ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4370

TECHNICAL REPORT
TR-2281-ENV

Final Technical Report
DEMONSTRATION AND VALIDATION OF A REGENERATED CELLULOSE DIALYSIS MEMBRANE DIFFUSION SAMPLER FOR MONITORING GROUND WATER QUALITY AND REMEDIATION PROGRESS AT DoD SITES (ER-0313)

by

U.S. Geological Survey, Trenton, New Jersey
Naval Facilities Engineering Service Center, Port Hueneme, California
Battelle, Columbus, Ohio

August 30, 2007

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0811*

1. REPORT DATE *(DD-MM-YYYY)* AUGUST 2007	2. REPORT TYPE TECHNICAL REPORT - FINAL	3. DATES COVERED *(From – To)*

4. TITLE AND SUBTITLE **FINAL TECHNICAL REPORT** **DEMONSTRATION AND VALIDATION OF A REGENERATED CELLULOSE DIALYSIS MEMBRANE DIFFUSION SAMPLER FOR MONITORING GROUND WATER QUALITY AND REMEDIATION PROGRESS AT DOD SITES (ER-0313)**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Thomas E. Imbrigiotta, U.S. Geological Survey, Trenton, NJ** **Joseph S. Trotsky, Naval Facilities Engineering Service Center, Port Hueneme, California** **Matthew C. Place, Battelle, Columbus, Ohio**	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESSES Commanding Officer Naval Facilities Engineering Service Center 1100 23rd Ave Port Hueneme, CA 93043-4370 US Geological Survey 810 Bear Tavern Road, Suite 206 West Trenton, NJ 08628	8. PERFORMING ORGANIZATION REPORT NUMBER **TR-2281-ENV**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Environmental Security Technology Certification Program 901 North Stuart Street, Suite 303 Arlington, VA 22203	10. SPONSOR/MONITORS ACRONYM(S) ESTCP 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This final technical report documents the demonstration and validation of regenerated cellulose dialysis membrane diffusion samplers for use in collecting ground water samples for a range of inorganic and organic water-quality parameters. This project, ER-0313, was funded by the Environmental Security Technology Certification Program (ESTCP). The primary objectives of the project were; (1) to determine the usefulness of dialysis samplers in collecting a range of organic and inorganic water quality constituents from ground water, (2) to determine the optimum equilibration times for these constituents to diffuse into the dialysis sampler, (3) to compare water quality results and sampling costs from samples collected with dialysis samplers to samples collected with a low-flow purging technique and polyethylene diffusion bag (PDB) samplers, and (4) to transfer the technology while gaining regulatory acceptance. Field comparisons were conducted at three Department of Defense (DoD) sites: (1) Naval Air Engineering Station (NAES) Lakehurst, NJ, (2) Naval Base Ventura County (NBVC), Port Hueneme and Pt. Mugu, CA, and (3) Naval Air Warfare Center (NAWC) West Trenton, NJ. Dialysis samplers were found to cost significantly less than samples collected with a low-flow purging procedure. Field sampling time was reduced by a factor of more than six times, compared to low-flow purging. The total sampling costs per sample was estimated to be three times less, compared to low-flow purging.

15. SUBJECT TERMS

Environmental Security Technology Certification Program (ESTCP); regenerated cellulose dialysis membrane samplers; dialysis samplers; final report; diffusion sampling; PDB samplers; ER-0313

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF **PAGES**	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
U	U	U			

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Final Technical Report

for

Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Ground Water Quality and Remediation Progress at DoD Sites (ER-0313)

by

U.S. Geological Survey
810 Bear Tavern Road, Suite 206
West Trenton, NJ 08628

Naval Facilities Engineering Service Center
1100 23rd Avenue
Port Hueneme, CA 93043-4370

Battelle
505 King Avenue
Columbus, OH 43201

ESTCP
Environmental Security
Technology Certification
Program

August 30, 2007

CONTENTS

FIGURES

TABLES

ABBREVIATIONS AND ACRONYMS

BTEX	Benzene, toluene, ethylbenzene, and xylenes
COC	Contaminant of concern
Dialysis	Regenerated cellulose dialysis membrane
DOC	Dissolved organic carbon
DoD	Department of Defense
GC-MS	Gas chromatography-mass spectrometry
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
ICP-MS	Inductively coupled plasma – mass spectrometry
ITRC	Interstate Technology Regulatory Council
LRL	Laboratory reporting level
LDPE	Low-density polyethylene
MDL	Minimum detection limit
MNA	Monitored natural attenuation
MTBE	Methyl tert-butyl ether
NAES	Naval Air Engineering Station
NAWC	Naval Air Warfare Center
NBVC	Naval Base Ventura County
NFESC	Naval Facilities Engineering Service Center
NJDEP	New Jersey Department of Environmental Protection
NTU	Nephelometric turbidity units
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PDB	Polyethylene diffusion bag
PVC	Polyvinyl chloride
QA/QC	Quality assurance/quality control
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
TDS	Total dissolved solids
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	Volatile organic compound

ACKNOWLEDGMENTS

Thomas Imbrigiotta of USGS, Joey Trotsky of NFESC, and Matt Place of Battelle all contributed to the writing of this report. John Dupont of DHL Analytical was responsible for arranging the efficient and consistent analysis of the samples collected in this study. Jeff Dale of the U.S. Navy was instrumental in encouraging and supporting the initial work on dialysis samplers at the NAWC West Trenton, New Jersey site that eventually led to this demonstration. Michael Figura of the U.S. Navy supplied well construction information and water-quality data and arranged access to the wells sampled at NAES Lakehurst, New Jersey. Ernest Lory, Dale Lorenzana, and Joseph Saenz of the U.S. Navy supplied well construction information and water-quality data and arranged access to the wells sampled at NBVC Port Hueneme, California. Steve Granade of the U.S. Navy supplied well construction information and water-quality data and arranged access to wells sampled at NBVC Point Mugu, California. Eric Best, Rob Rosman, Bonnie Gray, and Christine Wieben of the USGS helped in the collection of samples for this project. Theodore Ehlke of USGS and Ron Hoeppel of NFESC were instrumental in conceiving, proposing, and obtaining funding for this project.

EXECUTIVE SUMMARY

This final technical report documents the demonstration and validation of regenerated cellulose dialysis membrane diffusion samplers (dialysis samplers) for use in collecting ground water samples for a range of inorganic and organic water-quality parameters. This project, ER-0313, was funded by the Environmental Security Technology Certification Program (ESTCP). The primary objectives of the project were; (1) to determine the usefulness of dialysis samplers in collecting a range of organic and inorganic water quality constituents from ground water, (2) to determine the optimum equilibration times for these constituents to diffuse into the dialysis sampler, (3) to compare water quality results and sampling costs from samples collected with dialysis samplers to samples collected with a low-flow purging technique and polyethylene diffusion bag (PDB) samplers, and (4) to transfer the technology while gaining regulatory acceptance. Equilibration times were determined in bench-scale testing for major cations and anions, a suite of trace elements, volatile organic compounds (VOCs), and several natural attenuation parameters. Field comparisons were conducted at three Department of Defense (DoD) sites: (1) Naval Air Engineering Station (NAES) Lakehurst, New Jersey, (2) Naval Base Ventura County (NBVC), Port Hueneme and Point Mugu, California, and (3) Naval Air Warfare Center (NAWC) West Trenton, New Jersey. Samples collected with the three sampling techniques were compared graphically and statistically to determine the significance of any differences found.

Seven bench-scale equilibration tests were conducted that evaluated 22 cations and trace elements, 59 VOCs, 6 anions, silica, dissolved organic carbon, methane, and sulfide using ground water collected from the three field sites. Greater than 95% equilibrium was reached in regenerated cellulose dialysis membrane diffusion samplers within 1 to 3 days for all VOCs, all anions, silica, dissolved organic carbon, methane, and sulfide, and within 3 to 7 days for most cations and trace elements. Dialysis samplers equilibrated in a slightly shorter time period when inorganic constituent concentrations were higher. Lower temperatures were found to have a small effect in that they lengthened equilibration times for several inorganic constituents from 3 days to 7 days and several VOCs from 1 day to 3 days. The only parameters that did not equilibrate in the dialysis samplers were mercury, silver, and tin, which all took greater than 28 days to equilibrate. Because of their longer equilibration times, mercury, silver, and tin were not evaluated in the field comparisons. No trace elements or VOC concentrations were detected in the bench-scale test blanks, indicating that there was no desorption of any of these constituents from the dialysis membrane. Coefficients of variation for triplicate dialysis sampler analyses were generally less than 10% for most inorganics and less than 18% for all VOCs. Based on the results of the bench-scale testing, a 7-day equilibration time was chosen for dialysis samplers in the field demonstration.

The experimental design of the field demonstration was to sample ground water from 6 to 8 wells per site at the three DoD sites with each of three sampling methods; the dialysis sampler, the PDB sampler, and low-flow purging using a variable-speed submersible pump. Samples were collected at the same depth in each well using all three sampling techniques. In all cases, the dialysis and PDB 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 least one week. After the

diffusion samplers were retrieved and sampled, the pump 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 were analyzed at the same laboratory for the same suite of inorganic and organic water-quality constituents.

Results of the analyses for most VOCs showed excellent agreement between concentrations collected with dialysis samplers and PDB samplers and between concentrations collected with dialysis samplers and low-flow purging. For all 24 VOCs detected in the field demonstration, statistical testing showed dialysis samplers recovered median concentrations that were not significantly different from median concentrations recovered by PDB samplers. For 21 of 24 VOCs detected in the field demonstration, identical statistical testing showed dialysis samplers recovered median concentrations that were not significantly different from median concentrations recovered by low-flow purging. Results of the analyses for most inorganic constituents also showed excellent agreement between concentrations collected with dialysis samplers and low-flow purging. For 28 of 30 inorganic constituents, statistical testing showed dialysis samplers recovered median concentrations of inorganic constituents that were not significantly different from median concentrations recovered by low-flow purging.

Dialysis samplers were deployed in wells at the depth where the highest mass flux passed through the open interval. Vertical profiling by either hydraulic or chemical methods, or preferably both, was used to determine this depth. Dialysis samplers made with regenerated cellulose dialysis membrane must be kept hydrated between the time they are constructed and deployed. Purported limitations of dialysis 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.

Water samples collected with dialysis samplers were found to cost significantly less than samples collected with a low-flow purging procedure. Specifically, field sampling time (and hence field labor costs) were reduced by a factor of more than six times when dialysis samplers were used compared to low-flow purging. Overall, the total sampling costs per sample were estimated to be three times less for a sample collected with a dialysis sampler and one collected by low-flow purging. Besides being able to collect samples more inexpensively for a wide variety of inorganic and organic constituents in ground water, dialysis samplers were found to have the additional advantages that they were (1) 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 ground water samples, and (4) eliminated cross-contamination between wells because they were disposable.

1.0 INTRODUCTION

1.1 Background

Collection of ground-water samples for long-term monitoring or to assess remedial progress at contaminated Department of Defense (DoD) sites is very costly in terms of manpower, time, and equipment requirements. Currently, the standard technique for ground water 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 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 to prevent cross-contamination. 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 ground water samples with portable pumps or bailers is that the installation and removal of these sampling devices frequently results in increased turbidity in the ground water 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 ground water, 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 ground water sampling field time, equipment decontamination costs, and purge-water treatment costs, as well as 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 in a well. 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 is restricted in the volume of sample it can collect at a depth 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 (MNA) (such as nitrate, iron, sulfate, or alkalinity), highly soluble organic compounds (such as methyl tert-butyl ether (MTBE) or acetone), or most semi-volatile organic compounds (such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs)) (Interstate Technology Regulatory Council (ITRC), 2004).

Because it is usually necessary to collect samples for both inorganic and organic constituents when monitoring water quality and the progress of remediation at contaminated DoD sites, 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). This type of diffusion membrane sampler is constructed from commercially available tubular regenerated cellulose dialysis membrane. The dialysis membrane allows the passage of both dissolved inorganic and organic contaminants from ground water into the sampler. The regenerated cellulose dialysis membrane 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 dialysis 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 dialysis samplers are relatively low in cost, only slightly more than PDB samplers, and are disposable after one use. Dialysis samplers have been used to sample wells for major cations, anions and chlorinated VOCs. Demonstration of these regenerated cellulose dialysis membrane diffusion samplers for additional inorganic and organic constituents was performed as part of this project.

For the sake of brevity, throughout this report the regenerated cellulose dialysis membrane diffusion sampler will be referred to simply as the dialysis sampler.

1.2 Objectives of the Demonstration

1.2.1 Objectives of the Project

The purpose of this project was to demonstrate and validate the usefulness of regenerated cellulose dialysis membrane diffusion samplers for monitoring ground water at DoD sites. The main objectives of the project were as follows:

(1) To determine if the dialysis sampler will collect statistically valid samples for a variety of organic and inorganic chemical constituents relevant to the DoD for which there is no current information available,

(2) To determine the optimum equilibration period for these contaminants to diffuse into a dialysis sampler,

(3) To compare the sampling efficiency and cost of the dialysis sampler to quantitatively recover these contaminants from wells at field sites with samples collected using a PDB

sampler (for VOCs only), and the standard low-flow purging technique (for all ground water constituents), and

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

Objectives (1) and (2) were addressed during the pre-demonstration bench-scale testing at the USGS facility in West Trenton, New Jersey. The data generated during the field demonstration primarily were used to address objectives (3) and (4).

1.2.2 Objective of the Demonstration

The primary objective of the demonstration was to compare the sampling efficiency and cost of dialysis samplers in collecting ground water samples for a wide range of chemical constituents from wells at DoD field sites with the sampling efficiency and cost of the standard low-flow purging technique and PDB samplers (for VOCs only). Comparisons were done at the three sites that were used during the pre-demonstration portion of this study: (1) Naval Air Engineering Station (NAES) Lakehurst, New Jersey, (2) Naval Base Ventura County (NBVC), Port Hueneme and Point Mugu, California, and (3) Naval Air Warfare Center (NAWC) West Trenton, New Jersey. The chemical constituents that were sampled and compared included trace metals, VOCs, MTBE, and natural attenuation parameters. The field testing was conducted to demonstrate that samples collected using the dialysis samplers are less costly overall, generate less sampling derived wastewater, and produce samples of equal quality to those collected by low-flow purging. Moreover, the field testing evaluated whether the dialysis samplers collect samples containing more VOCs than the PDB samplers.

1.3 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; and Air Force 124 Plume Location and Source Identification; 131 Improved Remediation Monitoring Technologies; 1608 Find and Track Organic Contaminant Plumes; 1703 Technology to Track Transport and Fate of Heavy Metals; 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.

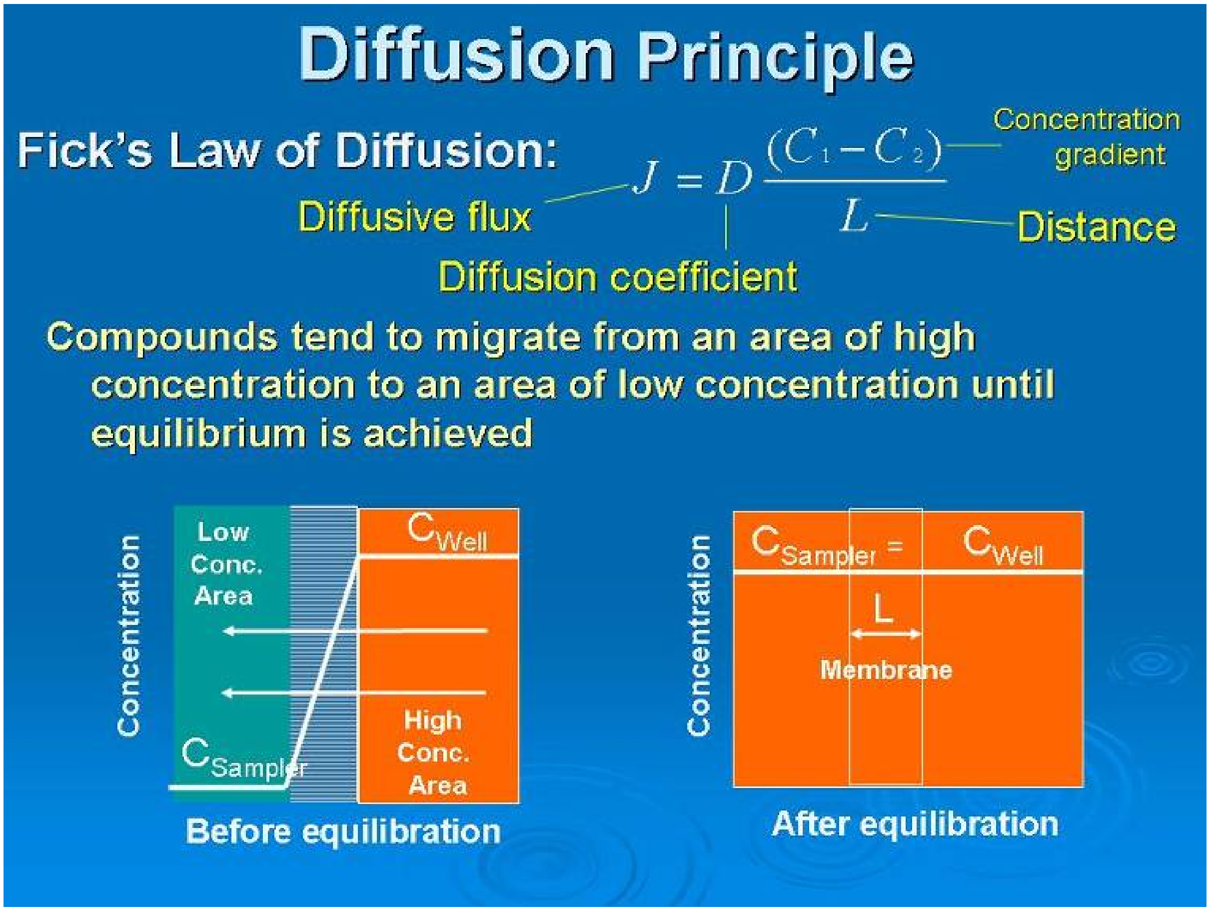
1.4 Stakeholder/End-User Issues

The most important stakeholder/end-user issue is whether the dialysis samplers can gain acceptance by State and Federal regulators as a stand-alone method for sampling wells for the contaminants tested. The publication of the findings of this demonstration plan should significantly increase the regulator’s acceptance of the dialysis samplers.

