lab, but this seems unlikely since most of the bench-scale test blanks were below detection limits for this compound. No explosives compounds were detected in the low-flow purging blank except trace amounts of RDX (<1.0 μg/L), HMX (<0.17 μg/L), and 4-amino-2,4-dintrotoluene (<0.08 μg/L) (Table 11). The latter two compounds were above their detection limits, but below their reporting limits. Again, it is possible that the laboratory deionized water used in the low-flow blank was somehow slightly contaminated with these compounds. It is also possible that the low-flow pump head tubing was not flushed sufficiently after sampling a well containing these explosives compounds. Use of a clean length of pump head tubing is recommended prior to each well.

Duplicate Samples

One set of duplicate samples was collected with both the RCDM sampler and the low-flow purge pump at the APG site for perchlorate. The coefficient of variation of the RCDM sampler duplicates was <4% and the low-flow purge pump duplicates was <6%.

Three sets of duplicate samples were collected with both sampling techniques at Picatinny Arsenal for explosives compounds. Seven different explosive compounds were detected in the duplicate samples. The average coefficient of variation for duplicate RCDM samplers for these compounds was <5%. The average coefficient of variation for duplicate low-flow samples for these compounds was <12%.

The lower coefficients of variation for the RCDM sampler at both sites indicate that these diffusion samplers collect slightly more reproducible samples than low-flow purging. However, all of the observed sampling variations were well within acceptable sampling guidelines.

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7.0 PERFORMANCE ASSESSMENT

The effectiveness of these demonstration studies was qualitatively and quantitatively evaluated by comparing the perchlorate and explosives compounds chemical data collected using the RCDM sampler against data collected from low-flow purging. Graphical comparisons of the data were done using 1:1 plots and statistical comparisons of the data were done using the Wilcoxon signed-rank test. An evaluation of whether the performance objectives of the field demonstration were met is discussed as well as deployment considerations for use of RCDM samplers for the detected compounds.

7.1 EVALUATION OF FIELD COMPARISON RESULTS FOR PERCHLORATE

7.1.1 Graphical Analysis of Perchlorate Results

The results for perchlorate concentrations found above detection limits during the APG field demonstration were evaluated graphically by constructing a 1:1 correspondence plot. The concentration of perchlorate obtained with the RCDM sampler in a well was plotted versus the concentration obtained with low-flow purging in the same well. This correspondence plot is given below.

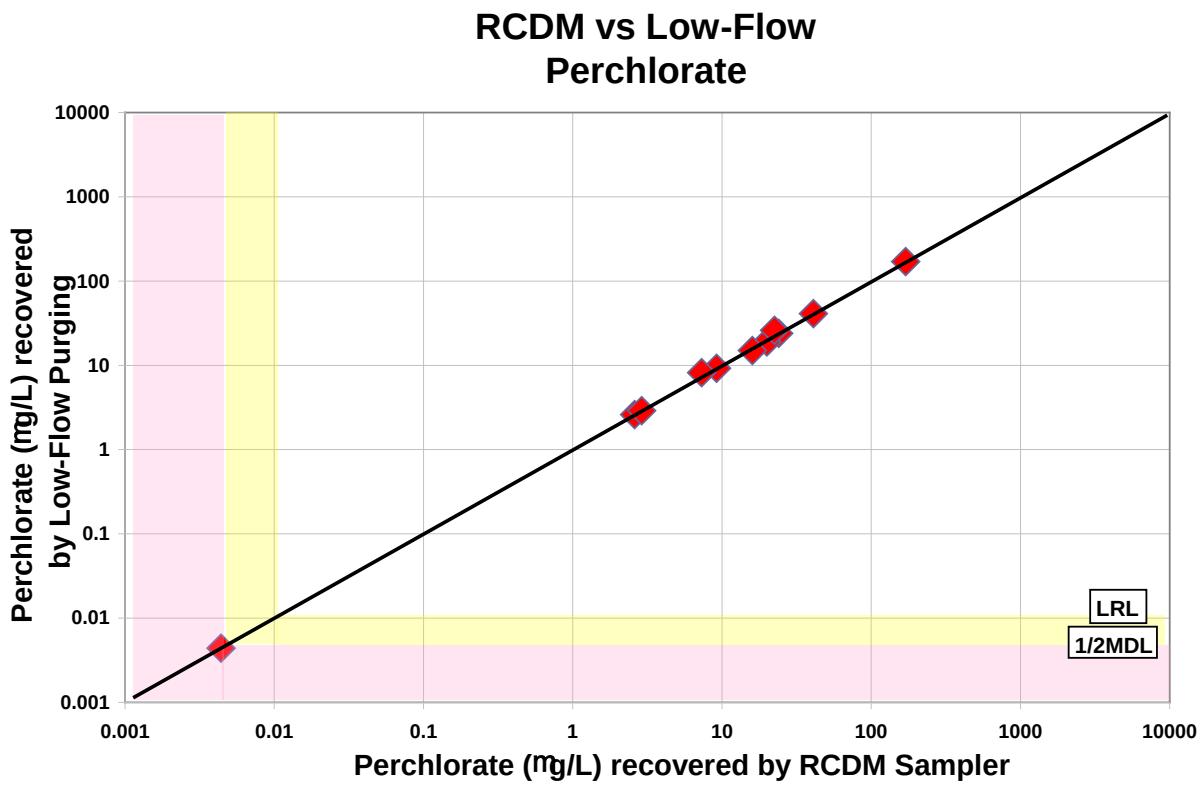

Figure 12. RCDM sampler versus low-flow purging results for perchlorate.

The plot of RCDM sampler versus low-flow purging results (Figure 12) shows excellent agreement between concentrations obtained using both sampling techniques starting at the detection limit and going up over four orders of magnitude in concentration. The data points were closely grouped on or near the 1:1 correspondence line. These results confirmed that the two sampling techniques collected nearly identical samples from wells in the field demonstration.

7.1.2 Statistical Comparison of Perchlorate Results

7.1.2.1 Correlation Analysis of Perchlorate

Pearson's correlation coefficient (r) was calculated by running a least-squares regression for all field comparison results between the RCDM sampler and low-flow purging for perchlorate (SPLUS, 2002). The results are provided in Table 12. The correlation between concentrations sampled with the RCDM sampler and concentrations sampled with low-flow purging was strongly positive (0.99). The high correlation value indicates that the data collected by different sampling techniques were closely and consistently matched.

Table 12. Correlation of sampling techniques for perchlorate.

Compound	n	RCDM vs. Low-Flow Purging	
		r	LSRE
Perchlorate	10	0.99	y=0.99x+0.24

RCDM = regenerated cellulose dialysis membrane
vs. = versus
n = number of comparisons correlated
r = Pearson's correlation coefficient
LSRE = least-squares regression equation

The least-squares regression equation listed in Table 12 can also be used as another indicator of how well the two distributions being compared match. If the two distributions match exactly, the slope would be 1 and the intercept should be 0. The regression slope and intercept for the perchlorate data indicates excellent agreement between RCDM samplers and low-flow purging.

7.1.2.2 Normality Testing for Perchlorate Results

The perchlorate concentration data from all 10 wells sampled in the field comparison study were tested to determine if the data distributions were normal distributions. This was accomplished by a univariate analysis that included the construction of box plots and the application of the Kolmogorov-Smirnov goodness-of-fit test (S-PLUS, 2002). Wells where at least one sampling technique had a value above detection were included in this analysis. A Kolmogorov-Smirnov test statistic of 0.05 or less indicated that the data distribution was significantly different from the normal distribution. The perchlorate data were not normally distributed. Because the perchlorate results were not normally distributed, non-parametric statistical testing of the data was conducted. Non-parametric statistics do not require normal data distributions.

7.1.2.3 Wilcoxon Signed-Rank Test on Perchlorate

Perchlorate concentration data collected with the two different sampling techniques were compared using a non-parametric Wilcoxon signed-rank test. The results of the testing are given in Table 13 below. No significant difference was found between samples collected with the RCDM sampler and low-flow purging. These results indicate that RCDM samplers were able to collect perchlorate as accurately as low-flow purging over a range of concentrations.

Table 13. Statistical comparison of perchlorate concentrations by the RCDM sampler and low-flow purging using the Wilcoxon signed-rank test.

Constituents where no significant difference was found between samples collected with the RCDM sampler and low-flow purging (at $p<0.05$; the 95% confidence level)
Perchlorate (10)[1]

[1] Number of comparisons above the minimum detection limit.

7.1.2.4 Concentration Range Measured for Perchlorate

Because it is useful to know the concentration ranges over which RCDM samplers can function, the concentration range for detected perchlorate measured by the RCDM samplers in this demonstration study is given in Table 14. Because the wells sampled in this study were not contaminated over a wide range of concentrations, the full concentration range of use for RCDM samplers is most likely larger than that shown in Table 14.

Table 14. Ranges of concentrations measured using RCDM samplers for perchlorate.

Constituent Detected	Concentration Range Measured		Units
	Low	High	
Perchlorate	2.6	170	µg/L

µg/L = micrograms per liter

7.2 EVALUATION OF FIELD COMPARISON RESULTS FOR EXPLOSIVES COMPOUNDS

7.2.1 Graphical Analysis of Explosives Compounds

Results for the six explosives compounds found at above detection-limit concentrations greater than four times during the field comparison portion of the study were evaluated graphically using 1:1 correspondence plots. Up to 11 comparisons were plotted on each graph if the explosive compound was found in all eight wells and three duplicate samples. Ideally, if both the RCDM sampler and low-flow purging collected an explosive compound equally, all points from the field comparison sampling (red symbols) would fall on the 1:1 correspondence line. However, because sampling and analytical variations did occur, the data points for most explosives compounds were scattered around the line. The closer the scatter in the data points was to the 1:1 line, the more comparable the data produced by the two sampling techniques. Plots for all constituents included in this group are given in Figures 13 thru 18.