2.0 TECHNOLOGY DESCRIPTION

2.1 Technology Development and Application

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 ground water. 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 2-1). 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 diffusion of chemicals across a membrane.



Diffusion Principle

Fick's Law of Diffusion:

$$J = D\frac{(C_1 - C_2)}{L}$$

Concentration gradient

Diffusive flux

Distance

Diffusion coefficient

Compounds tend to migrate from an area of high concentration to an area of low concentration until equilibrium is achieved

Before equilibration

After equilibration

Figure 2-1. Diffusion Across a Membrane (Fick's Law of Diffusion)

Once the diffusion sampler has reached equilibrium, it is then 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 so that they do not allow the passage of suspended particulates into the sampler.

The dialysis samplers tested during this demonstration were constructed of regenerated cellulose. The membrane was obtained from Membrane Filtration Products, Inc., Sequin, Texas.[1] The membrane has a nominal molecular weight cut off of 8,000 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 a particular well and site.

Various components of the dialysis sampler are shown in Figures 2-2 through 2-5. Figure 2-2 shows the components of the sampler prior to assembly; Figure 2-3 shows the sampler partially constructed prior to being filled with deionized water, and Figure 2-4 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 dialysis sampler is pictured in Figure 2-5. 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 regenerated cellulose dialysis membranes and demonstrated that dialysis membranes could equilibrate with selected inorganics and VOCs in the laboratory. Imbrigiotta et al. (2002) used these dialysis samplers in actual field sampling at the NAWC West Trenton, NJ site during 2000-2002 and found that 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 dialysis sampler and tested it at several field sites and found that it compared well to low-flow purge samples for several aromatic VOCs. These dialysis samplers could potentially be used to replace pump sampling at virtually all DoD sites that require long-term monitoring of dissolved inorganic species and VOCs.

---

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

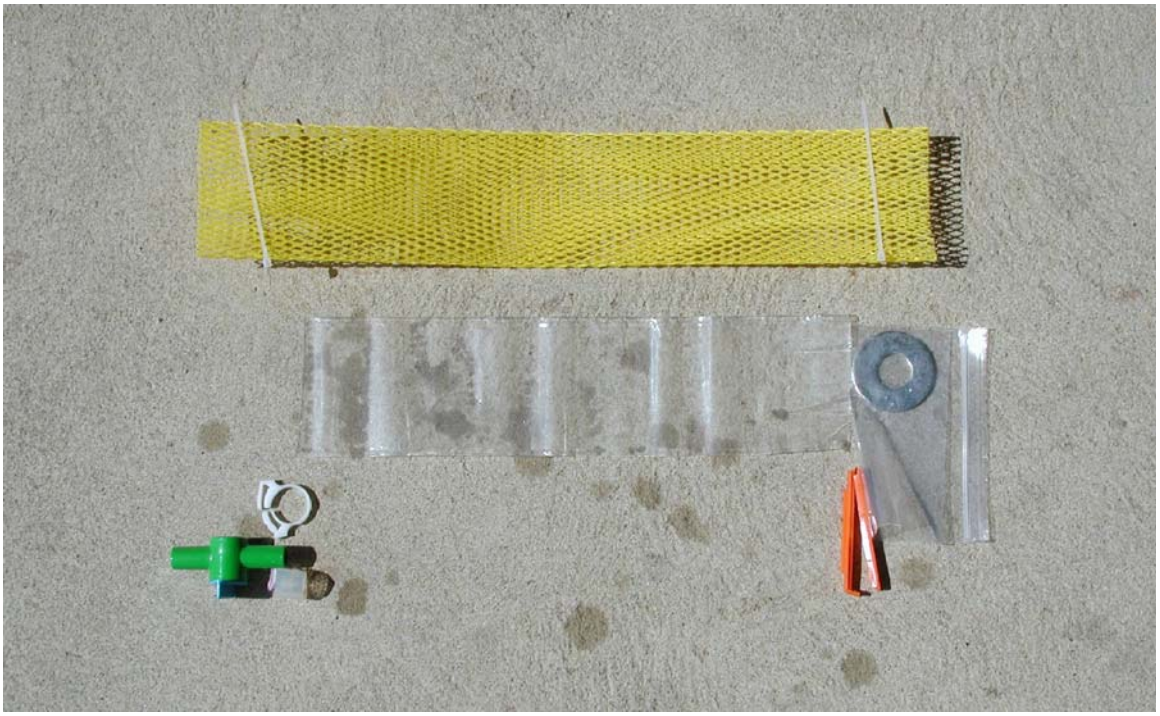


Figure 2-2. Disassembled Regenerated Cellulose Dialysis Membrane Diffusion Sampler, Showing Component Parts

Figure 2-3. Partially Assembled Regenerated Cellulose Dialysis Membrane Diffusion Sampler, Showing Protective Mesh and PVC Pipe External to the Membrane

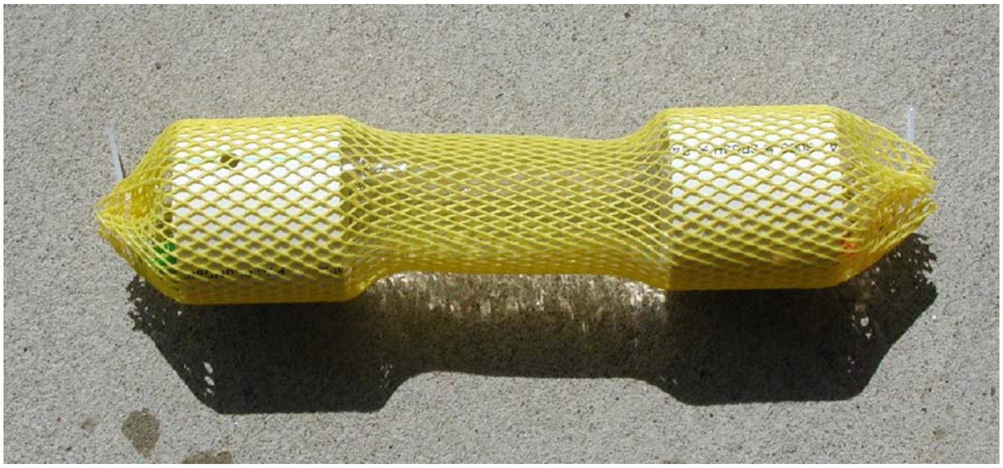


Figure 2-4. Assembled Regenerated Cellulose Dialysis Membrane Diffusion Sampler with PVC Pipe Sections External to the Membrane

Figure 2-5. Regenerated Cellulose Dialysis Membrane Diffusion Sampler With Perforated PVC Pipe Support Inside the Membrane

2.2 Previous Testing of the Technology

Prior to the start of the field demonstration, the dialysis sampler was used successfully in laboratory tests and in limited field tests for collecting chlorinated VOCs and selected dissolved inorganic ground water constituents (Ehlke et al. 2004; Imbrigiotta et al. 2002). When these samplers were evaluated during three annual sampling events (9 to 15 wells per event) at NAWC, West Trenton, New Jersey, using 1-week equilibration times, they showed good correlation with low-flow purging and modified conventional purging (high-flow purging followed by low-flow purging) results for both chlorinated VOCs and selected inorganic constituents. The results of statistical analyses showed no significant difference at the 95% confidence level between sampling techniques for all constituents tested.

Laboratory testing of equilibration times for selected anions and trace elements was also conducted by Vroblesky et al. (2002). They found that within 1-4 days all tested constituents reached equilibrium with the test ground water in their experiments. Leblanc (2003) tested the dialysis membranes for permeability to explosive compounds and found that 75-80% equilibration of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) concentrations were reached within 12 days at 4 ºC. More recently, Harter and Talozi (2004) found equilibration of specific conductance and nitrate was attained in 1-4 days at 21 ºC. Also, Parker and Mulherin (2006) conducted laboratory equilibration tests for HMX, 1,3,5-trinitrobenzene, RDX, and TNT (2,4,6-trinitrotoluene) at room temperature and found these explosive compounds equilibrated in dialysis samplers within 7 to 14 days.

Dialysis samplers have also been successfully tested in the field on a limited basis at Naval Air Station Fort Worth Joint Reserve Base, Texas (Vroblesky et al. 2002), at Hickam Air Force Base (AFB), Hawaii (Vroblesky and Pravecek, 2002), and at Andersen AFB, Guam (Vroblesky et al. 2003). These tests involved comparing dialysis samplers to PDB samplers for fuel-related VOCs and to low-flow purging for selected inorganic ions and trace elements. Their results showed good comparability for the dialysis samplers to the other sampling techniques for most compounds tested using a 2-week equilibration period. The authors pointed out that a shorter equilibrium period may have been possible for the dialysis samplers and would be advantageous so as to minimize the potential for membrane biodegradation, iron fouling, and gradual loss of sampler water volume. The latter can occur in high ionic strength ground water. Studies conducted by various researchers (Ehlke et al. 2004; Ronen et al. 1987; Magaritz et al. 1989; Vroblesky et al. 2002; Harter and Talozi, 2004) indicated that for most organic and inorganic chemical species, the equilibrium period is probably considerably less than 2 weeks.

Since the start of the field demonstration, a study by Harter and Talozi (2004) found that nitrate and specific conductance were sampled equally well by dialysis samplers and a conventional purging method. More recently, a study comparing a number of different diffusion samplers and purging technologies was conducted in 20 wells at McClellan Air Force Base, Sacramento, California (Parsons, 2005). Dialysis samplers, PDB samplers, rigid porous polyethylene samplers, polysulfone samplers, a downhole thief sampler, a disposable point-source bailer sampler, low-flow purging, and conventional purging were compared in samples analyzed for anions, trace metals, hexavalent chromium, 1, 4-dioxane, and VOCs. Results of the Parsons (2005) study indicated that dialysis samplers recovered concentrations of VOCs, anions, 1,4-

dioxane, and hexavalent chromium as well as or better than low-flow purging. Parsons (2005) noted that dialysis samplers generally recovered lower concentrations of trace metals than low-flow purging in their tests, although results for specific trace metals were not given. Overall, the dialysis sampler was rated equal to low-flow purging in Parsons (2005).

Extensive laboratory testing was conducted in the pre-demonstration portion of this project. The bench-scale testing was performed to determine the time required to reach equilibrium between the ground water (outside the dialysis sampler) and the water sample (inside the dialysis sampler). The overview of the results of the pre-demonstration testing is presented in Section 3.4 of this report.

2.3 Factors Affecting Cost and Performance

The number of wells that must be sampled at a site may affect the cost of deploying dialysis samplers due to savings that can be realized by economy of scale if a large number of samplers must be constructed at one time. A number of design parameters, such as, the diameter of the wells being sampled, the length of the open interval of the wells, and the volume of water needed for analysis, influence the size and cost of the dialysis samplers needed at a particular site. However, the cost for modifying the size of the dialysis samplers should be small and would not be expected to change the overall cost of a project significantly. Wells that have screens longer than 5 feet should be vertically profiled both chemically and hydraulically prior to sampling with passive sampling techniques (ITRC, 2004). The cost of vertically profiling (chemically and geophysically) needs to be calculated into the cost of sampling wells with these techniques.

Factors affecting the performance of the dialysis samplers include: the properties of chemical constituents to be sampled (for example, type of constituent – inorganic or organic, hydrophobicity or hydrophilicity) and the properties of the ground water (such as, ionic strength or temperature).

2.4 Advantages and Limitations of the Technology

The advantages and limitations of the dialysis sampler, the PDB sampler and low-flow purging are compared in Table 2-1.

Table 2-1. Advantages and Limitations of the Technology

Regenerated Cellulose Dialysis Membrane Diffusion Sampler (Dialysis)	Polyethylene Diffusion Bag Sampler (PDB)	Low-Flow Purging
Advantages		
No purge water is produced to drum, transport, or treat.	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.	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.	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 is minimized for field personnel.	Time in field can be 0.75-1.5 hours waiting for field parameters to stabilize.
Dialysis membrane is fairly inexpensive; slightly more than LDPE, but still far less than the cost of a pump setup.	LDPE membrane is very inexpensive.	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 only be used to sample for VOCs and methane.	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.	LDPE membrane does not need to be cleaned and can be kept dry or wet prior to use.	Pump must be cleaned prior to use.
Dialysis samplers lose water with time due to the nature of the dialysis process.	LDPE samplers do not lose water with time.	Not applicable.
Dialysis membranes are subject to attack by bacteria and fungi.	LDPE membranes are not attacked by bacteria and fungi.	Pumps are not affected by bacteria and fungi.
Sample volume is finite.	Sample volume is finite.	Sample volume is not limited.

The limitations of the dialysis 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 (<14 days). Results of tests conducted as part of this investigation supporting this statement will be discussed in more detail in sections 4.4.2.2.3 and 4.4.2.2.4.

3.0 DEMONSTRATION DESIGN

This section provides the primary performance criteria, the criteria and requirements used in selecting the test sites, test site description, pre-demonstration testing and analysis, testing and evaluation plan, selection of analytical and testing methods, and selection of analytical/testing laboratories.

3.1 Performance Objectives

The overall performance objective of this demonstration project was to evaluate the performance of dialysis samplers versus low-flow purging and PDB samplers and to compare their costs. The performance was evaluated by comparing the water-quality results from samples collected at the same depth using the three sampling techniques in a series of wells at three test sites. The primary performance criteria, expected performance, and actual performance objectives achieved are tabulated in Table 3-1 and are discussed in more detail in Section 4.

Table 3-1. Performance Objectives [Dialysis sampler, regenerated cellulose dialysis membrane sampler; PDB, polyethylene diffusion bag; $p<0.05$, 95 percent confidence level]

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met?
Qualitative	Dialysis samplers recover the same chemical parameters as low-flow purging and PDB samplers in the same well.	Chemical parameters detected in PDB and low-flow purging are the same detected by the dialysis sampler.	Yes.
	Dialysis membrane integrity is maintained over the course of equilibration.	No perforations noted during the course of the test.	Yes.
Quantitative	Dialysis samplers recover concentrations that are the same as those recovered by low-flow purging.	No significant difference (at $p<0.05$) between chemical concentrations recovered by the dialysis sampler and low-flow purging.	Yes, for 55 of 60 (92%) organic and inorganic compounds compared.
	Dialysis samplers recover concentrations that are the same as those recovered by PDB samplers.	No significant difference (at $p<0.05$) between chemical concentrations recovered by the dialysis sampler and the PDB sampler.	Yes, for 27 of 28 (96%) volatile organic compounds compared.
	Sensitivity – Dialysis samplers can sample low concentrations.	Concentrations within 2-5 times the detection limit can be detected.	Yes.
	Dialysis and PDB samplers take significantly less field time to collect samples than low-flow purging.	Comparison of field time required to sample dialysis and PDB samplers versus low-flow purging should be 5 times shorter.	Yes.

3.2 Selecting Test Sites

Field comparison demonstrations were done at the same three sites that were sampled for the pre-demonstration portion of this project; NAES Lakehurst, New Jersey, NBVC, Port Hueneme and Point Mugu, California, and NAWC West Trenton, New Jersey. These sites were chosen because of 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 water-quality analyses for a range of inorganic and organic contaminants of interest to this project, and
(4) the ground water at the sites had a wide range of concentrations of contaminants.

Based on these criteria, the chemical constituents analyzed for in samples collected from the three sites and the concentration ranges of the chemical constituents are shown in Table 3-2.

Table 3-2. List Of Sampled Sites [NAES, Naval Air Engineering Station; NJ, New Jersey; BTEX, benzene, toluene, ethylbenzene, and xylenes; VOCs, volatile organic compounds; µg/L, micrograms per liter; NBVC, Naval Base Ventura County; CA, California; MTBE, methyl-tert-butyl ether; NAWC, Naval Air Warfare Center]

Site	Chemical Constituents	Concentration Ranges
NAES, Lakehurst, NJ	Trace metals, BTEX VOCs	VOCs <1-700 µg/L Trace metals <1-40,000 µg/L Methane <1-5,600 µg/L Sulfide <10-1,300 µg/L
NBVC, Port Hueneme, CA NBVC, Point Mugu, CA	BTEX, MTBE Trace metals	VOCs <1-8,000 µg/L Trace metals <1-7,000 µg/L Methane <1-3,000 µg/L Sulfide <10-7,500 µg/L
NAWC, West Trenton, NJ	Chlorinated VOCs, trace metals, monitored natural attenuation parameters (sulfide, methane)	VOCs <1-32,000 µg/L Trace metals <1-7,700 µg/L Methane <1-50 µg/L Sulfide <10-120 µg/L

3.3 Test Site Descriptions

Naval Air Engineering Station (NAES) Lakehurst, New Jersey is located approximately 15 miles west of the Atlantic coast in south-central New Jersey. The wells that were sampled for the field demonstration are screened in a shallow unconsolidated sand-and-gravel aquifer in the coastal plain of New Jersey (Figures 3-1 and 3-2). Ground water flows generally west to east towards a wetland area on the eastern side of the base. The primary contaminants at this site are aromatic VOCs (BTEX compounds) and trace metals. The ground water at this site had fairly low ionic strength with total dissolved solids (TDS) concentrations ranging from <10 to 280 milligrams per liter (mg/L). The Standard Industrial Classification (SIC) codes for these areas are 5541 (gasoline filling stations-retail) and 8711 (engineering services: industrial, civil, electrical, mechanical, petroleum, marine, and design).

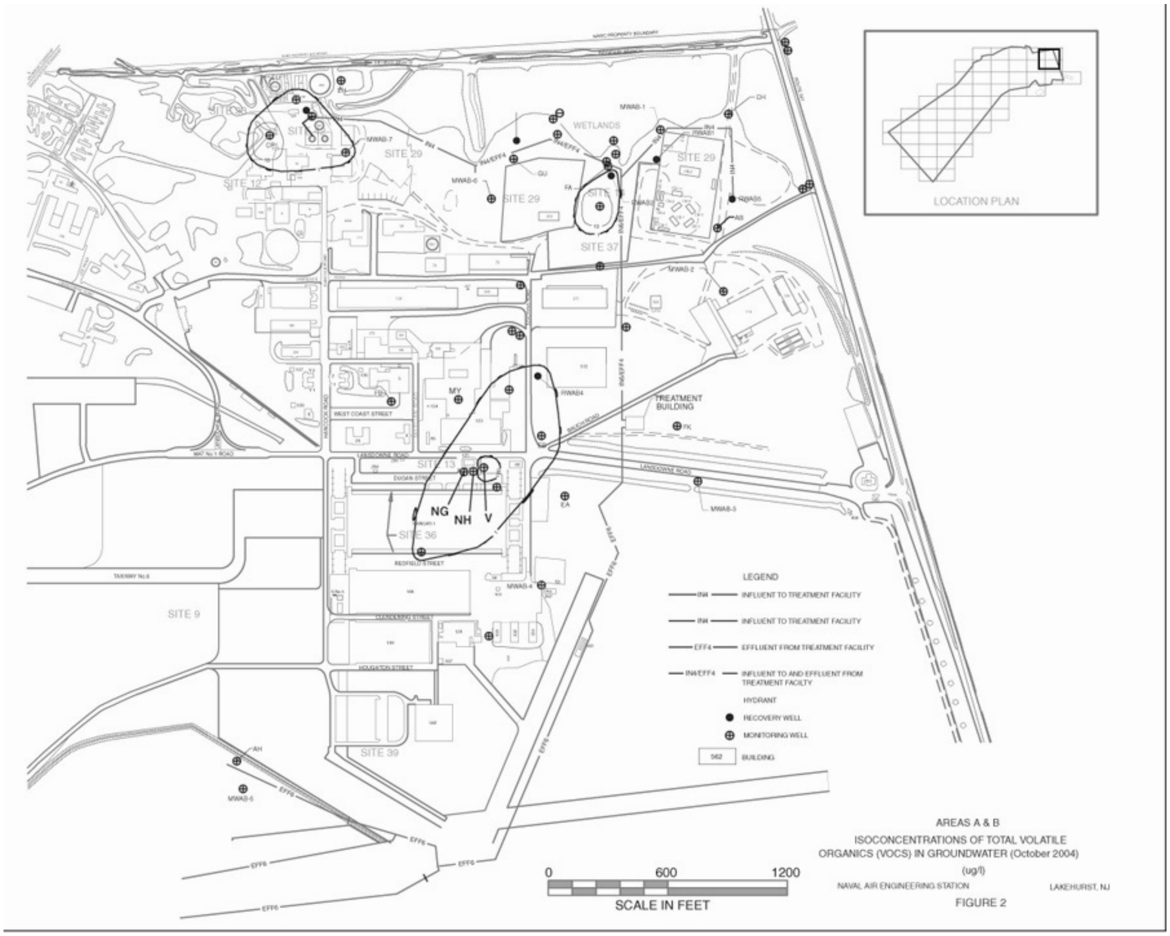


Figure 3-1. Wells Sampled As Part Of The Field Demonstration In Areas A and B At The Naval Air Engineering Station, Lakehurst, New Jersey.

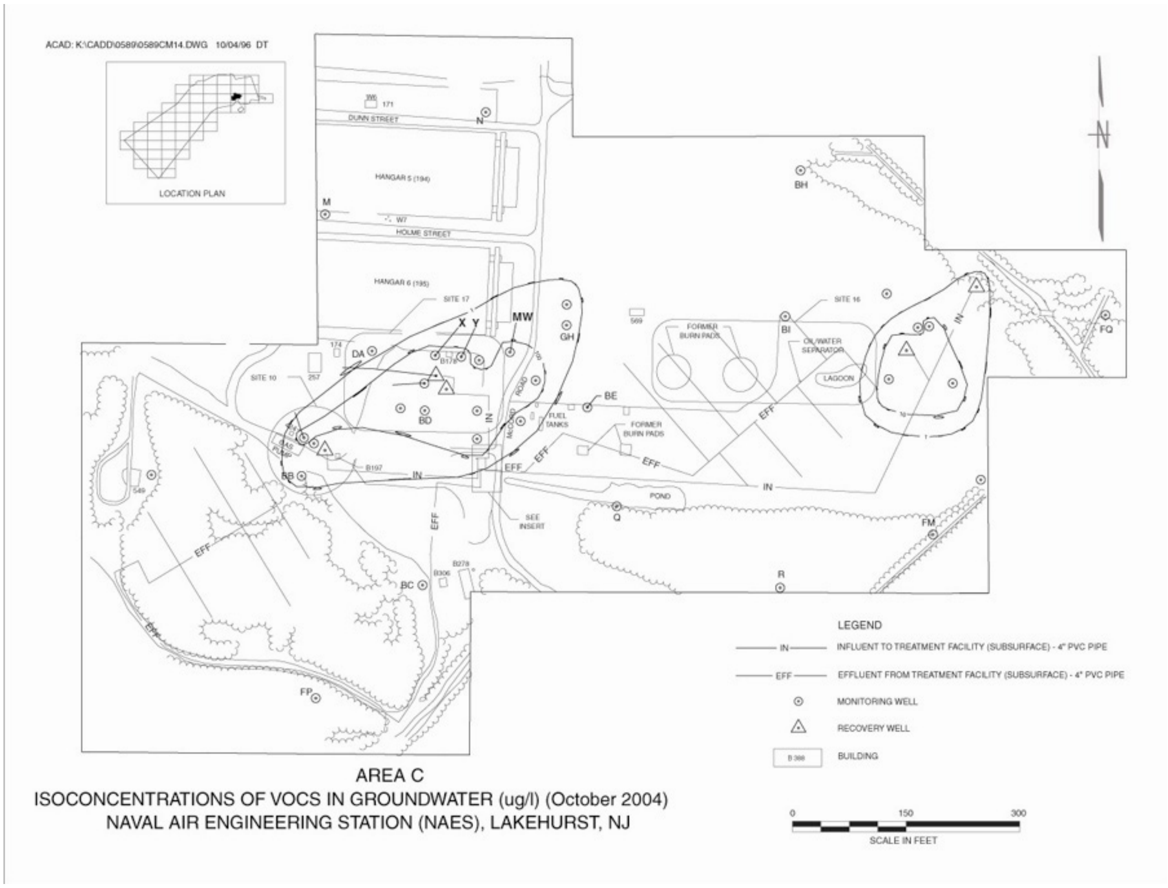


Figure 3-2. Wells Sampled As Part Of The Field Demonstration In Area C At The Naval Air Engineering Station, Lakehurst, New Jersey.

Naval Base Ventura County (NBVC), Port Hueneme and Point Mugu, are located within 1 mile of the Pacific coast near Oxnard, California. The wells that were sampled as part of the demonstration are screened in a shallow sand-and-gravel aquifer (Figures 3-3 and 3-4). Ground water generally flows from northeast to southwest towards the Pacific Ocean. The primary contaminants at Port Hueneme are aromatic VOCs (BTEX compounds) and MTBE. The contaminants of concern at Point Mugu are trace metals. The ground water at the NBVC sites had fairly high ionic strength with TDS concentrations ranging from 744 to 2320 mg/L. The SIC codes for these areas are 5541 (gasoline filling stations-retail) and 3559 (metal finishing equipment for plating, except rolling mill lines-mfg).

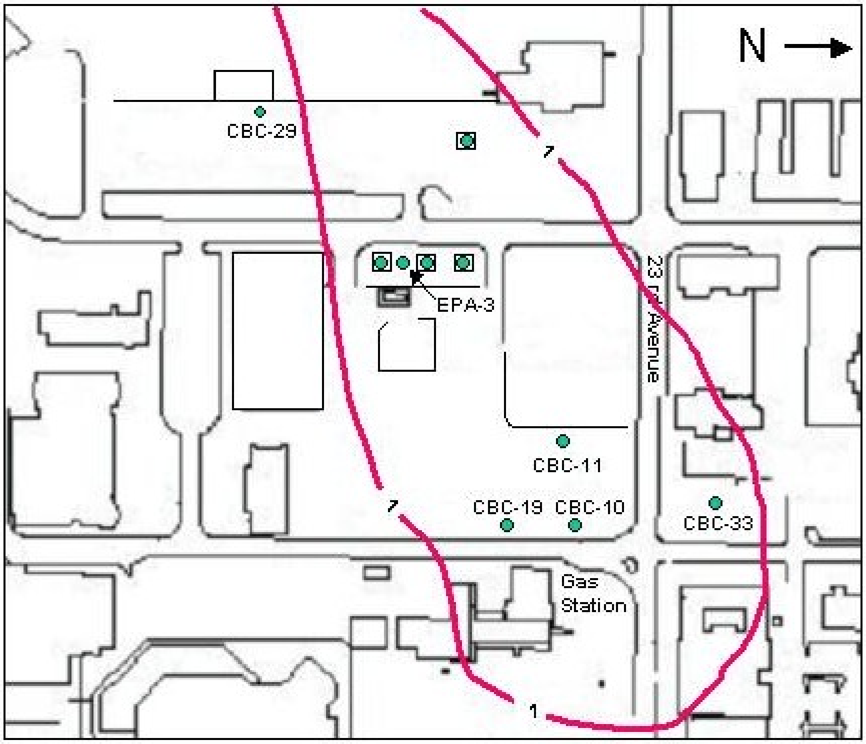


Figure 3-3. Wells Sampled As Part Of The Field Demonstration At Naval Base Ventura County, Port Hueneme, California

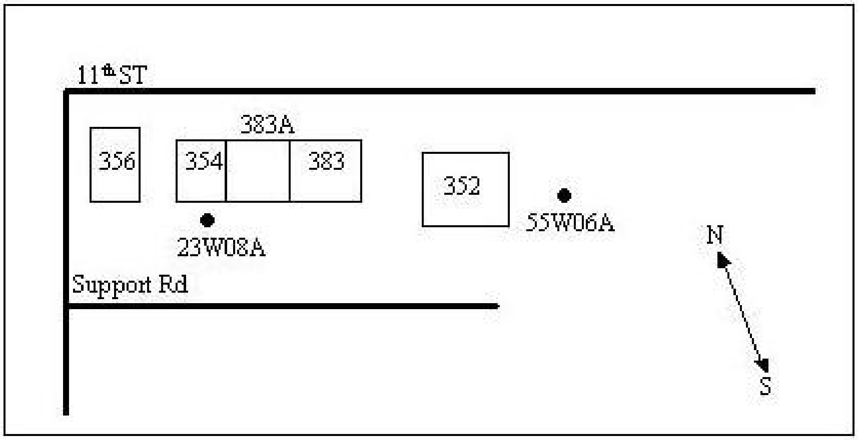


Figure 3-4. Wells Sampled As Part Of The Field Demonstration At Naval Base Ventura County, Point Mugu, California

Naval Air Warfare Center (NAWC) is located 5 miles north of Trenton in west-central New Jersey. The wells that were sampled as part of the demonstration are fractured bedrock wells set in the Lockatong formation of the Newark Basin which is composed primarily of mudstones and siltstones (Figure 3-5). Ground water flow is generally northeast to southwest across the site along the strike of the bedrock fractures towards the Delaware River. The primary chemicals of interest at NAWC are chlorinated VOCs and monitored natural attenuation parameters, such as methane, carbon dioxide, sulfide, sulfate, and dissolved iron. The ground water at this site had fairly low ionic strength with TDS concentrations ranging from 58 to 485 mg/L. The SIC codes for this site include 3724 (engines and engine parts, aircraft: internal combustion and jet propulsion-mfg), 8711 (engineering services: industrial, civil, electrical, mechanical, petroleum, marine, and design), 3569 (testing chambers for altitude, temperature, ordnance, and power-mfg), and 3724 (cooling systems, aircraft engine-mfg).

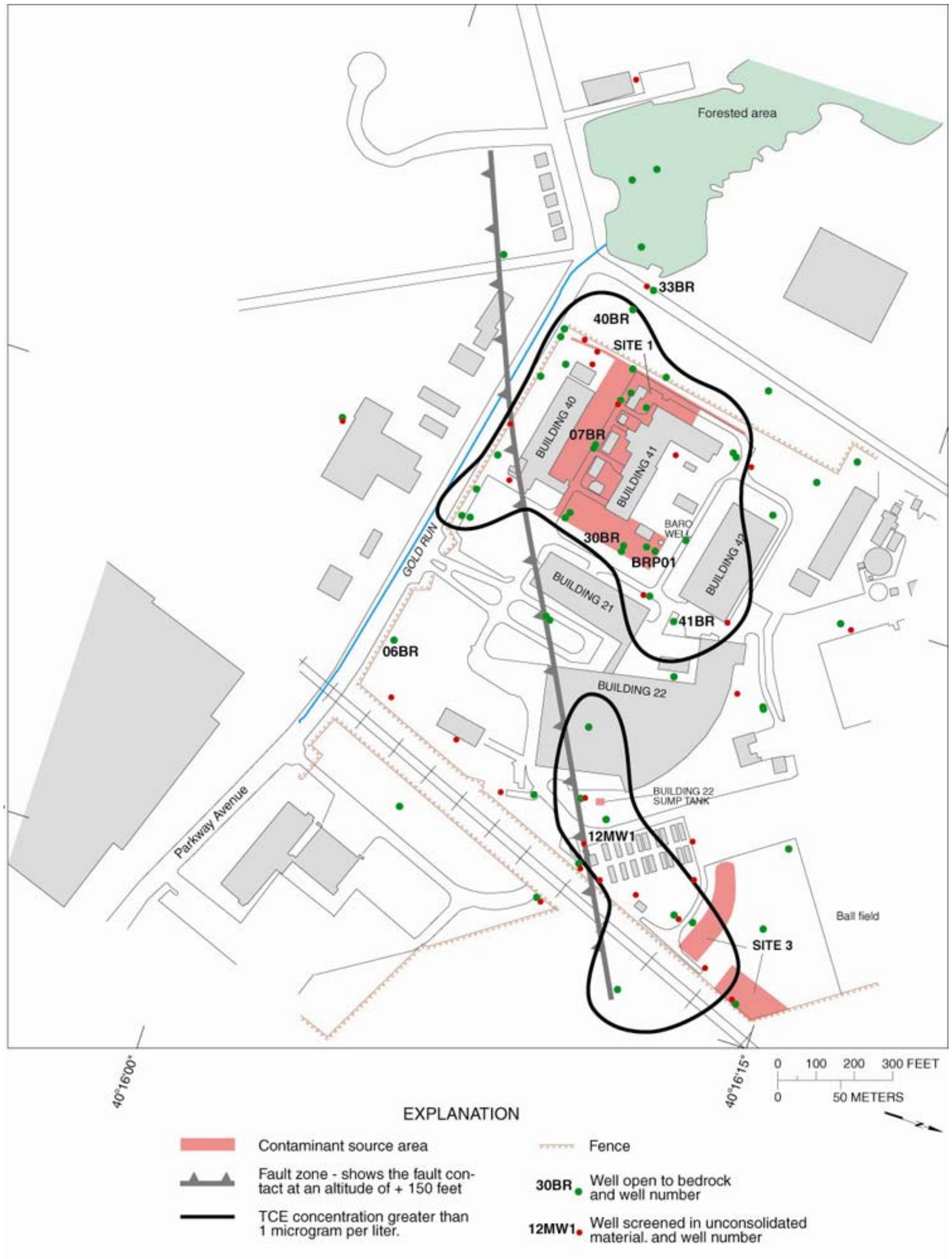


Figure 3-5. Wells Sampled As Part Of The Field Demonstration At Naval Air Warfare Center, West Trenton, New Jersey.

3.4 Pre-Demonstration Testing and Analysis

A significant portion of this project involved pre-demonstration testing of which chemical constituents would diffuse through the dialysis membrane and how long these chemicals would take to attain equilibrium with the ground water. An Interim Progress Report was written and submitted to ESTCP in September 2004 detailing the results of the pre-demonstration testing completed prior to that date. Additional bench-scale work involving testing the effect of different water temperatures and concentrations on equilibration times, and testing the suitability of other chemical constituents to diffuse through the dialysis membrane were completed after the September 2004 progress report. A summary of all pre-demonstration testing, including the more recent results, is given in this section.