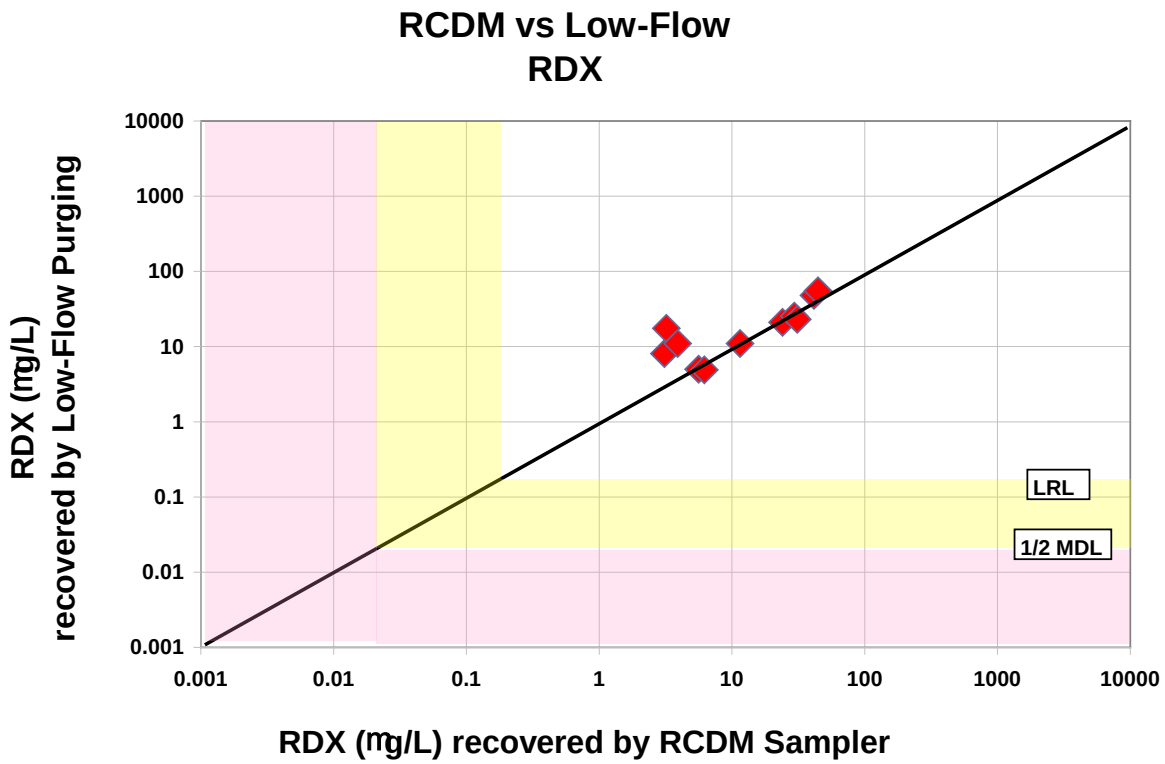

Figure 13. RCDM sampler versus low-flow purging results for RDX.

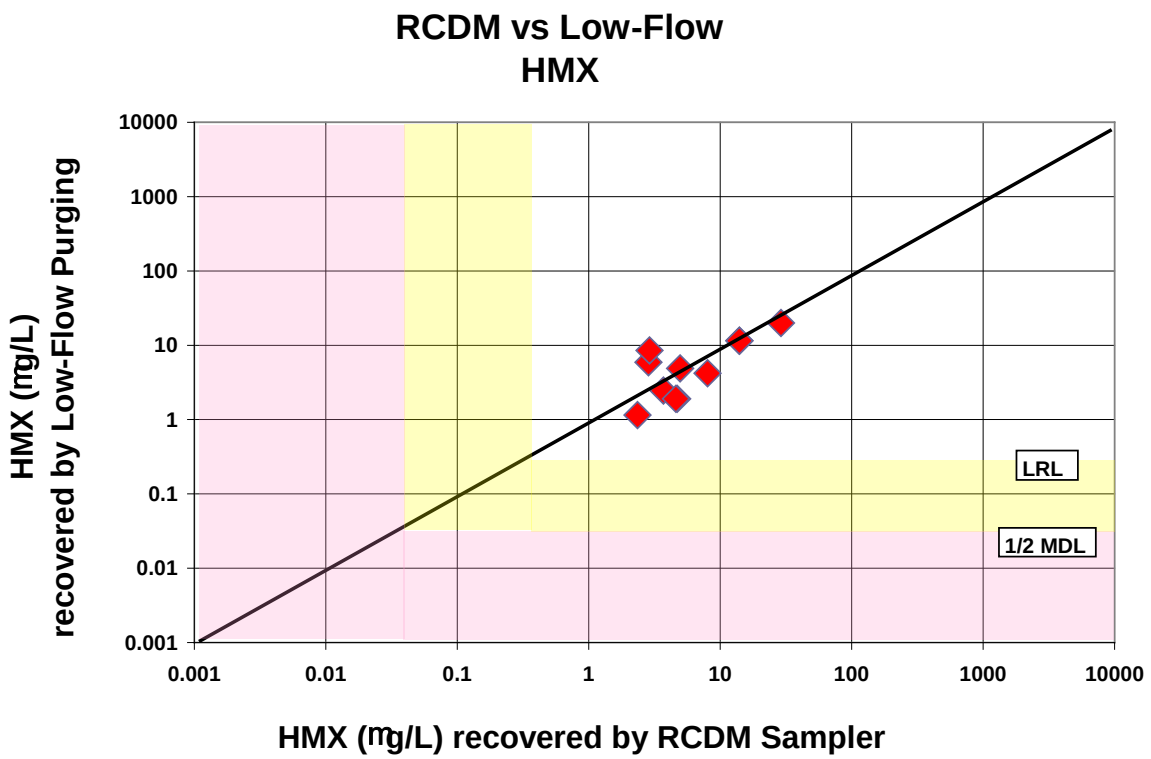

Figure 14. RCDM sampler versus low-flow purging results for HMX.

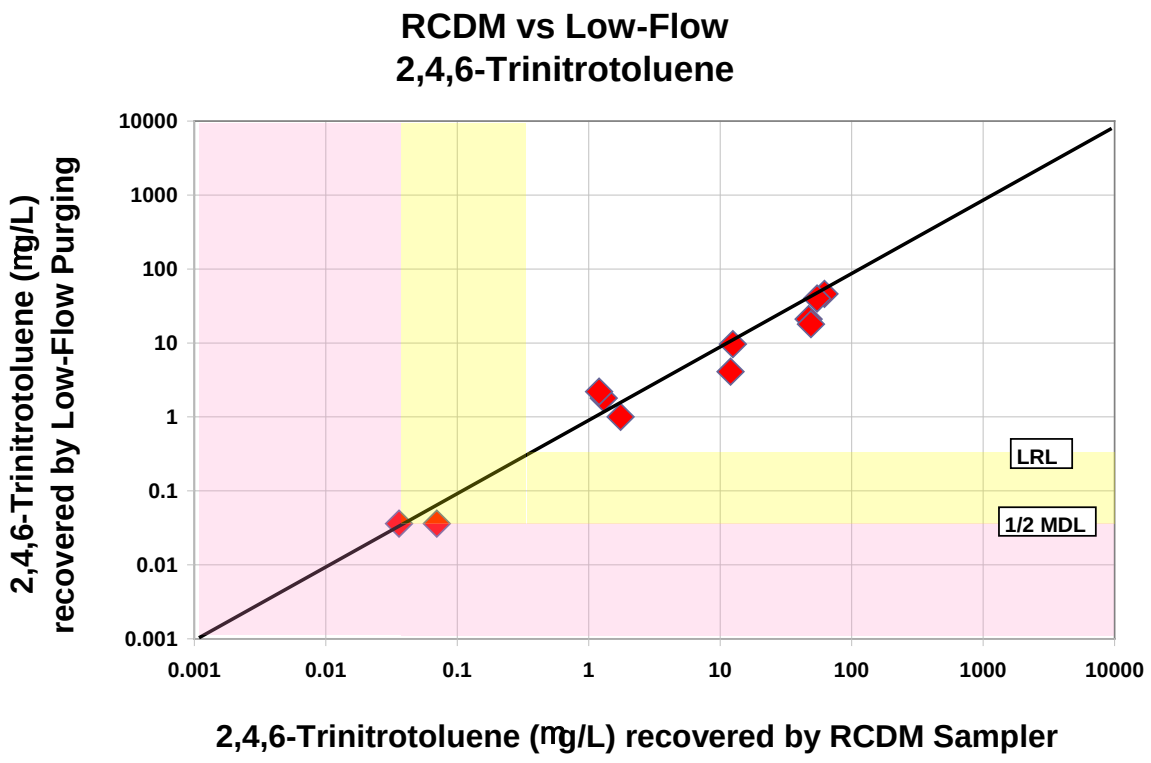

Figure 15. RCDM sampler versus low-flow purging results for 2,4,6-trinitrotoluene.