During the pre-demonstration portion of this project, water samples from the chosen field sites were collected and brought back to the laboratory to conduct bench-scale equilibration tests. Seven bench-scale equilibration tests were conducted that evaluated 22 cations and trace metals, 59 VOCs, 6 anions, silica, dissolved organic carbon, methane, and sulfide (Table 3-3). During the bench-scale testing, dialysis samplers filled with deoxygenated deionized water were placed into containers containing ground water field samples that had been spiked with known concentrations of the chemicals being tested. Ground-water test solutions were stirred once per day for the duration of the testing to minimize any concentration stratification. After specified times (0, 1, 3, 7, 14, and 28 days of equilibration), a dialysis sampler was removed and sampled. A sample of the ground water test solution was also collected at each time step. 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 dialysis sampler to be at least 95% of the concentration in the ground water test solution outside the sampler. Initially, all tests were run at room temperature (21^{o}C). However, because ground water temperatures across the continental U.S. are usually lower than this, parts of several tests were conducted at 10 ^{o}C in an incubator. In addition, the effect of concentration was evaluated by varying the concentrations of the chemical constituents used in portions of selected tests. The equilibration times determined for the chemical constituents in the bench-scale tests were used to guide the time needed for the dialysis samplers to equilibrate in the wells during the field demonstration.

Table 3-3. Chemical Constituents Tested In Bench-Scale Tests

Bench-Scale Test 1 (200 μg/L; 21°C)			
Aluminum	Calcium	Lead	Nickel
Arsenic	Chromium	Magnesium	Potassium
Barium	Copper	Manganese	Sodium
Cadmium	Iron	Mercury	Zinc
Bench-Scale Test 2 (100 μg/L; 21°C)			
1,1,1,2-Tetrachloroethane	1,2-Dichloropropane	Chlorobenzene	n-Propylbenzene
1,1,1-Trichloroethane	1,3,5-Trimethybenzene	Chloroethane	Naphthalene
1,1,2,2-Tetrachlorethane	1,3-Dichlorobenzene	Chloroform	o-Xylene
1,1,2-Trichlroethane	1,3-Dichloropropane	Chloromethane	p-Isopropyltoluene
1,1-Dichloroethane	1,4-Dichlorobenzene	cis-1,2-Dichloroethene	sec-Butylbenzene
1,1-Dichloroethene	2,2-Dichloropropane	Dibromochloromethane	Styrene
1,1-Dichloropropene	2-Chlorotoluene	Dibromomethane	tert-Butylbenzene
1,2,3-Trichlorobenzene	4-Chlorotoluene	Dichlorodifluoromethane	Terachloroethene
1,2,3-Trichloropropane	Benzene	Ethylbenzene	Toluene
1,2,4-Trichlorobenzene	Bromobenzene	Hexachlorobutadiene	trans-1,2-Dichloroehene
1,2,4-trimethylbenzene	Bromochloromethane	Isopropylbenzene	Trichloroethene
1,2-Dibromo-3-chloropropane	Bromodichloromethane	m-Xylene	Trichlorofluoromethane
1,2-Dibromoethane	Bromoform	p-Xylene	Vinyl chloride
1,2-Dichlorobenzene	Bromomethane	Methylene chloride	
1,2-Dichloroethane	Carbon tetrachloride	n-Butylbenzene	
Bench-Scale Test 3 (1-600 mg/L; 21°C)			
Alkalinity/Bicarbonate *(50-500 mg/L)*	Chloride *(100 mg/L)*	Fluoride *(1 mg/L)*	Silica *(2-25 mg/L)*
Bromide *(1 mg/L)*	Dissolved organic carbon (sodium benzoate) *(5 mg/L)*	Nitrate as N *(3 mg/L)*	Sulfate *(20-600 mg/L)*
Bench-Scale Test 4 (30-100 μg/L; 10°C and 21°C)			
All compounds tested in bench-scale test 2 *(30 μg/L)*		methyl tert-butyl ether *(100 μg/L)*	
Bench-Scale Test 5 (30-100 μg/L; 21°C)			
Methane	Sulfide		
Bench-Scale Test 6 (10-200 μg/L; 10°C and 21°C)			
All elements tested in Bench-Scale Test 1		Selenium	Tin
Antimony	Molybdenum	Silver	Vanadium
Bench-Scale Test 7 (100 μg/L; 10°C and 21°C)			
Sulfide			

Equilibrium was reached in dialysis samplers within:

- 1 to 3 days for arsenic, aluminium, potassium, sodium, and selenium,
- 3 to 7 days for barium, calcium, cadmium, chromium, copper, iron, magnesium, manganese, nickel, lead, vanadium, and zinc, and
- 28 days or more for mercury, silver, and tin,

at temperatures tested (10 °C and 21 °C). The effect of temperature was small but observable in that some cations and trace elements took longer to equilibrate (1 day compared to 3 days or 3 days compared to 7 days) when tested at 10 °C compared to 21 °C. In all cases, except for mercury, silver, and tin, equilibration of cations and trace elements was achieved within one week. In addition, it was found that cations and trace elements present at high concentrations tended to equilibrate slightly faster than when they were present at low concentrations. However, all cations and trace elements, except mercury, sliver, and tin, equilibrated within one week at all concentrations tested.

The reasons mercury, silver, and tin did not equilibrate within the same time frame as all the other cations and trace elements tested are uncertain. All three were severely affected by the colder test temperature (10 °C). These metals are known to form complexes with humic and fulvic acids present in natural waters. It is possible that these complexes take longer to diffuse through the dialysis membrane. Organic complexes would be expected to move slower than smaller ions at reduced temperatures. Because of long equilibration times, mercury, silver, and tin were not evaluated in the field comparisons.

Cations and trace elements were not detected in the blanks, indicating that there was no desorption of these elements from the dialysis membrane. Coefficients of variation for triplicate analyses of water from the dialysis sampler were <6% for most cations and trace elements tested. Only silver, iron, and mercury had higher variations, 5-7%, 6-10%, and 14-17%, respectively.

Equilibrium was reached in dialysis samplers within

- 1 to 3 days for 59 VOCs tested.

The VOCs were compounds included in the USEPA SW-846 8260B analysis, including MTBE. The effect of temperature was slight in that most VOCs equilibrated in one day at 21 °C and in three days at 10 °C. Decreasing the concentrations of VOCs from 100 μg/L to 25 μg/L did not affect the equilibration time of VOCs in the dialysis samplers. No desorption of VOCs was found from any of the dialysis sampler blanks. Coefficients of variation of triplicate analyses of water from the dialysis sampler for 51 of the 59 VOCs were less than 5%. All VOCs had coefficients of variation less than 18%.

In general, VOCs equilibrated faster than many cations and trace elements given ground water of the same temperature. Because the diffusion mechanism is the same, the differing equilibration rates may have resulted from trace elements forming less mobile organic complexes or the fact that dialysis membranes normally carry a slight negative electrostatic charge. Because most VOCs are neutral molecules they were not affected by this charge on the membrane. However, the inorganic constituents were primarily present in ground water as charged species, so they may have been affected by the charge on the membrane. Positively charged species may be attracted by the negative electrostatic charge of the membranes. Thus, diffusion rates for some cations and trace elements through the membrane could have been slowed by this exchange phenomenon which acted on these constituents in addition to the primary driving force of the concentration gradient across the membrane.

Equilibrium was reached in dialysis samplers within:

- 1 day for bromide, chloride, and nitrate, and
- 1 to 3 days for alkalinity (bicarbonate), fluoride, sulfate, silica, and dissolved organic carbon.

Bench-scale test 3 was carried out at 21 ^{o}C only so no effect of temperature could be determined. A few anions (alkalinity and sulfate) were present in higher concentrations in samples from the Port Hueneme site compared to samples from the New Jersey sites. For these anions, higher concentrations tended to equilibrate slightly faster (1 day versus 3 days). No desorption of anions, silica, or dissolved organic carbon was observed from the dialysis samplers, except for a few very low concentrations of chloride (<1.6 mg/L), fluoride (<0.18 mg/L), and sulfate (<1.1 mg/L) in isolated samples. Coefficients of variation of triplicate analyses of water from dialysis samplers were less than 7% for all anions, silica, and dissolved organic carbon.

Equilibrium was reached in dialysis samplers within:

- 1 day for methane, and
- 1 day for sulfide in one test and an indeterminate length of time in another test.

Bench-scale test 5 for methane was carried out only at 21 ^{o}C so no temperature effect could be determined. No concentration effect was noted for methane. Concentrations of 1 μg/L methane were detected consistently in the dialysis sampler blanks which may be due to methane not being completely removed from the deionized water used in the test solutions. Coefficients of variation of triplicate dialysis samplers were less than 9%.

It is believed that bench-scale test 7 for sulfide gave inconsistent results because the containers failed to remain sealed after the first few days of the tests. One test reached equilibrium after only one day, but then could not maintain equilibration over the duration of the test. The second test reached approximately 60% equilibrium after one day, but then it too could not maintain equilibration over the rest of the test. If sulfide from the test solutions was volatilizing and leaking from the containers, this would set up a concentration gradient of sulfide out of the dialysis sampler into the test solution and could account for these findings. Sulfide was initially not present in the dialysis sampler blanks, but was detected at day 3 and thereafter at concentrations ranging from 10-24 μg/L. One possible explanation is that sulfide desorbed from the dialysis sampler over time. Another possible explanation is that sulfide leaking from the other containers contaminated the adjacent blank test containers. Coefficients of variation of triplicate analyses of water from dialysis samplers ranged from 27-65% primarily because most values were at or near the detection limit. Because rapid sulfide equilibration was achieved in one test, this parameter was included in the field comparison testing.

The findings of all pre-demonstration plan bench-scale testing are summarized in Table 3-4.

Table 3-4. Summary Of All Bench-Scale Testing Results: Suitability And Equilibration Times Of All Chemicals Tested.

Favorable Bench-Scale Equilibration Testing Results		
VOCs (1-3 day equilibration times at 10°C and 21°C)		
1,1,1-Trichloroethane	cis-1,2-Dichloroethene	1,2-Dibromo-3-chloropropane
1,1,2,2-Tetrachloroethane	Dibromomethane	1,3,5-Trimethylbenzene
1,1,2-Trichloroethane	Dichlorodifluoromethane	1,3-Dichloropropane
1,1-Dichloroethene	Ethylbenzene	2,2-Dichloropropane
1,2,3-Trichloropropane	m-Xylene	2-Chlorotoluene
1,2,4-Trimethylbenzene	Naphthalene	4-Chlorotoluene
1,2-Dibromoethane	o-Xylene	Bromobenzene
1,2-Dichlorobenzene	p-Xylene	Bromochloromethane
1,2-Dichloroethane	Tetrachloroethene	Bromomethane
1,2-Dichloropropane	Toluene	Hexachlorobutadiene
1,3-Dichlorobenzene	trans-1,2-Dichloroethene	Isopropylbenzene
1,4-Dichlorobenzene	Trichloroethene	Methyl tert-butyl ether
Benzene	Trichlorofluoromethane	Methylene chloride
Bromodichloromethane	Vinyl chloride	n-Butylbenzene
Bromoform	1,1,1,2-Tetrachloroethane	n-Propylbenzene
Carbon tetrachloride	1,1-Dichloroethane	p-Isopropyltoluene
Chlorobenzene	Dibromochloromethane	sec-Butylbenzene
Chloroethane	1,1-Dichloropropene	Styrene
Chloroform	1,2,3-Trichlorobenzene	tert-Butylbenzene
Chloromethane	1,2,4-Trichlorobenzene	
Cations and Trace Elements (1-7 day equilibration times at 10°C and 21°C)		
Calcium	Barium	Molybdenum
Magnesium	Cadmium	Nickel
Potassium	Chromium	Selenium
Sodium	Copper	Vanadium
Aluminum	Iron	Zinc
Arsenic	Lead	
Antimony	Manganese	
Anions (1-3 day equilibration times at 21°C)		
Bicarbonate/Alkalinity	Chloride	Nitrate
Bromide	Fluoride	Sulfate
Other Constituents (1-3 day equilibration times at 10°C and 21°C)		
Dissolved organic carbon	Silica	Methane
Sulfide		

Table 3-4. Summary Of All Bench-Scale Testing Results: Suitability And Equilibration Times Of All Chemicals Tested (Continued).

Unfavorable Bench-Scale Equilibration Testing Results		
(Greater than 28 day equilibration times at 10°C and 21°C)		
Mercury	Silver	Tin

3.5 Testing and Evaluation Plan.

This section provides information on the demonstration installation and start-up, the period of operation, residual handling, requirements for use of the technology, experimental design, sampling plan, demobilization, analytical test methods, and analytical laboratories used in this field demonstration. Additionally, details are given on the sampler construction, sampler deployment, sample frequency, tested chemical constituents, sample collection, sample preservation, field sample handling procedures, sampler cleaning, quality assurance/quality control procedures, sample analysis, and analytical calibration procedures used. This field demonstration project did not involve any treatment of materials, cleanup activities, structural decontamination, or the use of any major equipment.

3.5.1 Demonstration Installation and Start-up

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. Dialysis samplers and PDB samplers were constructed within 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. If contaminated purge water had to be drummed at a site, the Site Manager was contacted in advance of the start of the field test to obtain the drums and make arrangements for transport and treatment of the purge water collected. The wells sampled during the field demonstrations are shown in Figures 3-1 to 3-5.

3.5.2 Period of Operations

The period of operations at each of the field demonstration sites is given in Table 3-5 below. A total of four field demonstrations were conducted at the three field sites. The dialysis and PDB samplers were deployed in the test wells at least one week prior to the collection of samples. On the sample collection date, the dialysis and PDB samplers were removed from the test wells and sampled prior to the pump installation and collection of samples by low-flow purging.

Table 3-5. Periods Of Operations At Field Demonstration Sites

Site	Diffusion Sampler Deployment Dates	Sample Collection Dates
NAES, Lakehurst, NJ	December 14, 2004	December 21-22, 2004
NBVC, Port Hueneme, CA NBVC, Point Mugu, CA	February 22-24, 2005	March 2-4, 2005
NAWC, West Trenton, NJ	April 19-21, 2005	April 26, 2005 and May 4-5, 2005
NAES, Lakehurst, NJ	June 29, 2005	July 6-8, 2005

3.5.3 Amount/Treatment Rate of Material to be Treated

Under this demonstration no treatment of environmental media was performed.

3.5.4 Residuals Handling

Almost all of the water contained in the dialysis samplers and the PDB samplers was used to fill sample containers and sent to the laboratory for analysis. Essentially no residuals were produced by sampling these samplers. The empty dialysis and PDB samplers were properly disposed of at each site.

Low-flow pumping of each well 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 at each site were followed.

3.5.5 Requirements for Use of the Technology

Dialysis 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. Dialysis samplers can be installed easily by one person and retrieved and sampled easily by two persons. Dialysis samplers require that ground water be moving through the open interval of a well past the sampler to collect a sample representative of the ground water in the aquifer.

Dialysis samplers, as well as PDB samplers and 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. This depth should be determined if at all possible by vertical profiling the open interval of the 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.

If the open interval of a well is 5 feet (ft) or less, no vertical profiling is deemed necessary and the dialysis or PDB 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 dialysis 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. The depth where the concentration times the input flow is greatest is the depth of highest mass influx.

The length of a dialysis sampler should be determined by several factors. A dialysis sampler's length should enclose the volume needed for the analyses that will be conducted on the sampled water. The length of a dialysis sampler should be limited to the shortest of the following constraints; (1) 5 ft, (2) the open interval being sampled, or (3) the length of the zone of highest mass flux present in the open interval.

3.5.6 Experimental Design

The experimental design of the field demonstration was to sample ground water from 6 to 8 wells per test site at the three test sites with each of three sampling methods -- the dialysis sampler, the PDB sampler, and low-flow purging using a variable-speed submersible pump. Samples were collected at the same depth in each well using all three sampling techniques. Analytical results were compared both graphically (using 1:1 correspondence plots) and statistically (using analysis of variance (ANOVA) techniques) to determine if there were significant differences between samples collected with each sampling method by chemical constituent. Results for chemical constituents present at more than one site were combined to increase the power of the statistical comparisons to determine if differences existed between sampling methods.

Ground water containing major cations and anions, trace elements, VOCs, dissolved gases, sulfide, silica, total dissolved solids, and dissolved organic carbon was sampled at the three sites included in the field demonstration plan. Concentrations typically ranged from the detection limit up to 2 to 4 orders of magnitude higher for most chemical constituents. Ground waters with a range of ionic strengths (TDS from 32 to 2080 mg/L), pH's (4.8 to 8.9), temperatures (13.1 to 25.4 ^{o}C), and dissolved oxygen concentrations (<0.1 to 9.3 mg/L) were sampled in the field demonstrations.

Table 3-6 details 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. This table also shows that a total of four field comparison demonstrations were conducted at the three field sites over the course of this study.