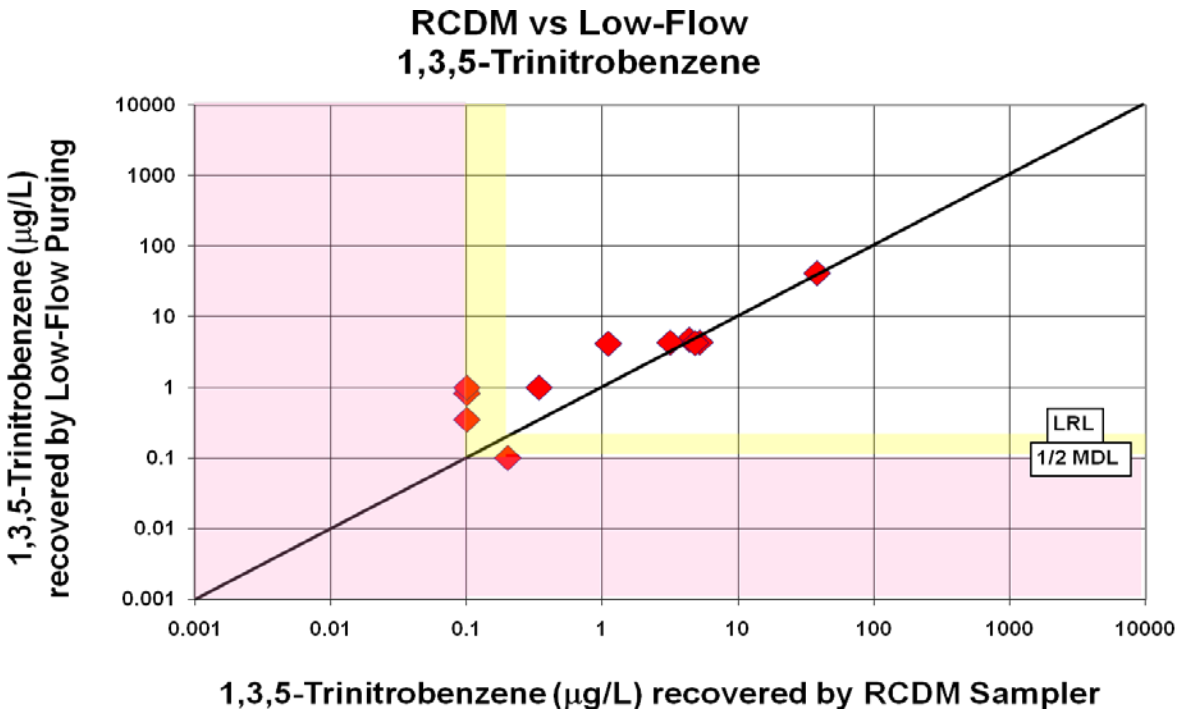

Figure 16. RCDM sampler versus low-flow purging results for 1,3,5-trinitrobenzene.

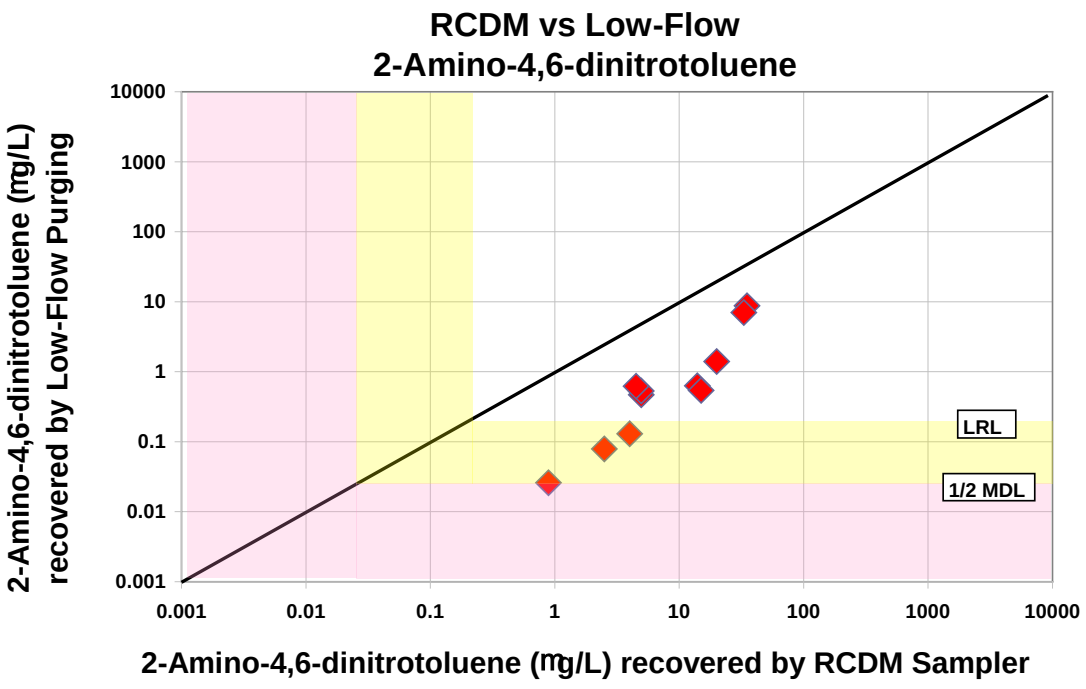

Figure 17. RCDM sampler versus low-flow purging results for 2-Amino-4,6-dinitrotoluene.

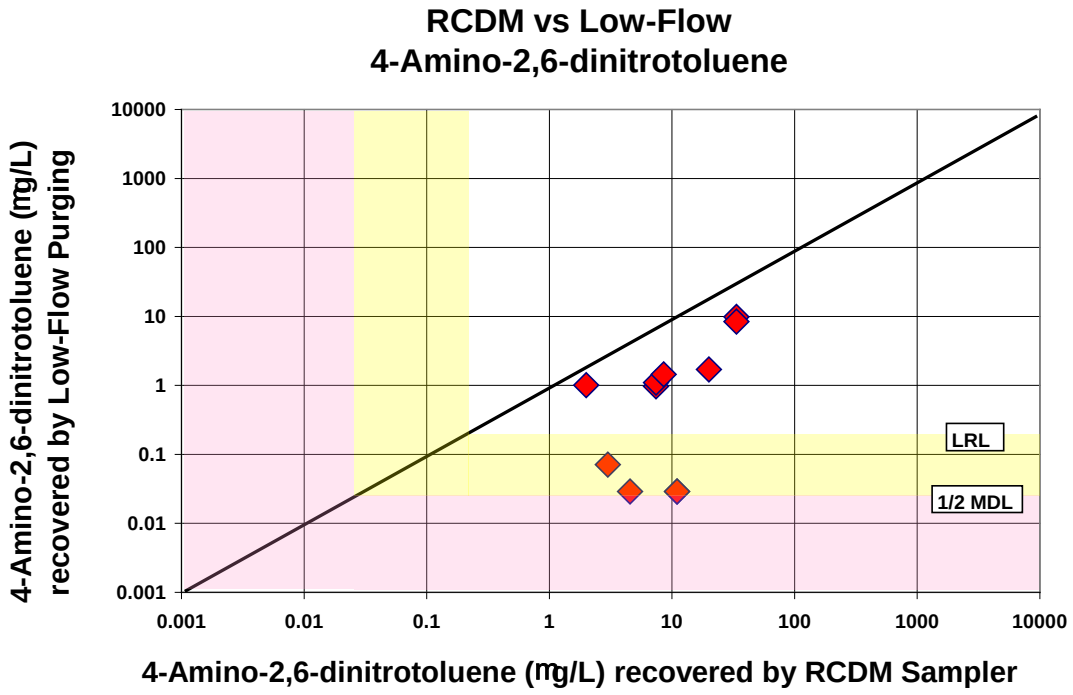

Figure 18. RCDM sampler versus low-flow purging results for 4-Amino-2,6-dinitrotoluene.

The plots of RCDM sampler results versus low-flow purging results for RDX, HMX, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene all show generally excellent agreement between concentrations obtained using both sampling techniques starting at the detection limit and going up over two to three orders of magnitude in concentration. The data points were closely grouped on or near the 1:1 correspondence line. These results confirmed that the two sampling techniques collected nearly identical samples for these explosives compounds from wells in the field demonstration.

The plots of RCDM sampler results versus low-flow purging results for 2-Amino-4,6-dinitrotoluene and 4-Amino-2,6-dinitrotoluene did not show close agreement between concentrations obtained using both sampling techniques. Although the concentration comparisons trended approximately parallel to the 1:1 correspondence line, most of the points fell below the line for both of these compounds. These results indicated that higher concentrations of these two explosives compounds were found in the RCDM samples than in the corresponding low-flow purge samples. A possible explanation for this phenomenon is that the amino groups present on both of these compounds sorb strongly to the dialysis membrane and cause locally higher concentrations inside the RCDM sampler. These results indicate that RCDM samplers should only be used for qualitative identification of these compounds not quantitative concentrations.

7.2.2 Statistical Comparison of Explosives Compounds Results

7.2.2.1 Correlation Analysis of Explosives Compounds

Pearson's correlation coefficients (r) were calculated by running least-squares regressions for all field comparison results between the RCDM sampler and low-flow purging for the six compounds found in four or more wells (SPLUS, 2002). The results are provided in Table 15. The correlations between concentrations sampled with the RCDM sampler and concentrations sampled with low-flow purging were all strongly positive (0.90 to 0.99). The high correlation values indicate that the data collected by different sampling techniques were closely and consistently matched over a range of concentrations.