Table 3-6. Wells Sampled During The Field Demonstrations

[ft blse, feet below land surface elevation; PVC, polyvinyl chloride; Dialysis, regenerated cellulose dialysis membrane diffusion sampler; PDB, polyethylene diffusion bag sampler; low-flow, low-flow purging; Dup, duplicate; Dialysis 1 and Dialysis 2, in one 2-inch diameter well (EPA3) the dialysis sampler consisted of two bags to collect a sufficient sample volume]

Site and Date	Well Name	Well Dia-meter (inches)	Casing Mater-ial	Total Depth (ft blse)	Open Interval Depth (ft blse)	Water Level (ft blse)	Sampling Technique	Sample Depth (ft blse)
NAES Lakehurst, NJ December 2004	V	2	PVC	49	34-49	34.25	Dialysis Dialysis-Dup PDB Low-Flow	34.9 – 38.2 38.2 – 41.5 41.5 – 42.8 37.9
(See Figures 3-1 and 3-2)	NH	2	PVC	46	31-46	34.52	Dialysis PDB Low Flow	36.3 – 39.6 39.6 – 41.0 39.0
	NG	2	PVC	46	31-46	34.25	Dialysis PDB PDB Low-Flow	36.4 – 39.7 39.7 – 41.1 41.1 – 42.4 39.0
	MW	2	PVC	22	2-22	6.63	Dialysis PDB Low-Flow	8.0 – 11.3 11..3 – 12.7 10.0
	X	2	PVC	17	2-17	6.87	Dialysis PDB Low-Flow	7.2 – 10.5 10.5 – 11.9 9.2
	Y	2	PVC	17	2-17	6.80	Dialysis PDB Low-Flow	7.4 – 10.7 10.7 – 12.2 9.4
NBVC Port Hueneme, and Point Mugu, CA March 2005	CBC33	4	PVC	25	5-25	11.84	Dialysis PDB Low-Flow	15 – 17 17 – 18 16
(See Figure 3-3 and 3-4)	EPA3	2	PVC	27	7-27	9.12	Dialysis 1 Dialysis 2 PDB PDB-Dup Low-Flow	14 – 16 16 – 18 18 – 19 19 – 20 15
	CBC29	4	PVC	25	5-25	7.05	Dialysis PDB Low-Flow	13 – 15 15 – 16 14
	55W06A	4	PVC	14	4-14	2.49	Dialysis PDB Low-Flow	8 – 10 10 – 11 9
	23W08A	4	PVC	14	4-14	3.44	Dialysis PDB Low-Flow	8 – 10 10 – 11 9

Table 3-6. Wells Sampled During The Field Demonstrations (Continued)

Site and Date	Well Name	Well Dia-meter (inches)	Casing Mater-ial	Total Depth (ft blse)	Open Interval Depth (ft blse)	Water Level (ft blse)	Sampling Technique	Sample Depth (ft blse)
NBVC Port Hueneme and Point Mugu, CA March 2005 (continued)	CBC19	4	PVC	25	5-25	8.10	Dialysis Dialysis-Dup PDB PDB-Dup Low-Flow Low-Flow-Dup	18 – 20 19 – 21 20 – 21 21 – 22 20 20
(See Figures 3-3 and 3-4)	CBC11	4	PVC	25	5-25	7.78	Dialysis PDB Low-Flow	13 – 15 15 – 16 14
	CBC10	4	PVC	25	5-25	8.37	Dialysis PDB Low-Flow	12 – 14 14 – 15 13
NAWC West Trenton, NJ April-May 2005	06BR	6	Steel	77	52-77	2.77	Dialysis PDB Low-Flow	60.5 – 62 60 – 60.5 61
(See Figure 3-5)	07BR	6	Steel	54	39-54	7.66	Dialysis PDB Low-Flow	39.5 – 41 39 – 39.5 40
	30BR	6	Steel	110	85-110	9.25	Dialysis PDB Low-Flow	104.5 – 106 104 – 104.5 105
	33BR	6	Steel	45	30-45	8.60	Dialysis PDB Low-Flow	32.5 – 34 32 – 32.5 33
	40BR	4	Steel	120	95-120	11.66	Dialysis Dialysis-Dup PDB PDB-Dup Low-Flow Low-Flow-Dup	97.5 – 99 97.5 - 99 97 – 97.5 97 – 97.5 103 103
	41BR	4	Steel	110	85-110	5.60	Dialysis PDB Low-Flow	90.5 – 92 90 – 90.5 91
	BRP01	6	Steel	60	21-60	5.61	Dialysis PDB Low-Flow	52.5 – 54 52 – 52.5 53
	12MW1	4	PVC	15	5-15	9.19	Dialysis PDB Low-Flow	10.5 – 12 10 – 10.5 12
NAES Lakehurst, NJ July 2005 (See Figures 3-1 and 3-2)	V	2	PVC	49	34-49	33.78	Dialysis Dialysis-Dup PDB PDB-Dup Low-Flow Low-Flow-Dup	38 - 41 42 - 45 37 – 38 41 - 42 39 39

Table 3-6. 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)
NAES Lakehurst, NJ July 2005 (continued)	NH	2	PVC	46	31-46	33.90	Dialysis PDB Low Flow	37 - 40 36 - 37 39
(See Figures 3-1 and 3-2)	NG	2	PVC	46	31-46	33.64	Dialysis PDB Low-Flow	37 - 40 36 - 37 39
	MW	2	PVC	22	2-22	6.80	Dialysis PDB Low-Flow	11 - 14 10 - 11 13
	X	2	PVC	17	2-17	7.13	Dialysis PDB Low-Flow	11 - 14 10 - 11 13
	Y	2	PVC	17	2-17	7.04	Dialysis PDB Low-Flow	11 - 14 10 - 11 13

3.5.7 Sampling Plan

3.5.7.1 Sampler Construction

The dialysis membrane samplers tested during this demonstration were constructed of regenerated cellulose. The pre-cleaned membrane was obtained from Membrane Filtration Products, Inc., Sequin, Texas. The membrane has a nominal molecular weight cut off of 8,000 Daltons with a pore size of 18 Å. The 100-mm width membrane has a filled diameter of 63.7 mm, a volume of 31.8 mL/cm, and comes in rolls 5 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 purchased pre-cleaned to eliminate any possible contamination with trace metals and sulfides. The membrane was cut into lengths appropriate for the volume needed for analyses at a particular well and site. The membrane is either clamped or tied in a knot to close one end and clamped to a PVC valve at the opposite end. The membrane is slipped inside a protective polyethylene mesh and filled with nitrogen-sparged deionized water through the valve. With the valve closed, cable ties are used to close the ends of the mesh trapping the dialysis bag inside. Weights can be included inside the protective mesh or attached externally. The sampler is attached to a disposable or dedicated polyethylene rope for suspension in a well.

Dialysis samplers and PDB samplers were constructed in the USGS laboratory in West Trenton, New Jersey, within one week of being deployed in wells at each field site. For the sites in New Jersey, both types of diffusion samplers were stored in PVC tubes filled with nitrogen-sparged deionized water, transported to the field site in these tubes. For the California site, both types of diffusion samplers were stored in flexible polyethylene tubes filled with nitrogen-spared deionized water, packed in a cooler, and delivered overnight to NFESC in Port Hueneme, California.

3.5.7.2 Sampler Deployment

Diffusion samplers were deployed in wells at the depths of highest mass flux of the primary chemicals of concern at each site. Depths were chosen based on vertical profiling results, knowledge of the well construction, and water-chemistry results from the pre-demonstration plan sampling. Chemical vertical profiling was conducted on wells at each of the sites. Selected wells were hydraulically profiled with a borehole flow meter at the Lakehurst and West Trenton sites. At the Port Hueneme/Point Mugu site, packer test data of the open interval of selected wells was available from previous studies.

Dialysis and PDB samplers were deployed side by side in wells where the casing diameter allowed (6-inch wells) or as close as possible to one another vertically in wells where the diameter was too narrow (4-inch and 2-inch wells). Duplicate samplers were similarly deployed, side-by-side where possible or as close vertically as possible. For the first two field comparisons, PDB samplers were encased in a separate mesh bag and suspended just above or below the dialysis samplers. In the final two field comparisons, the PDB samplers were included in the top of the same mesh bag that held the dialysis sampler in an attempt to suspend them at more nearly the same depth. The low-flow purge pump was deployed at a depth that corresponded with approximately the center of the primary dialysis sampler in each well to try and sample the same zone in the well.

3.5.7.3 Sample Frequency

Samples were collected twice from wells at the Lakehurst site and once from the wells at the Port Hueneme/Point Mugu site and the West Trenton site during the course of the field demonstrations. The dates each site was sampled are given in Table 3-5.

3.5.7.4 Tested Chemical Constituents

Samples were collected from each well at each site and analyzed for basically the same list of chemical constituents which included major cations and anions, trace elements, VOCs, dissolved gases, sulfide, silica, total dissolved solids, and dissolved organic carbon. Some samples were not analyzed for all constituents on the list if it was known from past results that the water did not contain those constituents at measurable concentrations. Two chemical constituents, ethene and carbon dioxide, were not tested for equilibration times in the bench-scale tests but were measured in the field samples because they came out on the same dissolved gas analysis as methane. A complete list of sampled chemical constituents and their minimum detection limits is given in Table 3-7.

Table 3-7. Chemical Constituents Tested For In Samples From The Field Demonstrations
[MDLs, minimum detection limits; μg/L, micrograms per liter; mg/L, milligrams per liter]

VOCs (MDLs 0.1-5.0 μg/L)		
1,1,1-Trichloroethane	cis-1,2-Dichloroethene	1,2-Dibromo-3-chloropropane
1,1,2,2-Tetrachloroethane	Dibromomethane	1,3,5-Trimethylbenzene
1,1,2-Trichloroethane	Dichlorodifluoromethane	1,3-Dichloropropane
1,1-Dichloroethene	Ethylbenzene	2,2-Dichloropropane
1,2,3-Trichloropropane	m-Xylene	2-Chlorotoluene
1,2,4-Trimethylbenzene	Naphthalene	4-Chlorotoluene
1,2-Dibromoethane	o-Xylene	Bromobenzene
1,2-Dichlorobenzene	p-Xylene	Bromochloromethane
1,2-Dichloroethane	Tetrachloroethene	Bromomethane
1,2-Dichloropropane	Toluene	Hexachlorobutadiene
1,3-Dichlorobenzene	trans-1,2-Dichloroethene	Isopropylbenzene
1,4-Dichlorobenzene	Trichloroethene	Methyl tert-butyl ether
Benzene	Trichlorofluoromethane	Methylene chloride
Bromodichloromethane	Vinyl chloride	n-Butylbenzene
Bromoform	1,1,1,2-Tetrachloroethane	n-Propylbenzene
Carbon tetrachloride	1,1-Dichloroethane	p-Isopropyltoluene
Chlorobenzene	Dibromochloromethane	sec-Butylbenzene
Chloroethane	1,1-Dichloropropene	Styrene
Chloroform	1,2,3-Trichlorobenzene	tert-Butylbenzene
Chloromethane	1,2,4-Trichlorobenzene	Acetone
Cations and Trace Elements (MDLs 0.3-100 μg/L)		
Calcium *(100 μg/L)*	Barium *(3 μg/L)*	Molybdenum *(2 μg/L)*
Magnesium *(100 μg/L)*	Cadmium *(0.3 μg/L)*	Nickel *(3 μg/L)*
Potassium *(100 μg/L)*	Chromium *(2 μg/L)*	Selenium *(2 μg/L)*
Sodium *(100 μg/L)*	Copper *(2 μg/L)*	Vanadium *(3 μg/L)*
Aluminum *(10 μg/L)*	Iron *(50 μg/L)*	Zinc *(2 μg/L)*
Arsenic *(2 μg/L)*	Lead *(0.3 μg/L)*	
Antimony *(0.8 μg/L)*	Manganese *(3 μg/L)*	
Anions (MDLs 0.1-10 mg/L)		
Bicarbonate/Alkalinity *(10 mg/L)*	Chloride *(0.3 mg/L)*	Nitrate *(0.1 mg/L)*
Bromide *(0.1 mg/L)*	Fluoride *(0.1 mg/L)*	Sulfate *(1 mg/L)*
Other Constituents (MDLs 0.0001-10 mg/L)		
Dissolved organic carbon *(0.3 mg/L)*	Silica *(1 mg/L)*	Sulfide *(10 μg/L)*
Methane *(1 μg/L)*	Ethene *(0.1 μg/L)*	Carbon dioxide *(1 mg/L)*
Total dissolved solids *(10 mg/L)*		

3.5.7.5 Sample Collection

The dialysis and PDB samplers were allowed to equilibrate for at least one week. This was the shortest common period determined during the bench-scale testing necessary for equilibration to take place for all the chemical constituents being sampled.

After the equilibration period, the field comparison sampling was conducted at each site. At the beginning of each field demonstration for 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 dialysis and PDB samplers were retrieved from each well and samples were collected immediately in appropriate containers. 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 3-6. Removal Of Diffusion Sampler From A Well Prior To Sampling

Figure 3-7. Low-Flow Purging Set Up For A 4-Inch Diameter Well. A Submersible Pump Is Being Used To Purge And An Electric Tape Is Being Used To Monitor Drawdown

Figure 3-8. Flow Chamber And Multi-Parameter Instrument Used For Monitoring Field Parameters During Low-Flow Purging

Thereafter, a variable-speed stainless-steel low-flow purge pump equipped with Teflon-lined polyethylene discharge tubing was lowered into the well and approximately centered at the depth at which the dialysis sampler was suspended during its equilibration. Low-flow purging at 500-1000 mL/min was conducted as per the USEPA protocol (Puls and Barcelona, 1996) 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. Field parameters were considered to be stabilized when three successive readings taken five minutes apart were within +/-0.1 ^{o}C for temperature, +/-0.1 units for pH, +/-5% for conductance in 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 purge 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.

In all, 22 wells were sampled during the field demonstrations that resulted in a maximum total of 28 field comparisons per chemical constituent. Major cations and anions, silica, carbon dioxide, dissolved organic carbon (DOC), and TDS were present in almost all wells and therefore could be compared near the maximum number of times (26 to 28). However, because detectable and quantifiable concentrations of most VOCs and trace elements were not present in all wells sampled, fewer comparisons of these constituents could be made overall. All wells sampled in this study are given in Table 3-6.

3.5.7.6 Sample Preservation

Unfiltered VOC samples were collected and preserved with 1:1 HCl to pH <2 to prevent biodegradation prior to analysis. Unfiltered methane, ethene, and carbon dioxide samples were collected and preserved with $HgCl_2$ to prevent biodegradation prior to analysis. Samples for analysis of dissolved inorganic chemical constituents, TDS, and DOC were filtered using a 0.45-μm pore-diameter polyethersulfone in-line capsule filter, and preserved appropriately. Samples for analysis of cations and trace elements were preserved with 1:1 HNO_3 to pH <2 to prevent sorption to the container walls. Anions were preserved by chilling to 4^{o}C, DOC samples were preserved with H_3PO_4 to prevent biodegradation, and sulfide samples were preserved with sodium hydroxide and zinc acetate.

3.5.7.7 Field Sample Handling Procedures and Notes

Preprinted waterproof sample container labels were filled out by field personnel using a permanent marker at the time of sample collection and attached to all sample bottles. The sample labels included appropriate information, like date, time, site, well ID, field personnel initials, preservative, and type of sample. The field data from the field forms and the results of analyses of both field and laboratory samples were transferred to electronic data files prior to evaluation of results. Duplicate samples were given a unique sample ID and were handled by the same procedure as other samples collected in the field.

All samples were placed on ice while in the field. At the end of each day, samples were repacked with fresh ice in coolers, standard chain-of-custody forms were filled out, and the samples were shipped by overnight courier to the analytical laboratory.

3.5.7.8 Sampler Cleaning

New clean diffusion samplers were used when sampling each well. The low-flow purge pump was decontaminated initially and between wells and new clean Teflon-lined polyethylene tubing was attached before each new well was purged and sampled. The pump was decontaminated between wells by successive rinses with a dilute solution of detergent, deionized water, 5% methanol, and deionized water. Wells were sampled in the order from least contaminated to most contaminate at each site to further reduce potential cross-contamination.

3.5.7.9 Quality Assurance/Quality Control Procedures

All probes used in the multi-parameter instrument were calibrated each day prior to use in the field according to the procedures outlined in the multi-parameter instrument manual. Calibration data were recorded on the field forms each day.

Trip blanks, equipment wash blanks, and duplicate analyses were collected during the field demonstrations to meet the data-quality objectives. One duplicate dialysis sample, one duplicate PDB sample, and one duplicate low-flow purge sample were collected during each field demonstration (approximately 10% of samples). One equipment wash blank was collected from the low-flow purge pump each sampling day at each field site. One dialysis sampler and one PDB sampler that were suspended in deionized water for a week were sampled as dialysis and PDB sampler equipment blanks at each field demonstration site. Deionized-water trip blanks for VOCs were included in coolers being shipped to the laboratory. The deionized water used to clean the low-flow purge pump and to fill the diffusion samplers was analyzed at two sites. Replicates and blanks were analyzed for the same set of chemical constituents at the laboratory as the other samples in the same set. All analyses for the same chemical constituent were completed by the same laboratory.

The general accuracy of the results were checked by comparing the concentrations from the field demonstration samples to concentrations obtained in the pre-demonstration plan samples from the same wells. Precision was checked by comparing the results from duplicate samples from each of the sampling devices in at least one well per site. The sampling and analytical variation in concentration of duplicate samples for inorganic constituents should typically be within +/- 10-15%. The sampling and analytical variation in concentration of duplicate samples for VOCs should typically be within +/- 30%. Equipment wash blanks and trip blanks were collected and analyzed to check for any possible cross-contamination between wells or samples. If any cross-contamination was found, cleaning or sample-handling procedures were adjusted to eliminate the problem prior to the next sampling event. One VOC trip blank was analyzed during each of the four field comparisons.

3.5.7.10 Sample Analysis

Samples collected in the field demonstrations were analyzed at off-site laboratories. All chemical constituents listed in Table 3-7 except methane, ethene, carbon dioxide, and sulfide were analyzed at DHL Analytical in Round Rock, Texas using standard USEPA methods. Methane, ethene, carbon dioxide, and sulfide were analyzed at the USGS New Jersey District Laboratory in West Trenton, New Jersey using standard and modified USEPA methods. Detection limits for all chemical constituents are given in Table 3-7. Additional details of all the analytical procedures used are discussed in Section 3.6.