Table 15. Correlation of sampling techniques for explosives compounds.

Compound	n	RCDM vs. Low-Flow Purging	
		r	LSRE
RDX	11	0.91	y=0.96x+3.17
HMX	11	0.90	y=0.65x+1.37
2,4,6-trinitrotoluene	11	0.94	y=0.61x-0.30
1,3,5-trinitrobenzene	11	0.99	y=1.08x+0.46
2-Amino-4,6-dinitrotoluene	11	0.99	y=0.23x-1.04
4-Amino-2,6-dinitrotoluene	11	0.91	y=0.28x-1.39

RCDM = regenerated cellulose dialysis membrane
vs. = versus
n = number of comparisons correlated
r = Pearson's correlation coefficient
LSRE = least-squares regression equation

The least-squares regression equations listed in Table 15 are also used as another indicator of how well the two distributions being compared matched. If the two distributions match exactly, the slope would be 1 and the intercept would be 0. The regression slope for the first four compounds ranged from 0.61 to 1.08 indicating relatively good agreement between the best-fit lines for these compounds and the 1:1 correspondence line. For the latter two compounds, the slopes were much lower (0.23 and 0.28), indicating that the best-fit line differed substantially from the 1:1 correspondence line.

7.2.2.2 Normality Testing of Explosives Compounds Results

The explosives compounds concentration data from all eight wells sampled in the field comparison study were tested to determine if the data distributions were normal distributions. This was accomplished by a univariate analysis that included the construction of box plots and the application of the Kolmogorov-Smirnov goodness-of-fit test (S-PLUS, 2002). Wells where at least one sampling technique had value above detection were included in this analysis. A Kolmogorov-Smirnov test statistic of 0.05 or less indicated that the data distribution was significantly different from the normal distribution. All explosives compounds data were not normally distributed. Because the explosives compounds results were not normally distributed, non-parametric statistical testing of the data was conducted. Non-parametric statistics do not require normal data distributions.

7.2.2.3 Wilcoxon Signed-Rank Test on Explosives Compounds

Explosives compounds concentration data collected with the two different sampling techniques were compared using a non-parametric Wilcoxon signed-rank test. The results of the testing are given in Table 16 below. No significant difference in the recoveries of RDX, HMX, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene were found between samples collected with the RCDM samplers and low-flow purging. These results indicate that RCDM samplers were able to collect samples for these compounds as accurately as low-flow purging over a range of concentrations.

Table 16. Statistical comparison of explosives compounds concentrations by the RCDM sampler and low-flow purging using the Wilcoxon signed-rank test.

Constituents where no significant difference was found between samples collected with the RCDM sampler and low-flow purging (at p<0.05; the 95% confidence level)
RDX (8)[1]
HMX (8)
2,4,6-trinitrotoluene (6)
1,3,5-trinitorbenzene (7)
Constituents where a significant difference was found between samples collected with the RCDM sampler and low-flow purging (at p<0.05; the 95% confidence level)
2-Amino-4,6-dinitrotoluene (8)
4-Amino-2,6-dinitrotoluene (8)

[1] Number of comparisons for each constituent above the minimum detection limit.

The two constituents that showed a significant difference in this test were 2-Amino-4,6-dinitrotoluene and 4-Amino-2,6-dinitrotoluene. Higher concentrations of both of these compounds were found in the RCDM samples when compared to concentrations found in low-flow purge samples. These two compounds differed from the other explosives compounds in that they contained amino groups. There is some evidence that proteins containing amino groups are sorbed more strongly to RCDMs. If this occurred with the amino-containing explosives compounds, locally high concentrations of these compounds may be found inside the RCDM sampler. RCDM samplers should therefore only be used for qualitative detection of these compounds in groundwater wells.

7.2.2.4 Concentration Range Measured for Explosives Compounds

Because it is useful to know the concentration ranges over which RCDM samplers can function, the concentration range for detected explosives compounds measured by the RCDM samplers in this demonstration study is given in Table 17. However, the wells sampled in this study were not contaminated over a wide range of concentrations, so the full concentration range of use for RCDM samplers for these compounds is most likely larger than shown in Table 17.

Table 17. Ranges of concentrations measured using RCDM samplers for explosives compounds.

Compound Detected	Concentration Range Measured		Units
	Low	High	
RDX	0.57	55	µg/L
HMX	0.17	29	µg/L
2,4,6-trinitrotoluene	1.00	62	µg/L
1,3,5-trinitrobenzene	0.34	42	µg/L
2-Amino-4,6-dinitrobenzene	0.54	35	µg/L
4-Amino-2,6-dinitrobenzene	0.07	33.5	µg/L

µg/L micrograms per liter

7.3 PERFORMANCE ASSESSMENT OF THE RCDM SAMPLER

The performance of the RCDM sampler was assessed by determining if the performance objectives of the field demonstration from Table 2 were met. A summary of this assessment is given in Table 18 below. Each objective is discussed in more detail in subsequent sections.

Table 18. Performance Objectives

Performance Objective	Data Requirements	Success Criteria	Results
Qualitative Performance Objectives			
Determine if RCDM samplers equilibrate with perchlorate and explosives compounds in the laboratory.	List of chemical constituents that equilibrated in the RCDM samplers in bench-scale testing.	All compounds tested equilibrate through the dialysis membrane.	Criteria met.
Determine if RCDM samplers and low-flow purging collect the same chemical constituents in the same wells in the field.	List of chemical constituents recovered by both RCDM and low-flow purging in each well.	Detection of the same chemical constituents in field samples collected with both RCDM samplers low-flow purging.	Criteria met.
Determine if dialysis membrane integrity is maintained over the course of equilibration.	Observations of the RCDM samplers after removal from the well.	No perforations noted during the length of the test.	Criteria met.
Determine if RCDM samplers are easier to use than low-flow purging.	Observations of the field sampling personnel.	RCDM samplers should be as easy or easier to use than low-flow purging.	Criteria met.
Quantitative Performance Objectives			
Determine minimum equilibration times for RCDM samplers for perchlorate and explosives compounds.	Bench-scale test concentration data.	Minimum times to equilibration are determined. All compounds tested equilibrate in less than 4 weeks.	Criteria met. Perchlorate equilibrates within 1 day. Explosives compounds equilibrate within 7 days.
Determine if RCDM samplers and low-flow purging recover similar concentrations of detected perchlorate and explosives compounds in field samples.	Concentrations of perchlorate and explosives compounds in samples collected by both RCDM samplers and low-flow purging.	No significant difference (at $p<0.05$) between chemical concentrations recovered by the RCDM sampler and low-flow purging.	Criteria met for perchlorate and four of six detected explosive compounds compared in field demonstration test wells.
Determine if RCDM samplers can collect low concentration samples.	Concentrations of perchlorate and explosives compounds in samples collected by both RCDM samplers and low-flow purging.	Concentrations within 2 to 5 times the reporting limit can be detected.	Criteria met. Values between detection limit and reporting limit were reported for most compounds.
Determine reproducibility of RCDM and low-flow data.	Concentrations of perchlorate and explosives compounds collected by both RCDM samplers and low-flow purging.	Concentrations within +/- 15% for perchlorate and +/- 30% for explosives compounds.	Criteria met. <6% for perchlorate and <12% for explosives compounds.
Determine if use of RCDM samplers reduces field sample collection time compared to low-flow purging.	Length of time to collect samples in the field with the RCDM sampler and with low-flow purging (including installation, sample collection, and equipment decontamination).	Length of field time required to sample with RCDM samplers should be at least 25% shorter than low-flow purging.	Criteria met. RCDM sampler field sample collection time was 84% shorter than low-flow purging.
Determine if use of RCDM samplers reduces field sample collection costs compared to low-flow purging.	Records of costs for equipment and supplies and record of personnel field time.	Cost savings using RCDM samplers should be at least 25% less than low-flow purging.	Criteria met. 73% overall cost savings per sample over low-flow purging found.

RCDM = regenerated cellulose dialysis membrane
$p<0.05$ = 95 percent confidence level

7.3.1 Ability of RCDM Sampler to Equilibrate and Equilibration Times

Bench-scale testing showed that perchlorate diffused through the dialysis membrane and equilibrated within 1 day at both 10EC and 21EC. Bench-scale testing showed that 14 explosives compounds all diffused through the dialysis membrane and equilibrated within 7 days at the same temperatures. This indicated that RCDM samplers had the potential to sample for these compounds in the field and that they could equilibrate in less than 4 weeks. Four weeks is a conservative estimate for the life of the dialysis membrane in the field before bacteria will cause perforations in the membrane (Imbrigiotta et al., 2007).

7.3.2 Ability of RCDM Sampler to Detect the Same Compounds as Low-Flow Purging

In greater than 93% of all sample comparisons, the same compounds were detected with the RCDM sampler and low-flow purging in the same well. In the few cases where there was disagreement, and one sampling method detected a compound that the other did not, the concentrations measured were usually very close to the detection limit

7.3.3 Maintenance of Dialysis Membrane Integrity

No perforations of the dialysis membrane were noted in any of the RCDM samplers deployed and retrieved over the length of these field demonstrations. RCDM samplers for collection of perchlorate concentrations were deployed and retrieved after 1 week. RCDM samplers for collection of explosives compounds were deployed and retrieved after 2 weeks.

7.3.4 Ease of Use

Feedback from the personnel that deployed and retrieved the RCDM samplers and conducted the low-flow sampling at each well indicated that the RCDM samplers were considered much easier to use and sample with than low-flow purging. The major reasons cited were (1) there was less equipment to haul to the field with the RCDM sampler, (2) no decontamination was needed with the RCDM sampler, (3) installation and retrieval of the RCDM sampler was simple and easy for a technician to learn quickly with minimal training, and (4) use of an RCDM sampler saved a great deal of time in the field.

7.3.5 Agreement Between Analyte Concentrations Obtained with Both Sampling Methods

For perchlorate, the concentrations obtained with the RCDM sampler and with low-flow purging in 10 wells were compared statistically and found not to differ significantly at the 95% confidence level. A 1:1 correspondence plot was made and correlation coefficients and best-fit linear regression equations were calculated for the RCDM sampler and the low-flow purging concentration distributions. The comparison data plotted very close to the 1:1 correspondence line on the graph, the correlation was strongly positively ($r>0.99$), and the best fit linear regression equation had a slope very close to 1. These findings indicated that there was strong agreement between RCDM sampling results and low-flow purging results for perchlorate. It was concluded that RCDM samplers collected essentially identical samples of perchlorate as low-flow purging.

For RDX, HMX, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene, the concentrations obtained with the RCDM sampler and with low-flow purging in eight wells were compared statistically and found not to differ significantly at the 95% confidence level. One-to-one correspondence plots were made and correlation coefficients and best-fit linear regression equations were calculated for the RCDM sampler and low-flow purging concentration distributions. The comparison data plotted fairly close to the 1:1 correspondence line on the graphs for these explosives compounds. In addition, the correlation coefficients were strongly positive (0.90 to 0.99) and the best-fit linear regression equation had strongly positive slopes (0.61 to 1.08). These findings indicated that there was strong agreement between RCDM sampling results and low-flow purging results for RDX, HMX, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene. It was concluded that RCDM samplers were able to collect essentially identical samples of these four explosives compounds as low-flow purging.

For 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene, the concentrations obtained with the RCDM sampler and with low-flow purging in eight wells were compared statistically and found to differ significantly at the 95% confidence level. One-to-one correspondence plots were made and correlation coefficients and best-fit linear regression equations were calculated for the RCDM sampler and low-flow purging concentration distributions for these compounds. The comparison data consistently plotted below the 1:1 correspondence line on the graphs for these two explosives compounds, indicating that higher concentrations were measured in the RCDM samplers than in the low-flow samples. In addition, although the correlation coefficients were strongly positive (0.91 and 0.99), the best-fit linear regression equation had weakly positive slopes (0.23 and 0.28). These findings indicated that the RCDM data and the low-flow data did not match closely for these two compounds. There is a bias towards the RCDM samplers collecting higher concentrations of 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene than low-flow purging.

The cause of this bias may be due in part to these two compounds containing amino functional groups. There is evidence from laboratory dialysis work that selected proteins (containing amino functional groups) may be sorbed strongly to RCDMs by a mechanism called non-specific binding (Thermo Scientific, 2008; Boure and Vanholder, 2004). If this occurred with the amino-containing explosives compounds, locally higher concentrations of these compounds may have been caused on the dialysis membrane and consequently higher concentrations of these two compounds may have equilibrated inside the RCDM sampler.

It was concluded based on the results of the field demonstration that RCDM samplers were not able to collect quantitatively similar samples of these two explosives compounds as low-flow purging. However, it was also concluded that RCDM samplers could certainly be used to collected qualitative samples for 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene to determine their presence or absence in groundwater.

7.3.6 Sensitivity of RCDM Samplers

RCDM samplers demonstrated excellent sensitivity by detecting concentrations between the detection limit and the reporting limit for most of the explosives compounds in groundwater samples collected over the course of the study (Table 11). These concentrations were easily within two to five times the reporting limit for most explosives compounds.

RCDM samplers demonstrated excellent sensitivity for perchlorate also by detecting concentrations within two to five times the reporting limit in the samples with the lowest perchlorate concentrations measured in this project.

7.3.7 Reproducibility of RCDM Data

The guideline for this performance objective was to have coefficients of variation <15% for perchlorate and <30% for explosives compounds for duplicate samples collected with RCDM and low-flow purging. The coefficient of variation for duplicate RCDM samples collected for perchlorate at the APG site was <4%. The coefficient of variation for three sets of duplicate RCDM samples collected for seven explosives compounds at the Picatinny Arsenal site was <5%. These results show that RCDM samplers collected highly reproducible results for both perchlorate and explosives compounds.

The coefficient of variation for duplicate low-flow purging samples collected for perchlorate was <6%. The coefficient of variation for three sets of duplicate low-flow purging samples collected for 7 explosives compounds was <12%. These results show that low-flow purging collected highly reproducible results for both perchlorate and explosives compounds also.

The lower coefficients of variation for the RCDM sampler at both sites indicate that these diffusion samplers collect slightly more reproducible samples than low-flow purging. However, all of the observed sampling variations were well within acceptable sampling guidelines.

7.3.8 Reduced Sampling Time

The length of time to collect samples in the field with RCDM samplers (installation, retrieval, sampling) was compared with the time to collect samples in the field with low-flow purging (installation, purging, field parameter monitoring, sample collection, filtration, and equipment decontamination) at all wells sampled in the ER-200313 study. On average it was found to take 0.5 person-hours to deploy, retrieve, and sample an RCDM sampler. On average it was found to take 3.2 person-hours to complete all the steps necessary to collect a low-flow purge sample. Therefore, it was calculated to take 84% less time to collect samples using an RCDM sampler than using low-flow purging. This was one of the major advantages field personnel noted for use of RCDM samplers over low-flow purging.

7.3.9 Less Costly Sampling Method

Because the field sample collection time using RCDM samplers was greatly reduced compared to low-flow purging, the field sample collection costs using RCDM samplers were also greatly reduced compared to low-flow purging. Based on this and other savings in material costs, construction labor costs, and purge water disposal costs, an overall cost savings of 73% was determined using RCDM samplers over low-flow purging on a per sample basis. This cost savings easily exceed the desired 25% cost savings performance objective.

7.4 DISCUSSION OF FIELD COMPARISON RESULTS

7.4.1 Comparison of Results to Previous Studies

No previous studies on the usefulness of RCDM samplers to collect samples for perchlorate had been conducted. Very few previous studies on the usefulness of RCDM samplers to collect samples for explosives compounds had been done prior to this project.

Parker and Mulherin (2006) conducted laboratory equilibration tests for HMX, 1,3,5-trinitrobenzene, RDX, and 2,4,6-trinitrotoluene at room temperature and found these explosive compounds equilibrated in RCDM samplers within 7 to 14 days. Leblanc (2003) lab-tested the dialysis membranes for permeability to explosive compounds and found that 75 to 80% equilibration of RDX and HMX concentrations were reached within 12 days at 4 ºC.

LeBlanc (2003) also conducted field tests with his RCDM samplers by burying the samplers in the sediments of a lake near the Massachusetts Military Reservation, Cape Cod, MA in an attempt to determine if explosives compounds in groundwater from the base were discharging into the lake. Over 130 RCDM samplers were installed in the lake sediments and allowed to equilibrate for 13 to 27 days before retrieval and sampling. The results were compared with a like number of drive-point pore-water samples collected from the pore sediments of the lake adjacent to the locations where the RCDM samplers had been buried. Four explosives compounds were detected at low concentrations in samples from the RCDM samplers. No explosives compounds were detected in samples from the drive-point water samples. Because so few comparisons resulted, no conclusions were made about the applicability of RCDM samplers to quantitatively sample for explosives in this manner, but clearly the RCDM samplers did allow qualitative detection of several explosives compounds in the lake sediments.

The results of the current demonstration project agree with the findings of these previous studies and advance the knowledge of the usefulness of RCDM samplers in collection of samples for explosives and perchlorate. Bench-scale testing showed that concentrations of all explosives compounds in groundwater test solutions were found to equilibrate with concentrations in RCDM samplers suspended in this groundwater within 7 days at temperatures bracketing most of the groundwater temperatures in the continental United States. Field testing showed that concentrations of perchlorate, RDX, HMX, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene sampled with RCDM samplers were not significantly different than concentrations of these compounds sampled using low-flow purging.

7.5 RCDM SAMPLER USE CONSIDERATIONS

Several factors should be taken into considerations prior to the use of RCDM samplers at a field site. These considerations were discussed in detail in both the ESTCP Final Technical Report (Imbrigiotta et al., 2007) published during the first phase of this project and in the ESTCP Protocol (Imbrigiotta et al., 2008) published as part of the ER-200313 project. Because these factors were not necessarily tested in this field demonstration, the authors felt it important for the sake of completeness to include a synopsis of the discussion from these reports.