3.5.7.11 Analytical Calibration Procedures and Quality Control Checks

All calibration procedures for the analytical instrumentation used to analyze samples from the field demonstrations were completed by the analytical laboratories. USEPA analytical protocols were followed. External standards were used for all analyses. Reagent grade chemicals were used to prepare calibration curves. Calibration curves were determined by analyzing standards at three to five different concentrations. Regression by least-square method was conducted to obtain the calibration curves. Standard curves with r^2 values of 0.95 or more were considered to be acceptable for computation of resultant data. Appropriate blanks, standards, and replicate samples were analyzed to check for quality. All solvents and reagents used in the analyses were checked for purity by analyzing them as blanks through the entire analytical procedure.

3.5.8 Demobilization

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

3.6 Selection of Analytical/Testing Methods

The ground water samples taken for analysis were sent to DHL Analytical, which is a DoD-certified Battelle contract laboratory and the samples were analyzed using USEPA-approved methods (Table 3-8). Most of the analyses were conducted using USEPA SW-846 analytical protocols. Others analytes were analyzed as per USEPA drinking water analytical protocols. Analysis of VOC samples were conducted by USEPA SW-846 method 8260B purge-and-trap gas chromatography-mass spectrometry (GC-MS) (USEPA, 2003). Major anions and nutrients were analyzed by USEPA SW-846 method 9056 ion chromatography (USEPA, 2003). Major cations and trace metals were analyzed by USEPA SW-846 method 6020 inductively coupled plasma-mass spectrometry (ICP-MS) (USEPA, 2003). Dissolved organic carbon, dissolved methane, ethene, and carbon dioxide were analyzed by USEPA SW-846 methods 9060, and 3810, respectively (USEPA, 2003). Silica and sulfide were analyzed by USEPA methods 370.1 and 376.2 (NEMI, 2002). Total dissolved solids and total suspended solids were analyzed by USEPA methods 160.1 and 160.2 (NEMI, 2002). All analytical methods were chosen to have sufficiently low detection levels so that the differences between sample results could be recognized if present. Details of the above mentioned analytical techniques used in this plan are given in the references shown in Table 3-8.

Table 3-8. Analytical Methods for Chemical Constituents

Chemical Constituent	U.S. EPA Method No.	References
Volatile organic compounds	SW-846 8260B	**www.epa.gov/epaoswer/hazwaste/test/main.htm** - search for method 8260B
Major anions and nutrients	SW-846 9056	**www.epa.gov/epaoswer/hazwaste/test/main.htm** - search for method 9056
Major cations and trace metals	SW-846 6020	**www.epa.gov/epaoswer/hazwaste/test/main.htm** - search for method 6020
Methane, ethene, carbon dioxide	SW-846 3810	**www.epa.gov/epaoswer/hazwaste/test/main.htm** - search for method 3810
Total dissolved solids	160.1	**www.nemi.gov** - search for total dissolved solids
Silica	370.1	**www.nemi.gov** - search for silica
Sulfide	376.2	**www.nemi.gov** - search for sulfide
Dissolved organic carbon	SW-846 9060	**www.epa.gov/epaoswer/hazwaste/test/main.htm** - search for method 9060
Alkalinity	310.1	**www.nemi.gov** - search for alkalinity

3.7 Selection of Analytical/Testing Laboratory

DHL Analytical, 2300 Double Creek Drive, Round Rock, Texas 78664, was selected to analyze the samples in this field demonstration because it was a DoD-certified Battelle contract laboratory. This laboratory had the capability to run all the needed analyses within the appropriate sample holding times, meet all quality assurance requirements, and provide results in a timely manner.

The USGS, 810 Bear Tavern Road, Suite 206, West Trenton, New Jersey 08628, was selected to analyze the samples collected in the field demonstrations for methane, ethene, carbon dioxide, and sulfide because it had the capability to run analyses for these constituents at lower detection limits than were available at the commercial laboratory.

3.8 Graphical Comparison Methods

Field results were evaluated by making 1:1 plots of the data for each chemical constituent for the dialysis sampler versus the PDB sampler and for the dialysis sampler versus low-flow purging. Ideally, if both sampling techniques work equally well in sampling for the constituent being plotted, all the points should lie on the 1:1 line. Although some deviation around the line is expected due to sampling and analytical variation, consistent deviation from the 1:1 relationship may indicate a sampling bias for a chemical constituent by one sampling method over another. These plots were presented as log-log plots because the chemical constituents found in the field comparison samples typically ranged from their detection limit up to 2 to 4 orders of magnitude higher in concentration. Analyses reported at less than the detection limit were assigned a value of one half the detection limit for the purposes of plotting the data.

3.9 Statistical Comparison Methods

A maximum of 28 well comparisons were conducted over the course of this study. Some chemical constituents, such as, major cations and anions, were present in almost all wells, so samples collected with the different sampling techniques could be compared close to the maximum number of times. However, many chemical constituents, such as, VOCs and trace elements, were not detected in every well because all sites were contaminated with different mixtures of these contaminants. These constituents, therefore, generated fewer detected concentrations to compare. Chemical constituents compared in 4 or more cases were included in the statistical comparisons.

3.9.1 Correlations.

Pearson's correlation coefficients were calculated for the two sets of data plotted on each 1:1 plot using a statistical software package (S-PLUS, 2002). Positive correlation coefficients greater than 0.50 indicate a positive relationship between the two sets of data. High correlation coefficients do not necessarily indicate that the relationship is 1:1.

3.9.2 Normality Testing.

Prior to any statistical testing of the data collected in the field demonstrations, the distribution of the data for each water-quality constituent was tested for normality. This was accomplished by running a univariate analysis, plotting box plots, and by applying a Kolmogorov-Smirnov goodness-of-fit test (S-PLUS, 2002). Chemical parameters from comparisons where at least one sampling technique had an above detection value 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. Parametric statistical tests require the data distribution to be normal to be valid. If the data distribution for a chemical constituent was not normal, non-parametric statistical tests were used to compare sets of results.

3.9.3 Kruskal-Wallis Rank Sum Test.

To compare three sets of VOC data, where the dialysis sampler, the PDB sampler, and low-flow purging were all used to collect samples at a site, a Kruskal-Wallis rank sum test was used (S-PLUS, 2002). This test is essentially a non-parametric one-way analysis of variance on the ranked data from the three data sets. Differences between data sets determined at a significance level of $p<0.05$ were considered significant. The Kruskal-Wallis test determined if there was a significant difference between the median concentrations recovered by the three sampling techniques. It did not tell how the sampling techniques differed.

3.9.4 Wilcoxon Signed-Rank Test.

To compare inorganic and non-VOC organic data, where only the dialysis sampler and low-flow purging were used to collect samples, a Wilcoxon signed-rank test was used (S-PLUS, 2002). This test is the non-parametric equivalent to a student's t-test on the ranked data from the two data sets. Differences determined at a significance level of $p<0.05$ were considered significant. The Wilcoxon test determined if there was a significant difference between the median concentrations recovered by the two sampling techniques.

3.9.5 Multi-factor Analysis of Variance (ANOVA) on Ranks.

If a significant difference was determined for a constituent with either the Kruskal-Wallis rank sum test or the Wilcoxon signed-rank test, a multiple factor analysis of variance on ranked data was run that included the variables of sampling site and sampling date as well as sampling technique (S-PLUS, 2002). This additional test helped determine which factor was the most important in explaining the differences found. If a significant difference was found, a Tukey multiple-comparison test was run to determine how the factors differed from each other.

4.0 PERFORMANCE ASSESSMENT

This section describes the performance criteria, performance confirmation methods, data analysis, interpretation and evaluation of the sampling techniques compared in the field demonstration.

4.1 Performance Criteria

The performance criteria, description, and type of performance criteria used in this field demonstration are listed in Table 4-1.

Table 4-1. Performance Criteria [vs., versus; dialysis, regenerated cellulose dialysis membrane sampler; PDB, polyethylene diffusion bag; VOC, volatile organic compounds]

Performance Criteria	Description	Type of Performance Criteria
Integrity and Durability	Confirm dialysis membrane remains intact over the course of the field test.	Primary Qualitative and Quantitative
Chemical Selectivity – Lab vs. Field	Confirm all lab-tested parameters diffuse into dialysis samplers in field tests.	Primary Qualitative
Chemical Selectivity – Dialysis vs. Low-Flow	Confirm all parameters measured in low-flow are also measured in dialysis samplers.	Primary Qualitative
Chemical Selectivity – Dialysis vs. PDB	Confirm all parameters measured in PDB sampler are also measured in dialysis samplers.	Primary Qualitative
Equal Recovery – Dialysis vs. Low-Flow	Confirm dialysis sampler recovery of chemicals of concern is not significantly different from low-flow purging recovery	Primary Quantitative
Equal Recovery – Dialysis vs PDB.	Confirm dialysis sampler recovery of VOC chemicals of concern is not significantly different from PDB sampler recovery	Primary Quantitative
Sensitivity	Confirm dialysis samplers can sample low concentrations	Primary Quantitative
Faster Sampling	Confirm dialysis samplers take significantly less time than low-flow purging	Primary Quantitative
Purge Water	Confirm dialysis sampler produces much less purge water than low-flow purging	Secondary Quantitative
Versatility	Confirm dialysis samplers work well under a variety of site conditions (hydrologic conditions, chemical conditions)	Secondary Qualitative
Ease of Use	Confirm dialysis samplers can be constructed, deployed, retrieved, and sampled by 2 persons with minimal training	Primary Qualitative
Scale-Up Constraints	Confirm there are no scale-up constraints for full-scale use	Secondary Qualitative

4.2 Performance Confirmation Methods

The performance of the tested sampling techniques was evaluated by graphically and statistically comparing the water-quality results from ground water samples collected with each method from the same depth in each well in the field demonstration. Dialysis sampler integrity was measured by weighing the samplers before deployment and after recovery from each well. The length of time it took to conduct various phases of a sampling technique was recorded on the field sheets. Table 4-2 summarizes the expected performance, performance confirmation methods used, and actual performance found during the demonstration project.

Table 4-2. Expected Performance and Performance Confirmation Methods [demo, demonstration; vs., versus; dialysis, regenerated cellulose dialysis membrane; PDB, polyethylene diffusion bag; Low-Flow, low-flow purging; VOC, volatile organic compounds; ANOVA, analysis of variance; $p<0.05$, at 95% confidence level]

Performance Criteria	Expected Performance Metric (pre-demo)	Performance Confirmation Method	Actual Performance (post-demo)
Primary – Qualitative			
Integrity and Durability	No membrane perforations during field testing.	Examine samplers at end of field testing.	Yes. No perforations or degradation were noted during the 7-14 day field tests.
Chemical Selectivity – Lab vs. Field	All lab-tested parameters should diffuse into dialysis samplers in field tests.	Compare lists of chemicals sampled in the field vs. lab.	Yes. Parameters that diffused into the dialysis samplers in the lab also diffused into the dialysis samplers in the field if present in the ground water.
Chemical Selectivity – Dialysis vs. Low-Flow	All parameters detected in low-flow are also measured in dialysis samplers.	Compare detected chemicals in low-flow and dialysis samplers.	Yes. All of the organic and inorganic chemical constituents detected with the low-flow purge method were also detected with the dialysis samplers.
Chemical Selectivity – Dialysis vs. PDB	All parameters measured in PDB samplers are also measured in dialysis samplers.	Compare detected chemicals in PDB and dialysis samplers.	Yes. All of the VOCs detected with the PDB samplers were also detected with the dialysis samplers.
Ease of Use	Dialysis samplers can be constructed, deployed, retrieved, and sampled by field personnel with minimal training.	Experience of field personnel.	Yes. The dialysis samplers were relatively easily constructed and deployed by one person with minimal training. The dialysis samplers were easily recovered and sampled from wells by 2 persons with minimal training.
Primary – Quantitative			
Integrity and Durability	There will be minimal weight loss of dialysis sampler during field test.	Weigh samplers at beginning and end of test.	Yes. A weight loss of <3% per week was measured in the dialysis samplers over the course of the 7-14 day field tests.
Equal Recovery – Dialysis vs. Low-Flow	Dialysis sampler concentrations will not be significantly different from low-flow purging concentrations.	Make 1:1 plots. Determine if significant differences in recovery were found using Kruskal-Wallis Test, Wilcoxon Test, or multi-factor ANOVA on	Yes. 1:1 plots (Appendix A) show good agreement between concentrations recovered with both sampling techniques. No significant difference (at $p<0.05$) due to sampling technique was

Performance Criteria	Expected Performance Metric (pre-demo)	Performance Confirmation Method	Actual Performance (post-demo)
		ranks.	found between concentrations recovered with the dialysis sampler and low-flow purging for 49 of 54 (91%) of the organic and inorganic constituents compared in the field demonstrations.
Equal Recovery – Dialysis vs. PDB	Dialysis sampler concentrations of VOC chemicals of concern will not be significantly different from PDB sampler concentrations.	Make 1:1 plots. Determine if significant differences in recovery were found using Wilcoxon Signed Rank Test or multi-factor ANOVA on ranks.	Yes. 1:1 plots (Appendix A) show good agreement between concentrations recovered with the dialysis sampler and PDB samplers. No significant difference (at $p<0.05$) due to sampling technique was found between concentrations recovered with the dialysis sampler and the PDB sampler for 24 of 24 (100%) of the volatile organic compounds compared.
Sensitivity	Dialysis samplers can sample low concentrations.	Concentrations within 2 times to 5 times detection limit are detected.	Yes. The data demonstrate that the dialysis samplers are capable of collecting samples at concentrations twice to five times the detection limit.
Faster Field Sampling	Dialysis samplers take significantly less time in the field than low-flow purging.	Compare time to sample w/dialysis to time to sample w/low-flow purging in the field.	Yes. Low-flow sampling required an average of 96 minutes to collect a sample; whereas, dialysis samplers required only 20 minutes to collect a single sample.
Secondary – Qualitative			
Purge Water	Dialysis sampler will produce much less purge water than low-flow.	Compare measured purge water production from dialysis samplers and low-flow.	Yes. Less than 0.025 liters of purge water were produced per well with the dialysis sampler and about 40 liters were produced per well with the low-flow purge technique.
Versatility	Dialysis samplers work well under a variety of site conditions (hydrologic conditions, chemical conditions)	Compare dialysis samplers to low-flow purging at sites with different hydrologic and chemical conditions	Yes. The dialysis samplers worked as well as low-flow purging in wells in both unconsolidated deposits and fractured bedrock and in wells with both high and low ionic strengths.
Scale-Up Constraints	There are no scale-up constraints for full-scale use	Experience of field personnel	Yes. There are no scale-up constraints for full-scale use of dialysis samplers in the field. However, the samplers are not yet available commercially so they must be constructed by project personnel.

4.3 Data Analysis, Interpretation, and Evaluation

The effectiveness of this demonstration study was qualitatively and quantitatively evaluated by comparing the chemical data collected using each of the three sampling techniques. The results of quality-control samples were evaluated. The results for each chemical constituent collected by pairs of sampling techniques were compared graphically using 1:1 plots. The concentration data for all chemical constituents were compared statistically. Deployment considerations for diffusion samplers in general and dialysis samplers in particular were evaluated.

4.3.1 Quality Assurance /Quality Control Sample Results

4.3.1.1 Trip blanks

No VOCs were detected in the trip blanks analyzed during two of the four field demonstrations. Only bromoform and trichlorofluoromethane were found at trace levels (above the minimum detection limit but below the laboratory reporting level) in trip blanks analyzed during the other two field demonstrations. Neither of these compounds was found in any of the field samples collected during these demonstrations, so their source was not the ground water that was sampled. These compounds are halogenated methanes and may have been in the source water used to produce the deionized water used in the trip blanks.

4.3.1.2 Equipment Wash Blanks

One wash blank was collected each day from the low-flow purge pump and submitted for analysis of VOCs, inorganics, DOC, and dissolved gases. Only trace amounts of a few VOCs were detected in any of the eight low-flow purge pump equipment blanks. Chloroform was detected in four of the eight low-flow purge pump equipment blanks. This is probably due to its presence in the tap water source for the deionizing cartridge system and its incomplete removal. Acetone was detected below reporting limits 3 times. Acetone is a common laboratory contaminant.

Low-flow pump equipment wash blanks analyzed for dissolved gases showed no detections. Low-flow pump equipment wash blanks analyzed for inorganics showed detections of a few trace elements in trace concentrations in only a few cases. Zinc, barium, and aluminum were detected in 7, 4, and 3, respectively, of the 9 equipment blanks analyzed for inorganics. A scan of the field data revealed that the samples collected after the wash blanks were not as high in concentration of these three trace elements as the blanks themselves. Analysis of the deionized water used to clean the pumps during two of the field demonstrations revealed trace to low concentrations of aluminum, barium, and silica which were apparently not removed by the deionizing system. The source of zinc in the low-flow pump blanks is unclear and maybe a laboratory contaminant.

DOC was detected in 6 of the 9 low-flow equipment wash blanks analyzed for this parameter. DOC showed the same pattern as the trace elements, in that, field samples collected after these wash blanks were usually not as high in concentration as the wash blanks. The cleaning procedure included the use of soap and methanol, both soluble organic compounds. It is possible that these cleaning compounds were not sufficiently flushed out of the pump by the amount of deionized water used in the field cleaning procedure. The fact that field samples collected after the wash blanks showed no contamination with DOC or the previously mentioned trace elements indicates that the low-flow purging process successfully flushed the wash water and any cleaning solutions out the pump over the course of the field parameter stabilization and low-flow sampling.