- The volume of water contained in an RCDM sampler can be adjusted by varying the length and diameter of the membrane used to construct it. Once constructed, the volume of the sampler is finite. For this reason, it is important to carefully determine the minimum volume of water needed for all the chemical analyses that will be run on a sample before sampler construction begins.
- The maximum length of an RCDM sampler should be limited to the shortest of the following constraints: 5 feet (ft), the open interval being sampled, or the length of the zone of highest mass flux present in the open interval.
- For 4-inch diameter wells, a sample volume of 1 liter can be contained in an RCDM sampler constructed with a 2.5-inch diameter membrane about 2-ft long.
- For 2-inch diameter wells, the maximum sample volume that can be contained in an RCDM sampler is limited to approximately 1 liter in a 1.5-inch diameter membrane that is 4.5-ft long.
- Deoxygenated deionized water should be used to fill and store RCDM samplers that will be deployed in anoxic wells to avoid altering the concentrations of redox active chemicals.
- RCDM samplers must (1) be submerged below the air/water interface in a well, (2) remain submerged and be allowed to equilibrate for an appropriate period of time for the chemicals of concern at a site, and (3) be sampled with a minimum of disturbance or aeration of the water inside to reduce the loss of volatile constituents or dissolved gases and to avoid changing the redox conditions of the groundwater sample.
- RCDM samplers require that groundwater be moving through the open interval of a well past the sampler to collect a sample representative of the groundwater in the aquifer.
- RCDM samplers require two trips to the field site to collect a sample; the first to deploy the sampler for equilibration, and the second to collect the sample. RCDM samplers can be installed easily by one person and retrieved and sampled easily by two persons.
- RCDM samplers, as well as low-flow purge pumps, should be deployed at the depth of highest mass influx of the chemical of primary concern in the open interval of a well.
- The depth of highest mass influx should be determined if at all possible by vertical profiling the open interval of the well. If the open interval of a well is 5 ft or less, no vertical profiling is deemed necessary and the RCDM sampler should be suspended at the mid-depth of the interval (ITRC, 2004). If the open interval of a well is greater than 5 ft, both chemical and hydraulic vertical profiling should be conducted. Chemical profiling is usually done by sampling equilibrated RCDM or PDB samplers that have been suspended at closely space depths (<5 ft apart) over the open interval of a well. Hydraulic profiling is usually done by borehole flow meter testing or packer testing over the open interval of a well. If

vertical profiling is not possible, knowledge of the site geology and past contamination history should be used to determine the depth of deployment.

- RCDM samplers must be kept hydrated once they are constructed. If allowed to dry out, the membrane's diffusion properties change, the material becomes stiff and brittle, and it essentially turns into cellophane.
- RCDM samplers lose less than 3% of their volume per week in wells with TDS up to 2300 mg/L because of the dialysis process. If sampler deployment times in the well are short (one to two weeks) this loss can be taken into account when constructing the sampler and should not impact the use of these samplers.
- RCDM is a bioactive membrane in that it can be degraded by bacteria and fungi. Observations from other field tests have shown that RCDM samplers can conservatively last 4 to 6 weeks in a well at ~15EC before biodegradation may compromise the membrane. If equilibration times for the chemicals of concern are short (one to two weeks) this should not restrict the use of these samplers in a well. If the equilibration times for the chemicals of concern are longer than 4 weeks, dialysis membranes should not be used in a well unless prior testing shows that they will survive the length of time without biodegrading. Warmer groundwater temperatures and high microbial populations can accelerate biodegradation.
- With regard to redox active chemicals, RCDM samplers recover statistically identical concentrations of dissolved iron as low-flow purging, whereas RCDM samplers recover statistically higher concentrations of dissolved sulfide than low-flow purging (Imbrigiotta et al., 2007). Thus, concentrations of sulfide collected with RCDM samplers should be considered high estimates of the actual sulfide concentrations in the groundwater.
- Differences between chemical concentrations collected with RCDM samplers and low-flow purging may be because sampling techniques use different mechanisms to collect samples. RCDM samplers can only equilibrate with chemical concentrations that are present at the depth at which they are suspended in an open interval under non-pumping conditions. Low-flow purging can collect samples that are drawn from different depths over the entire open interval or from areas of the aquifer adjacent to the open interval (Varljen et al., 2006; Gibs et al., 1993; Reilly and Gibs, 1993). The fact that different concentrations can be obtained with the different sampling techniques does not mean one method is right and the other is wrong. It just means that the methods are sampling different water from the same well (ITRC, 2004).

7.6 SUMMARY OF FIELD COMPARISON FINDINGS

7.6.1 Conclusions

The following bullets describe most of the significant findings from the field comparison work in this project.

- RCDM samplers made of RCDM can be used to collect quantitative concentrations for perchlorate, RDX, HMX, 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene, but should only be used to collect qualitative presence/absence data for 2-amino-4,6-dinitrotoluene or 4-amino-2,6-dinitrotoluene.
- A one-week deployment time was sufficient for equilibration of perchlorate, while a two-week deployment time was sufficient for equilibration of all explosives compounds monitored in the field demonstrations.
- For perchlorate, RDX, HMX, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene detected in wells sampled in the field demonstration, the graphs comparing RCDM sampler results to low-flow purging results showed a relatively tight grouping of data points around the 1:1 correspondence line, indicating good agreement between the two sampling techniques.
- Graphs for 2-amino-4,6-dinitrotoluene or 4-amino-2,6-dinitrotoluene comparing RCDM sampler results to low-flow purging results show poor grouping of data points around the 1:1 correspondence line, indicating that higher concentrations of these compounds were collected using RCDM samplers than low-flow purging.
- The correlation coefficients for perchlorate and all explosives compounds monitored in the field in this study were strongly positive between samples collected with RCDM samplers and low-flow purging.
- RCDM samplers recovered concentrations of perchlorate, RDX, HMX, 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene that were not statistically significantly different from concentrations recovered by low-flow purging.
- RCDM samplers recovered concentrations of 2-amino-4,6-dinitrotoluene or 4-amino-2,6-dinitrotoluene that were statistically significantly different from concentrations recovered by low-flow purging.

7.6.2 Criteria For Use of RCDM Samplers

The use of RCDM samplers would be advantageous over low-flow purging to sample wells for perchlorate or explosives compounds in the following situations:

(1) Where it would be difficult or impossible to bring in a pump and its power source (e.g., wells in remote wilderness areas, wells inside buildings),

(2) Where normal sampling activities would be extremely hazardous or inconvenient (e.g., wells in high traffic areas, wells in airport runway areas),

(3) Where it would be advantageous for sampling personnel to spend as short a period on site as possible (e.g., residential areas near military bases),

(4) Where collection, transport, and treatment of purge water would be costly, difficult, or undesirable due to safety concerns (e.g., wells at all hazardous waste sites, wells at remote hazardous waste sites, wells in populated areas near military bases),

(5) Where wells have water with high turbidity when purged due to their construction or the formation in which they are completed (e.g., incorrect screen size and filter pack), and

(6) At sites where large numbers of long-term monitoring wells must be sampled for known concentrations of both inorganic and organic compounds, including either perchlorate or explosives compounds.

RCDM samplers should not be used in the following situations:

(1) In wells where "total" or unfiltered samples must be collected,

(2) In small diameter wells that require a large sample volume (>1 liter), or

(3) In wells that must be sampled quantitatively for 2-amino-4,6-dintrotoluene or 4-amino-2,6-dinitrotoluene.

8.0 COST ASSESSMENT

8.1 COST MODEL

One of the objectives of this demonstration was to evaluate the cost savings produced by using RCDM samplers instead of traditional low-flow purging techniques. The costs for collecting samples with the RCDM sampler and low-flow purging have been estimated based on the costs experienced in both the laboratory and field portions of this project. Table 19 delineates the cost elements, data that must be tracked, and the estimated costs for each element that was considered in this cost model.

It should be noted that the site characterization costs may be greatly reduced if the investigator has worked at the site and already has recent information on the well construction, well depths, and contaminant concentrations. Ideally both chemical and hydraulic vertical profiling should be conducted on each well; however, up-front costs prior to the use of these sampling techniques may be reduced if the hydrogeology of the open intervals of the wells at the site is already well characterized. If this is the case, only the chemical vertical profiling need be done.

8.2 COST DRIVERS

The cost drivers are:

- The difference in cost of renting the low-flow pumping equipment versus purchasing RCDM sampler construction materials,
- The amount of time involved in pumping to stabilize field parameters prior to sample collection versus deployment and retrieval of the RCDM samplers prior to sample collection, and
- The remediation time frame for the cost comparison was considered to be 30 years.

8.3 COST ANALYSIS

The primary cost comparison has been conducted between the cost of constructing and using RCDM samplers, and the cost of renting and using low-flow purging equipment. Cost comparisons were made on both a per sample basis and on a per site basis. The costs for site characterization, chemical vertical profiling, and hydraulic vertical profiling were assumed to be one-time only costs that were needed for both sampling techniques in order to determine the proper sampling depth in a well. Because these costs were needed for both sampling methods, they were not included in the cost comparisons below.

Table 19. Cost model for RCDM samplers.