Dialysis sampler equipment blanks analyzed for VOCs in this study showed no detections in two field demonstrations and only trace concentrations of a few compounds in the other two field demonstrations. Dialysis sampler blanks analyzed for inorganics showed similar results to the low-flow purge wash blanks in that trace levels of zinc, barium, aluminum, and DOC were detected in them. Low concentrations of barium and aluminum were found to be present in the deionized water used to fill the dialysis samplers. DOC was found at below laboratory reporting level concentrations in two field demonstrations. Zinc was found in concentrations from 3 to 13 µg/L in the dialysis sampler equipment blanks collected at all 4 field demonstrations. The source of zinc was not the regenerated cellulose membrane (bench-scale blanks were clean) or the deionized water used to fill the dialysis samplers; therefore, it was probably desorbing from the galvanized weights used in the construction of the dialysis samplers.

PDB sampler equipment blanks analyzed for VOCs showed no detections during one field demonstration and near detection concentrations of only one compound during the other field demonstrations. Very high acetone concentrations were found in the PDB sampler blank at the NAWC site. Because similarly high acetone concentrations were found in all PDB sampler field samples collected at this site, it was concluded that the PDB samplers had been contaminated, perhaps while in storage in a refrigerator in the West Trenton, New Jersey laboratory prior to their use. PDB samplers have previously been found to have difficulty sampling for acetone and are not recommended for sampling this compound (Vroblesky, 2001a). For this reason, acetone was not evaluated in PDB samplers.

4.3.1.3 Duplicate Samples

One duplicate sample was collected using each sampling technique during each of the four field demonstrations. On average, duplicate samples collected by low-flow purging agreed within +/- 5% for inorganic constituents at all four field demonstrations. Low-flow duplicate samples agreed within +/- 15% for VOCs at three of the four field demonstrations. On average, duplicate samples collected with the dialysis sampler agreed within +/- 9% for inorganic constituents at all four of the field demonstrations. Dialysis sampler duplicate samples agreed within +/- 17% for VOCs at two of the four field demonstrations. Duplicate samples for VOCs collected with dialysis samplers had higher average variation (>20%) when the Lakehurst demonstration site was sampled. The Lakehurst site had 2-inch diameter wells with fuel-type contamination. Duplicate dialysis samplers could not be suspended at the same depth in these wells. Apparently, the small differences in depth between dialysis samplers resulted in large differences in VOC concentrations in the duplicate samplers at this site. Duplicate samples collected with PDB samplers agreed within +/- 21% at three of the field demonstrations. Similar to the dialysis samplers, the PDB sampler duplicates varied most at the Lakehurst demonstration site where narrow-diameter wells prevented the duplicate samplers from being suspended at the same depth.

4.3.2 Evaluation of Field Comparison Results for Volatile Organic Compounds

4.3.2.1 Graphical Analysis of VOCs

The results for 25 VOCs found at above-detection-limit concentrations at least four times during the field comparison portion of the study were evaluated graphically using 1:1 correspondence plots. For each compound two 1:1 plots were constructed; one of the concentrations obtained with the dialysis sampler compared to the concentrations obtained with the PDB sampler (blue symbols) and a second of concentrations obtained with the dialysis sampler compared to the concentrations obtained with the low-flow purging procedure (red symbols). Ideally, if both sampling techniques collected a VOC equally, all points from the field comparison sampling would fall on the 1:1 correspondence line. However, because sampling and analytical variations did occur, the data for most VOCs was 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. All of these correspondence plots are given in Appendix A. Selected plots will also be presented in this section for the sake of illustrating common findings.

Because the field comparison data typically varied from the detection limit of a compound to up to 3 to 4 orders of magnitude greater, all plots were shown as log-log plots. Each plot was divided into three parts. The white portion of each graph included all data points where both the sampling techniques being compared had concentrations above the laboratory reporting level (LRL) for the compound being plotted. Concentrations in this range had the greatest degree of confidence analytically. The yellow portion of each graph included all points where the concentrations for one or both of the sampling techniques were less than the laboratory reporting level but still above one half the minimum detection limit (1/2 MDL). One half the minimum-detection limit was plotted wherever a “less than the detection limit” value was obtained for an analysis. Concentrations in this range, while still valid, had a lower degree of confidence analytically because small sampling or analytical errors can have a large effect on the magnitude of these lower concentration values. The rose-colored portion of each graph included concentrations that were less than one half the minimum detection limit. No data points were plotted in the rose-colored section of any of the graphs.

4.3.2.1.1 Chlorinated VOCs. Vinyl chloride is an example of a chlorinated VOC that was detected in the field comparison samples. Vinyl chloride has a high Henry’s Law constant and a very high vapor pressure. Because of these characteristics, it is often difficult to obtain consistent results for vinyl chloride with pumped samples. The plot of dialysis sampler versus PDB sampler results (Figure 4-1) showed excellent agreement between concentrations obtained using both sampling techniques starting at the detection limit and going up over 4 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 diffusion samplers collected nearly identical samples from wells in the field demonstration.

The plot of dialysis sampler versus low-flow purging results (Figure 4-2) also showed excellent agreement between concentrations obtained using both sampling techniques, especially in the white portion of the graph. Except for a few data points in the yellow (low concentration) portion of the plot, most data comparison points were tightly grouped on or near the 1:1 line, extending from the detection limit and going up over 4 orders of magnitude in concentration.

These results show that the dialysis sampler and low-flow purging collected nearly identical samples from wells in the field also.

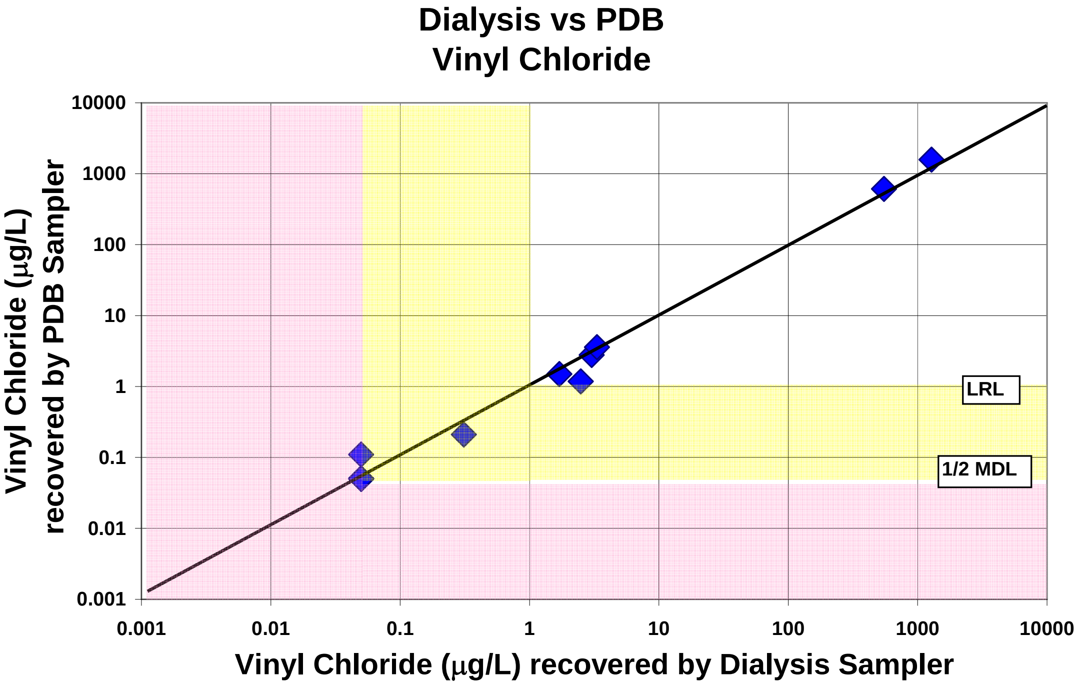


Figure 4-1. Dialysis Sampler Versus Polyethylene Diffusion Bag (PDB) Sampler Results For Vinyl Chloride

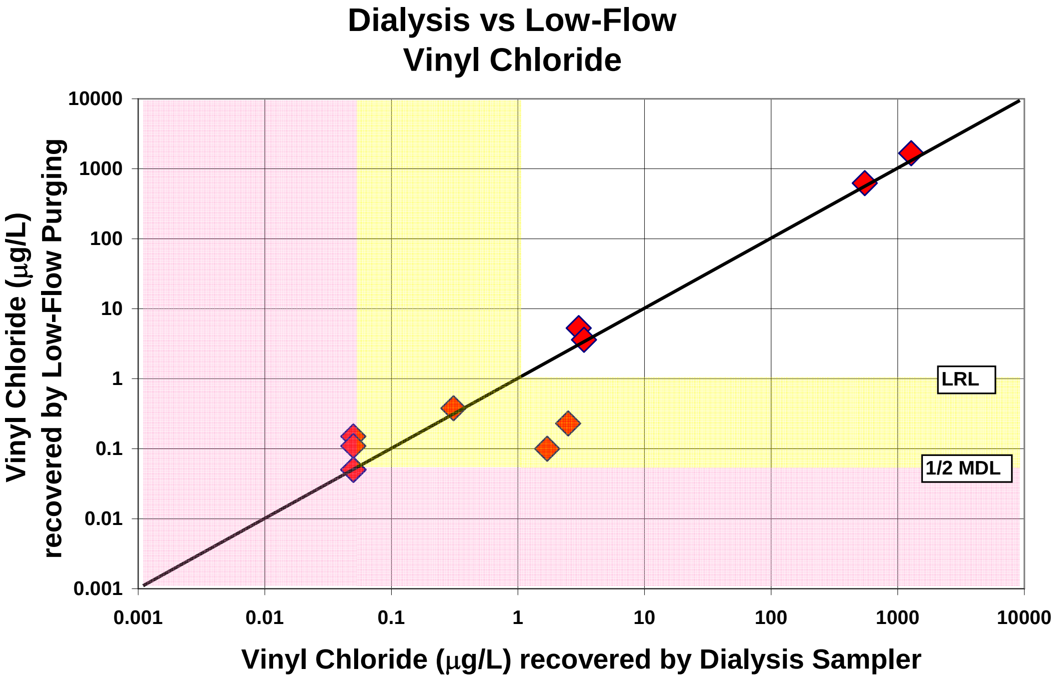


Figure 4-2. Dialysis Sampler Versus Low-Flow Purging Results For Vinyl Chloride.

These results were typical for most of the other chlorinated VOCs detected in this demonstration. The results for 1,1,1-trichloroethane, 1,1-dichloroethene, trichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, and dichlorodifluoromethane all showed similar close agreement between sampling techniques. The only chlorinated VOC that did not follow this pattern was chloroform. The 1:1 plots for chloroform (Figures A-13 and A-14) showed that there were very few data points to compare and all but one were below the laboratory reporting level. At these generally low concentrations, the chloroform comparison points appeared to be scattered around the 1:1 line.

4.3.2.1.2 Aromatic VOCs. Ethylbenzene is an example of an aromatic VOC detected in the field demonstration samples. The dialysis sampler versus PDB sampler results (Figure 4-3) matched very well indicating that the diffusion samplers were both collecting equivalent concentrations of ethylbenzene from wells in the field. The sampling techniques agree over the range from the detection limit to 3 to 4 orders of magnitude higher.

The dialysis sampler versus the low-flow purging results (Figure 4-4) also showed a close relationship for concentrations above the laboratory reporting level for ethylbenzene. However, at concentrations between the laboratory reporting level and the minimum detection limit, several instances were found where ethylbenzene was detected in the low-flow samples but not in the dialysis sampler. Given the fact that the dialysis and PDB samplers agreed well for this compound even at low concentrations, the most likely explanation for this observation was that even at low purging rates, ground water containing ethylbenzene was being drawn into these wells that was not present in the screened interval under unstressed conditions. The contaminant may be drawn in vertically from a depth other than the one the dialysis and PDB samplers were suspended at or from an area laterally adjacent to the screen.

When dialysis sampler results for other aromatic VOCs were plotted against low-flow purging results, several additional observations were made. The distribution of comparison points around the 1:1 correspondence line was generally more scattered than the distribution of comparison points around the 1:1 line for dialysis samplers versus PDB samplers. All aromatic VOCs had some comparison points scattered above, below, and/or on the 1:1 correspondence line for its plot. In the region of the graphs where both sampling techniques yielded above laboratory reporting level concentrations of an aromatic VOC (white area), some compounds (m,p-xylene, n-butylbenzene, t-butylbenzene, s-butylbenzene, naphthalene, and styrene) showed good agreement between dialysis and low-flow purging results. Similar to that found for ethylbenzene, some compounds (benzene, toluene, and o-xylene) had results that indicated dialysis samplers recovered generally higher concentrations than the low-flow purging technique. In addition, some compounds (1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, n-propylbenzene, isopropylbenzene, and p-isopropyltoluene) had results that indicated low-flow purging recovered generally higher concentrations of these compounds than dialysis samplers. In the region of the 1:1 plots where either or both the dialysis sampler and/or low-flow purging yielded concentrations between the laboratory reporting level and the minimum detection limit (yellow area), almost all graphs showed generally higher concentrations were recovered by low-flow purging.

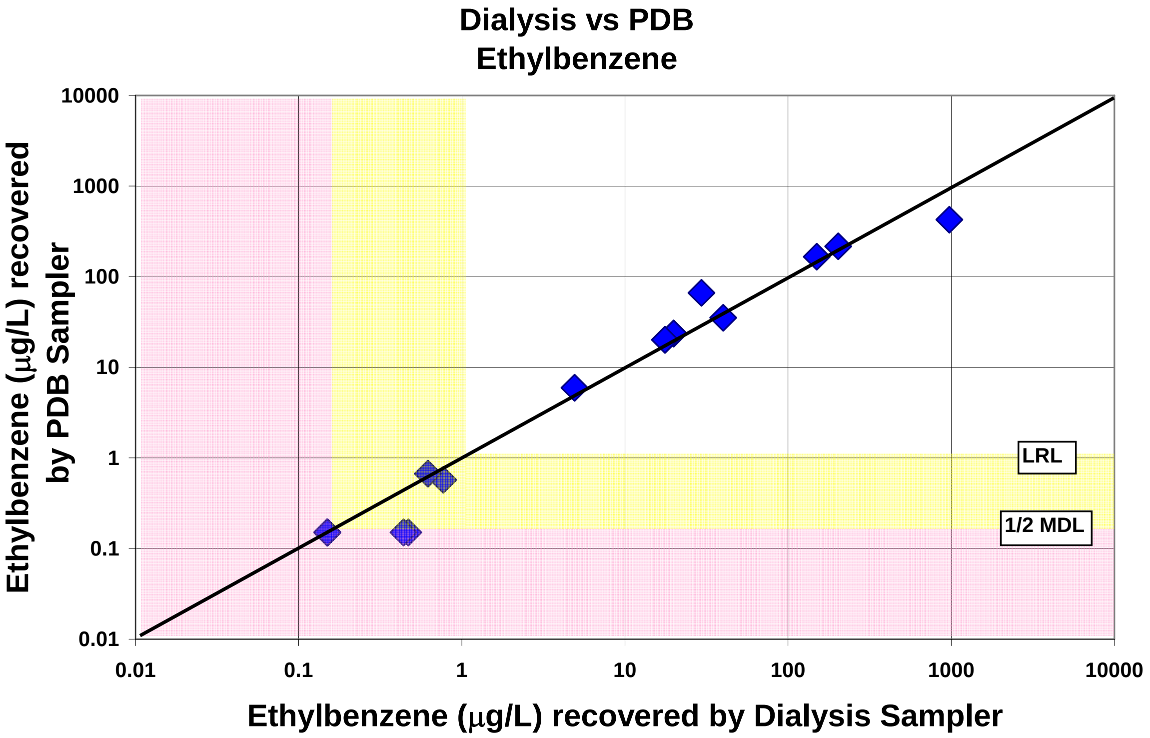


Figure 4-3. Dialysis Sampler Versus Polyethylene Diffusion Bag (PDB) Sampler Results For Ethylbenzene

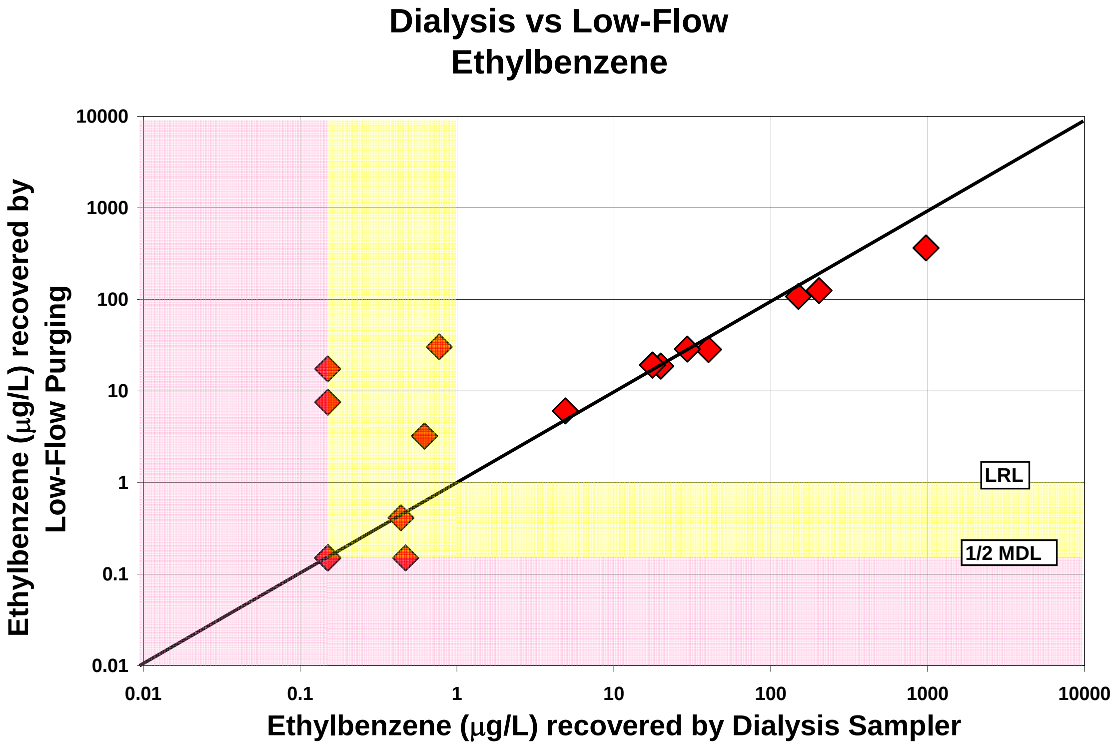


Figure 4-4. Dialysis Sampler Versus Low-Flow Purging Results For Ethylbenzene

The fact that the comparisons between the dialysis sampler and the PDB sampler usually yielded closer concentrations than between the dialysis sampler and low-flow purging was not unexpected. The diffusion samplers take point samples from the depth at which they are suspended in the well. Low-flow purge pumps, even if they are suspended at the same depth as the diffusion samplers, do not sample only from that depth. The process of pumping the well, even at low flow rates, draws water in from different depths in the aquifer over the open interval of the screen (Gibs et al. 1993; Reilly and Gibs, 1993; Britt, 2005; Varljen et al. 2006). The observations that some aromatics were sampled better by different sampling techniques will be statistically tested in section 4.3.2.4.