Cost Element	Data Tracked During the Demonstration	Costs	
Site characterization	Personnel time to obtain information on well construction, recent water chemistry, recent contaminant concentrations	Project person, 80 hrs	$8000
Vertical profiling – chemical	Personnel time to construct, deploy, and retrieve diffusion samplers; analytical costs; must be done once prior to diffusion sampling or low-flow purging (Assume 5 diffusion samplers per 20 ft open interval/well in 10 wells)	1 lab person, to construct 50 samplers, 8 hrs	$400
		1 field person to deploy 50 samplers, 2 hrs	$100
		1 field person to retrieve and collect 50 samples, 5 hrs	$250
		Analytical costs	$5000
Vertical profiling – hydraulic/geophysical	Personnel time to test open interval with a borehole flow meter, rental of equipment; should be done once prior to diffusion sampling or low-flow purging (Assume logging 10 wells)	Borehole flow meter rental, 40 hrs	$1000
		Geophysics person to log 10 wells, 24 hrs	$2400
		Geophysics person to analyze collected data, 16 hrs	$1600
Material costs – RCDM samplers	Costs of membrane, mesh, rope, stopcock, clamps, weights, regenerated cellulose lay-flat tubing (Assume 2 ft long by 2.5-inch diameter sampler in 10 wells)	Material costs (10 samplers)	$370
Construction costs – RCDM samplers	Personnel time to assemble sampler (Assume 0.75 hr/sampler for 10 samplers)	1 lab person, 7.5 hrs	$375
Operating costs – RCDM sampler	Field personnel time to deploy, retrieve, and collect sample; purge water disposal	1 field person to deploy 10 samplers, 2 hrs	$100
		2 field persons to retrieve and collect 10 samplers, 3.5 hrs	$175
		Purge water disposal	$0
Material costs – Low-flow purging	Rental of variable-speed submersible pump and control box, rental of generator, Teflon-lined polyethylene discharge tubing, extension cord, pump cleaning stand, pump cleaning supplies (deionized water, liquid detergent, methanol), 0.045 µm capsule filters for field filtration	Material costs	$1515
		Fuel for generator	$125
Construction costs – Low-flow purging	Personnel time to cut discharge tubing to length for 10 wells (Assume 10 min/well)	2 field persons, 3.5 hrs	$175
Operating costs – Low-flow purging	Field personnel time for purging and field parameter stabilization, collection of sample, filtration, pump decontamination, purge water disposal, pump maintenance costs (Assume 96 minutes/well sampling 10 wells)	2 field persons to purge and stabilize 10 wells	$1600
		Purge water disposal	$50

8.3.1 Basic Assumptions

For the cost comparison made on a per sample basis, the following assumptions were used:

- The average well sampled was a 4-in diameter well, having a depth to water of approximately 10 ft below land surface, a total well depth of 40 ft below land surface, and an average sampling depth of 35 ft below land surface.

- All RCDM samplers were assumed to be 2.5 inches in diameter and 2 ft in length and contained 1.7 L of sampleable groundwater.
- The minimum required volume of groundwater for a perchlorate analysis was assumed to be 0.25 L.
- The minimum required volume of groundwater for an explosives compounds analysis was 1.0 L.
- RCDM samplers were constructed by laboratory personnel, not purchased commercially.
- During sampling, essentially no purge water was produced using RCDM samplers, while approximately 40 L (10 gallons) of purge water was produced during each low-flow purge sampling.
- The low-flow purging sample will require field filtration whereas the RCDM samplers will not.
- The laboratory and field personnel earn $50/hour.

For the cost comparison made on a per site basis, the following assumptions were used:

- The sampling costs per well were applied to a typical site with 50 monitoring wells.
- The wells were sampled quarterly for a period of 30 years.

8.3.2 Cost Comparison per Sample

A detailed breakdown of materials, labor, and purge water disposal costs incurred in the use of RCDM samplers and low-flow purging on a per sample basis is given in the next two sections. The cost breakdown is summarized in Table 20.

8.3.2.1 RCDM Sampler Costs

RCDM Material Costs:
The material costs for a 2.5-in diameter by 2-ft long dialysis membrane, PVC supports, outer protective mesh, stopcock, clamp, weights, and suspension rope are given below:

Membrane ($9.75/ft)(2.5 ft)	$24.40
Protective mesh ($0.50/ft)(3 ft)	1.50
PVC supports ($0.25 ea)(2/sampler)	0.50
Weights ($0.24/wt)(10 wts/sampler)	2.40
Rope ($0.10/ft)(40 ft)	4.00
Stopcock ($3.00)(1/bag)	3.00
Miscellaneous (clamp, ties, etc)	0.50
Storage bag ($0.10/ft)(3 ft)	0.30
Total materials costs per RCDM sampler	**$36.60**

Note: This constructs a 2.5-inch diameter by 2-ft long sampler suitable for use in a 4-inch diameter well. Smaller dialysis membrane (1.25-inch diameter) can be purchased to make samplers that can be used in a 2-inch diameter well. The smaller diameter dialysis membrane costs approximately 25% less per unit length as the larger size and holds four times less volume. The material costs for a 1.25-inch diameter by 2-ft long RCDM sampler was calculated to be $30.30.

RCDM Construction Labor Cost:
The time for one person in the laboratory to construct one RCDM sampler was 45 minutes. This involved rinsing the membrane, cutting the membrane, tying a knot in one end of the membrane, cleaning the associated stopcock, clamp, internal support, cutting the PVC supports to length, cutting the protective mesh to length, cleaning and installing the weights, assembling the pieces, filling the dialysis membrane with nitrogen-sparged deionized water, and closing up the sampler on the ends with cable ties. Once the dialysis membrane was wetted, it had to remain so. To accomplish this, the sampler was inserted into a thicker-walled, larger-diameter polyethylene sleeve partially filled with deionized water and knotted at both ends for storage in the refrigerator.

Using a labor rate of $50/hour/person and the fact that it took 0.75 hours for one person to construct an RCDM sampler, the construction labor cost was calculated to be approximately $38.

RCDM Field Labor Cost:
To deploy a single RCDM sampler it took one person 10 minutes. To recover and sample a single RCDM sampler from a well, it took two persons approximately 10 minutes. Thus a total field labor time of 0.5 hours was required to collect one sample. At a labor rate of $50/hour/person, the field labor cost would be approximately $25.

RCDM Purge Water Disposal Costs:
Purge water disposal costs were estimated to be $0.50/gallon. Because only 0.025 L or 0.007 gallons of purge water were expected to be produced from each RCDM sampler upon sampling, the purge water disposal costs were calculated to be less than $0.01. Therefore, no additional costs were added for purge water disposal for the RCDM sampler.

Total Costs for an RCDM Sampler:
Total costs for materials, construction labor, and field labor for the collection of one sample using a 2.5-inch diameter by 2-ft long RCDM sampler were calculated to be $100/sample. (The total cost for a 1.25-inch by 2-ft long RCDM sampler was determined to be only slightly less at about $93/sample). These costs are itemized in Table 20 below.

8.3.2.2 Low-Flow Purging Costs

Low-Flow Purging Material Costs:
Material costs for a submersible pump capable of pumping approximately 35 ft of head were used in the low-flow purging cost estimate. Material costs were calculated using rental equipment because it would be difficult to depreciate the cost of purchased equipment over the life of the equipment. Based on the time require to prepare the pump and collect a sample (approximately 1.6 hours/sample in this study) and experience in field sampling, it was

realistically estimated that 15 samples could be collected per week (3 samples/day x 5 days) using such a pump to sample wells of this depth. Therefore, the weekly rental costs were divided by 15 in order to calculate the materials on a per sample basis. Teflon-lined polyethylene tubing was used as the discharge line for the pump. A 0.45 μ capsule filter was used in line to collect samples for dissolved constituents.

Pump rental ($240/week)	$16.00
Tubing ($2.00/foot) (40 feet)	80.00
Generator rental ($150/week)	10.00
Controller ($150/week)	10.00
Decontamination solutions	5.00
Fuel for generator (5 gal x $2.50/gal)	12.50
Capsule filter ($30 each)	30.00
Total material costs per low-flow sample	**$163.50**

Low-Flow Purging Construction Labor Costs:
The only construction labor cost associated with low-flow purging was measuring and cutting the new discharge tubing to length for each well. This was either done in the lab prior to going to the field or in the field as the pump was being installed. It was estimated that it would take 2 persons 10 minutes to accomplish this task. Therefore, the construction labor costs were calculated (0.17 hr x $50/hr/person x 2 persons) to be about $17/sample.

Low-Flow Purging Field Labor Costs:
Field labor costs using a low-flow purging pump were estimated based on the average time it took to sample wells in this study. On average, it required two persons 96 minutes (1.6 hours) to collect a single sample from a well using the low-flow purge technique. This time included setting the pump in the well at the appropriate depth, purging the well, monitoring field parameter stabilization, sample collection, sample filtration, removal of the pump from the well, and decontamination of the pump. At a labor rate of $50/hour/person, the total field labor cost would be (1.6 hours x $50/hour/person x 2 persons) or approximately $160/sample.

Purge Water Disposal Costs:
Purge water disposal costs were estimated to be $0.50/gallon. It was estimated that 10 gallons of purge water would probably be produced by low-flow purging in wells of this size and depth. The purge water disposal costs were calculated to be $5/well.

Total Costs for Low-Flow Purging:
Total costs for materials, construction labor, field labor, and purge water disposal for the collection of one sample using low-flow purging were calculated to be $346/sample. These costs are itemized in Table 20 below.

Table 20. Comparison of materials, construction labor, field labor, purge water disposal, and total costs per sample using an RCDM sampler and low-flow purging.

Costs/Sample	RCDM Sampler	Low-Flow Purging
Materials Cost	$37	$164
Construction Labor Cost	$38	$17
Field Labor Cost	$25	$160
Purge Water Disposal Cost	$0	$5
Total Cost/Sample	$100	$346

All cost comparisons have assumed that the RCDM samplers were produced by project personnel. These costs would be expected to drop significantly when the RCDM sampler is produced commercially.

Based on these estimates, a total cost savings of 71% would be realized by using an RCDM sampler to collect groundwater samples for perchlorate or explosives compounds rather than low-flow purging. Most of this savings is due to a significant reduction in field labor costs. Field labor costs alone were reduced by 84% when using an RCDM sampler over low-flow purging. These significant cost savings are a strong reason to consider the use of RCDM samplers at DoD sites, particularly sites undergoing long-term monitoring where the contamination is known and is compatible with this sampler.

8.3.3 Cost Comparison per Site

Table 21 summarizes the life-cycle costs of the two sampling technologies evaluated in this project when used to monitor a typical site over the period of 30 years. All the basic assumptions for these calculations are given in Section 8.3.1 and Table 20.

Table 21. Comparison of sampling costs over a 30-year period for RCDM samplers and low-flow purging.

Monitoring Costs	RCDM Sampler	Low-Flow Purging
Sampling Cost/Sample (from Table 20)	$100	$346
Samples(Wells)/Site	50	50
Sampling Costs per Site per Sampling Event	$5000	$17,300
Sampling Events per 30-year Period	120	120
Total Sampling Costs per Site per 30-year Period	$600,000	$2,076,000
Total Sampling Cost Savings per Site per 30-year Period over Low-Flow Purging	$1,476,000	---

The savings attained through the use of RCDM samplers instead of low-flow purging over the course of a 30-year long-term monitoring plan can be significant.

9.0 IMPLEMENTATION ISSUES

9.1 RCDM GUIDANCE AND PROTOCOLS

No technical guidance documents or protocols have been published that have dealt specifically with the use of RCDM samplers for collection of samples for perchlorate and explosives compounds. Most of the previously published RCDM sampler reports have given guidance on the construction and use of RCDM samplers for other types of elements or compounds. All reports mentioned below reflect in whole or in part, prior work done by the authors of this report.

The ESTCP Final Report from the first phase of the ER-200313 project (Imbrigiotta et al., 2007) that detailed the findings that RCDM samplers could successfully collect valid samples for VOCs, cations, anions, and most trace elements was published on the ESTCP website (www.serdp-estcp.org) and can be downloaded for free. The report contained the individual test results for the elements and compounds initially tested for sampling with RCDM samplers and how the RCDM samplers compared to PDB samplers and low-flow purging in recovery of these elements and compounds.

An ESTCP Protocol for construction and use of RCDM samplers was also published as part of the first phase of the ER-200313 project (Imbrigiotta et al., 2008). The Protocol contains details about the materials and methods that were used to construct the RCDM samplers in this project, issues that should be carefully considered prior to using RCDM samplers at a site, and deployment and recovery considerations for field use of RCDM samplers. This report was also published on the ESTCP website (www.serdp-estcp.org) and can be downloaded for free.

Both the Principal Investigator and Co-Principal Investigator of this project are members of the ITRC Diffusion Sampler Team. This is a national group of state regulators, representatives from branches of the military, federal investigators, industry consultants, and sampling equipment manufacturers that are interested in transferring diffusion sampler technology to the public arena. Participation in this group has allowed the ITRC to be directly informed of the progress of this work with RCDM samplers and to get feedback on its concerns about the use of the technology. In 2006, the authors contributed to an ITRC overview document on 14 passive sampling technologies including the RCDM sampler (ITRC, 2006). In 2007, an ITRC protocol document on the use of five passive samplers, one of which was the RCDM sampler, was written and published (ITRC, 2007). The authors wrote the section on the RCDM sampler based on their work on the first phase of the ESTCP ER-200313 project. This document provided guidance on how to deploy and collect samples using these samplers, and on the advantages, applicability, and limitations of these technologies. Both of these documents are available for free on the ITRC website (http://www.itrcweb.org/guidancedocument.asp?TID=12). The ITRC has included the RCDM sampler as one of the five passive sampling devices presented in its free online training course that has been given at least six times over the past 3 years (2008 to 2010). During each of these classes, 50 to 100 participants have been exposed to the capabilities and usefulness of the RCDM samplers as well as other passive samplers. Exposure from these classes has resulted in calls to the authors of this report from multiple consultants and state regulators seeking details on how to construct and use RCDM samplers. An archived copy of the most recent training session is available on the ITRC Diffusion Sampler Team website.

Technology transfer was accomplished through the Naval Facilities Engineering Command Engineering Services Center (NAVFAC ESC) by including the results of this demonstration on its website, in the NAVFAC Remedial Project Manager (RPM) newsletter, and in a Tech Data Sheet. The results were also included on the Federal Remediation Technologies Roundtable website. General RCDM sampler research findings have been presented at technical conferences including the Navy Cleanup Conference, the USGS-Department of Defense Environmental Conservation Conference (DODEC), and three poster presentations at the annual Partners in Environmental Technology Technical Symposium and Workshop (2005 to 2007). RCDM sampler research findings on sampling for perchlorate and explosives compounds have been presented at the USGS-USEPA Fractured Rock Workshop (2008), the USGS-USEPA Toxics Substances Hydrology Conference (2009) and the National Water-Quality Monitoring Council Conference (2010).

The NAVFAC ESC Tech Transfer Program and the NAVFAC Alternative Restoration Technology Team are very interested in passive samplers since they have the potential to be more cost effective and are green and sustainable. The August 10, 2009, DoD Green and Sustainable Remediation Memorandum specifically mentions the consideration of passive samplers where feasible. The Alternative Restoration Technology Team (ARTT) conducted a survey to learn about the use of passive samplers and identify barriers RPMs are experiencing. ARTT is planning to prepare a fact sheet or a handbook to discuss how and when to use passive samplers and highlight the cost and performance (including discussion of green and sustainability metrics), case studies, best practices, and lessons learned. The Technology Transfer program has plans to update the 2005 Tech Transfer "Passive Diffusion Sampler" web tool.

ASTM (American Society for Testing and Materials) is currently (2011) writing a protocol for use of passive sampling devices in general, RCDM samplers are included in this document. Once the ASTM protocol on passive samplers is published, the use of these samplers will be an accepted standard method for sampling groundwater.

9.2 LESSONS LEARNED

9.2.1 Regulatory Issues

Regulatory acceptance of diffusion/passive samplers is currently being done on a state by state basis. New Jersey was the only responding state that had published guidance on using a specific passive sampling technology (PDBs) for sampling VOCs in groundwater (New Jersey Department of Environmental Protection [NJDEP], 2005). The NJDEP guidance simply required that the open interval of a well be vertically profiled for VOC concentrations and subsequently sampled at the depth of the highest VOC concentration.

As an example, although the NJDEP PDB guidance does not specifically apply to RCDM samplers, the NJDEP site managers at the NAWC West Trenton, New Jersey site have adapted this guidance in their approval of RCDM use at this site. Initially, the NJDEP required a comparison study of RCDM sampler results to the results obtained using low-flow purging or high-flow purging sampling procedures. The NJDEP approved the use of RCDM samplers in 25 wells at the NAWC site based on these comparison studies. However, after the PDB guidance

was established (NJDEP, 2005), RCDM samplers were allowed in 15 additional wells at this site based primarily on doing the vertical VOC profiling required in the PDB guidance. The U.S. Navy is currently planning further comparison sampling in additional wells at the NAWC site. Based on the results of this comparison, NJDEP may approve the use of RCDM samplers as the sole sampling technique in additional wells at the NAWC site. The driving force behind the U.S. Navy's support for the implementation of this technology is the large cost savings in their long-term monitoring plan.

A survey sent to the ITRC's state contacts confirmed that there are some regulatory barriers (statutes, regulations, or guidance) that either prohibit or impede the use of passive sampler technologies (ITRC, 2007). Of the 16 states responding to the survey, 25% believed their state had a prohibition to use passive/diffusion sampling technologies because they required either three-well-volume purging or low-flow purging prior to groundwater sampling. Other states required that wells be purged, which precluded using passive sampler technologies. Most all states appeared receptive to the use of passive/diffusion sampling technologies, but required a comparison sampling demonstration to verify agreement with the currently used sampling technology.

9.2.2 End User Concerns

State regulators, environmental consultants, and the military can all be identified as end users of the results of this field demonstration. By far, the primary end user concern is whether the RCDM samplers will yield the same results as the low-flow purging or high-flow purging technologies currently in use at the site. Most state regulators will want to see a side-by-side comparison of RCDM samplers and whatever sampling technique is currently being employed at a site. This requires the collection and analysis of at least one to two sets of extra samples to accomplish the comparison, which can be costly to the site responsible party. In most cases, the comparison results will agree and the regulators should agree to use of the RCDM samplers. However, if the comparison results do not agree between the RCDM samplers and the purging sampling techniques, the state regulators may be reluctant to allow replacement of the current sampling technique with RCDM samplers. A large part of gaining acceptance of RCDM samplers at a site is educating the state regulators on how the samplers work and why the RCDM samplers may be giving valid results that do not agree exactly with the current sampling technique being used at the site. Publications on RCDM sampling such as the documents discussed in Section 9.1 will go a long way toward helping with this education process.

Limitations of the RCDM sampler technology were found to be minimal. Samplers made with RCDM must be kept hydrated between the time they are constructed and deployed. This is easily remedied by storing the RCDM sampler in a polyethylene sleeve partially filled with water. Purported limitations of RCDM samplers due to water volume loss with time in high ionic strength waters and due to biodegradation were not significant when equilibration times in wells were one to two weeks as was found in this study.

9.2.3 Procurement Issues

The fact that RCDM samplers are not currently commercially available is a stumbling block to having these samplers tested at more sites. Because there are currently (2011) no commercially available RCDM samplers of the type being tested in this demonstration, the samplers must be custom built by the user. One manufacturer was contacted about commercializing the RCDM sampler and was initially enthusiastic. However, they were also developing another passive sampler, so they have not moved forward as quickly on the RCDM sampler.

As mentioned earlier, an ASTM subcommittee on sampling methods is currently working on a protocol for the proper use of passive samplers. RCDM samplers are included as one of the samplers discussed in this document. When this protocol is published more interest in commercializing RCDM samplers is expected to be generated.

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APPENDIX A

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