4.3.2.1.3 Other VOCs. MTBE and acetone were also detected in the field demonstration samples. Only 5 wells containing MTBE were sampled in this study. The dialysis sampler versus PDB sampler results for MTBE (Figure 4-5) showed generally good agreement but with slightly higher concentrations recovered in 4 of 5 wells by the dialysis sampler. The MTBE plot for dialysis sampler versus low-flow purging results (Figure 4-6) was essentially identical to the dialysis sampler versus PDB sampler plot. The sampling techniques agreed over the range from the detection limit to 3 to 4 orders of magnitude higher. This finding was in contrast to previous findings that MTBE could not be reliably sampled by PDB samplers (Vroblesky, 2001; Vroblesky et al. 2002).

Acetone was detected in a number of wells sampled during the field demonstration. The plot of dialysis sampler versus low-flow purging results (Figure A-49) showed only one comparison point where both sampling techniques recovered concentrations above the laboratory reporting level. The distribution of acetone comparison points in the yellow (lower concentration) region of the 1:1 plot was characterized by some points being close to the line and many cases where acetone was detected with the dialysis sampler and not at all with low-flow purging and vice versa. These findings, coupled with the detections of acetone in several low-flow purge pump equipment blanks, seemed to indicate there were possible blanking problems for acetone. In addition, acetone was not one of the VOCs that had been tested for equilibration time in the bench-scale testing. For these reasons, acetone was not included in the statistical evaluation of VOC results between sampling techniques.

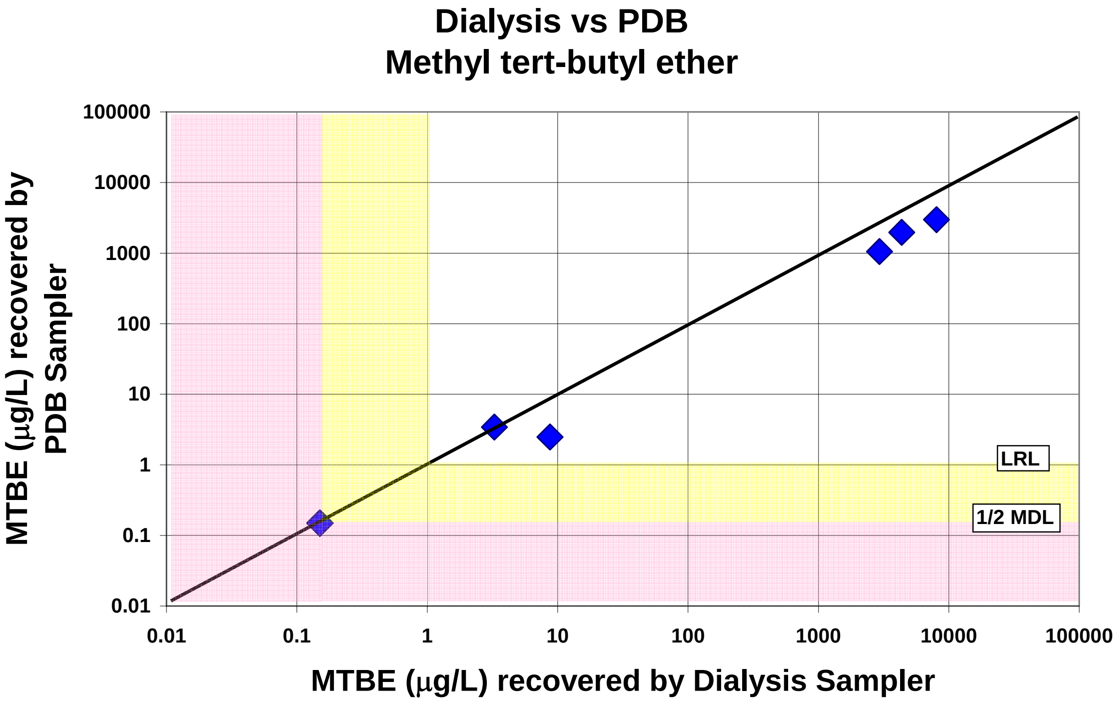


Figure 4-5. Dialysis Sampler Versus Polyethylene Diffusion Bag (PDB) Sampler Results For Methyl Tert-Butyl Ether

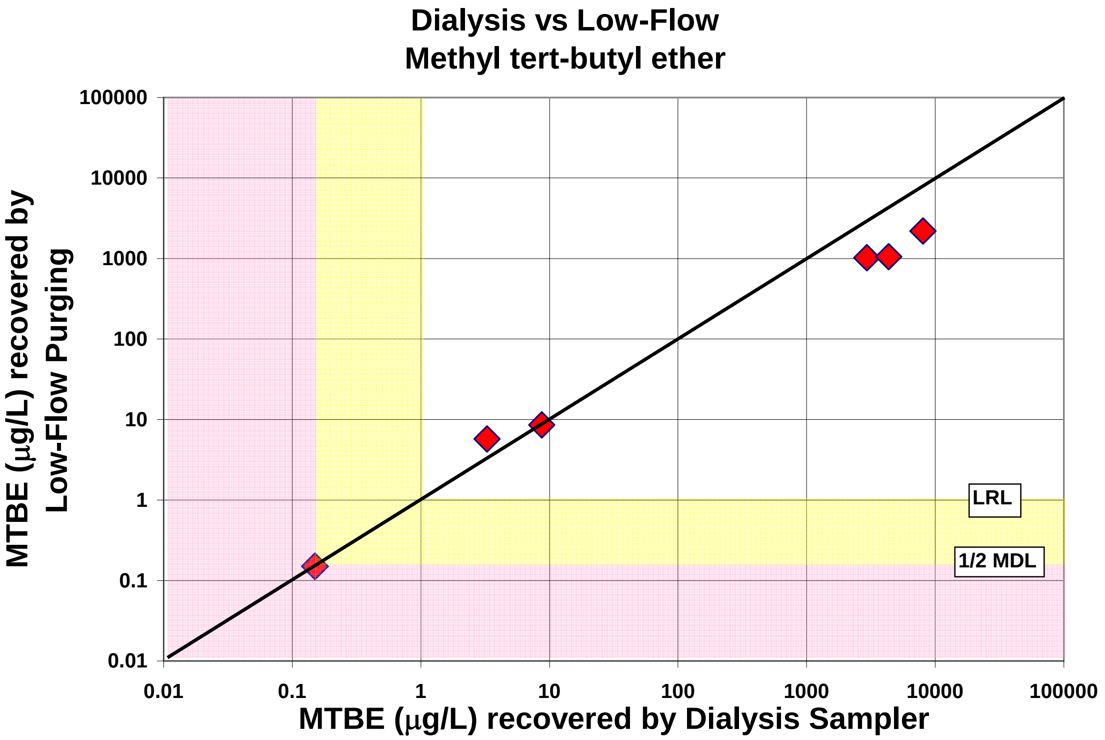


Figure 4-6. Dialysis SAmpler Versus Low-Flow Purging Results For Methyl Tert-Butyl Ether

4.3.2.2 Statistical Comparison of VOC Results

4.3.2.2.1 Correlation Analysis of VOCs. Pearson's correlation coefficients (r) were calculated by running least-squares regressions for all field comparison results between the dialysis sampler, PDB sampler, and low-flow purging for all volatile organic compounds (SPlus, 2002). The results are given in Table 4-3. Most correlations between concentrations sampled with the dialysis samplers and concentrations sampled with low-flow purging were strongly positive. For 20 of the 24 VOCs listed in Table 4-3, correlations coefficients exceeded 0.58. High correlation values indicated that the data collected by different sampling techniques were closely and consistently matched. Only chloroform (-0.84), n-butylbenzene (0.35), p-isopropyltoluene (0.28), and sec-butylbenzene (-0.40) had correlation coefficients below 0.58. These weaker or negative correlations were primarily due to (1) a low number of comparisons for each compound, (2) a few comparisons where each compound was found at above detection concentrations with the dialysis sampler and not with low-flow purging, and (3) several instances where the opposite was true.

All correlations between concentrations sampled with the dialysis samplers and concentrations sampled with PDB samplers were strongly positive. For all 24 VOCs listed in Table 4-3, correlations coefficients exceeded 0.57. High correlation values indicated that the data collected by these two sampling techniques were closely and consistently matched. This result was not unexpected since both were diffusion-type samplers.

Most correlations between concentrations sampled with low-flow purging and concentrations sampled with PDB samplers were strongly positive. For 21 of the 24 VOCs listed in Table 4-3, correlations coefficients exceeded 0.54. High correlation values indicated that the data collected by these two different sampling techniques were closely and consistently matched. Only chloroform (-0.52), n-butylbenzene (0.36), and sec-butylbenzene (-0.40) had correlation coefficients below 0.54. These weaker or negative correlations were primarily due to the same reasons mentioned above. These results were nearly identical to the correlation findings for dialysis sampler results versus low-flow purging results.

The least-squares regression equation for each correlation listed in Table 4-3 can also be used as another indicator of how well the two distributions being compared match. If the two distributions match exactly, the slope should be 1 and the intercept should be 0. Regression slopes between 1.75 and 0.25 were found for 22 of the 24 VOCs comparing the recoveries of the dialysis samplers and low-flow purging, for all 24 VOCs comparing the recoveries of the dialysis samplers and PDB samplers, and for 17 of the 24 VOCs comparing the recoveries of the PDB samplers and low-flow purging, indicating there was fairly good agreement for most compounds.

Table 4-3. Correlation Of Sampling Techniques By Volatile Organic Compound
[Dialysis, regenerated cellulose dialysis membrane sampler; LF, low-flow purging; PDB, polyethylene diffusion bag sampler; vs., versus; n, number of comparisons correlated; r, Pearson's correlation coefficient; LSRE, least-squares regression equation; yellow shading highlights r values less than 0.57]

		Dialysis vs. LF		**Dialysis vs. PDB**		**LF vs. PDB**	
Compound	**n**	**r**	**LSRE**	**r**	**LSRE**	**r**	**LSRE**
1,1,1-Trichloroethane	7	0.93	y=0.15x+0.59	0.88	y=0.86x+0.13	0.76	y=4.51x-2.0
1,1-Dichlorethene	10	0.99	y=1.24x-0.05	1.00	y=1.21x-0.29	1.00	y=0.97x-0.14
Trichloroethene	12	1.00	y=1.26x+44	1.00	y=1.28x-219	0.99	y=1.01x-252
cis-1,2-Dichloroethene	10	1.00	y=0.99x+39	1.00	y=1.08x+43	1.00	y=1.09x+0.90
trans-1,2-Dichloroethene	5	0.97	y=1.29x-0.31	0.95	y=1.25x-0.75	0.85	y=0.83x+5.4
Vinyl chloride	9	1.00	y=1.28x-6.5	1.00	y=1.22x-5.2	1.00	y=0.95x+1.2
Dichlorodifluoro-methane	4	1.00	y=1.40x-0.85	1.00	y=1.32x-0.81	1.00	y=0.95x-0.01
Chloroform	7	-0.84	y=-0.46x+1.1	0.84	y=0.76x+0.11	-0.52	y=-0.86x+1.3
Ethylbenzene	17	0.98	y=0.37x+15	0.94	y=0.45x+20	0.98	y=1.24x+0.82
Isopropylbenzene	17	0.64	y=0.45x+5.1	0.76	y=0.41x+3.1	0.72	y=0.56x+1.4
n-Propylbenzene	14	0.86	y=0.47x+6.8	0.78	y=0.31x+4.0	0.76	y=0.57x+0.73
n-Butylbenzene	9	0.35	y=0.37x+3.8	1.00	y=0.49x+0.09	0.36	y=0.17x-0.15
p-Isopropyltoluene	13	0.28	y=0.67x+2.8	0.57	y=0.53x+0.40	0.54	y=0.22x+0.54
sec-Butylbenzene	7	-0.40	y=-1.68x+53	1.00	y=0.99x+0.00	-0.40	y=-0.09x+0.83
tert-Butylbenzene	7	0.83	y=1.02x+1.1	0.99	y=1.00x+0.05	0.87	y=0.71x-0.39
Naphthalene	12	0.58	y=0.66x+30	0.77	y=0.64x+16	0.55	y=0.40x+25
1,2,4-Trimethylbenzene	17	0.69	y=0.75x+51	0.64	y=0.36x+28	0.79	y=0.41x+10
1,3,5-Trimethylbenzene	13	0.68	y=1.52x+8.5	0.77	y=0.83x+1.9	0.76	y=0.36x+2.5
Methyl tert-butyl ether	5	0.99	y=0.27x+33	0.99	y=0.38x+32	0.97	y=1.37x+24
Benzene	13	0.99	y=0.28x+21	1.00	y=0.62x+35	0.99	y=2.17x-6.5
Toluene	15	0.73	y=0.35x+10	0.97	y=1.62x-9.2	0.59	y=2.06x+19
m,p-Xylene	17	0.98	y=0.50x+29	0.86	y=0.37x+32	0.85	y=0.71x+12
o-Xylene	15	0.94	y=0.51x+7.6	0.66	y=0.48x+14	0.55	y=0.74x+12
Styrene	6	0.66	y=0.64x-0.09	0.65	y=0.63x+0.24	0.83	y=0.83x+0.46

4.3.2.2.2 Normality Testing for VOCs. The concentration data from all 24 volatile organic compounds detected 4 or more times 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). Chemical parameters from comparisons where at least one sampling technique had an above detection value 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. Initially, only 3 of the 24 volatile organic compounds were found to be normally distributed. A log-transformation was applied and the distributions retested. This resulted in only a slight improvement in that 5 of the 24 VOCs were then found to be normally distributed. Because the majority of VOC results were not normally distributed, non-parametric statistical testing of the data was conducted. Non-parametric statistics do not require normal data distributions.

4.3.2.2.3 Kruskal-Wallis Testing of VOC Results. VOC concentration data collected with the three different sampling techniques were compared using a non-parametric Kruskal-Wallis rank sum test. The results of the testing are given in Table 4-4 below. Only VOCs that had 4 or more field comparison data points with above minimum detection limit concentrations were included in this analysis. For 21 of 24 VOCs, no significant difference was found between samples collected with the dialysis sampler, PDB sampler, and low-flow purging. Thus, although some VOCs seemed to be recovered better with one sampling technique or the other on the 1:1 correspondence plots, these differences mostly turned out not to be significant statistically. These results indicate that for most VOCs, dialysis samplers accurately collected both chlorinated and aromatic VOCs that varied widely in volatility, solubility, and Henry's Law constant.

Table 4-4. Statistical Comparison Of VOC Concentrations Recovered By The Dialysis Sampler, PDB Sampler, And Low-Flow Purging Using The Kruskal-Wallis Test
[PDB; polyethylene diffusion bag; (at $p<0.05$); the presence or absence of differences are significant at the 95% confidence level for the number of comparisons]

VOCs where No Significant Difference was found between samples collected with the Dialysis sampler, PDB sampler, and Low-Flow Purging (at $p<0.05$)		
1,1,1-Trichloroethane (7)[1]	Ethylbenzene (17)	Benzene (13)
1,1-Dichlorethene (10)	Isopropylbenzene (17)	Toluene (15)
Trichloroethene (12)	n-Propylbenzene (14)	m,p-Xylene (17)
cis-1,2-Dichloroethene (10)	tert-Butylbenzene (7)	o-Xylene (15)
trans-1,2-Dichloroethene (5)	Naphthalene (12)	Styrene (6)
Vinyl chloride (9)	1,2,4-Trimethylbenzene (17)	
Dichlorodifluoromethane (4)	1,3,5-Trimethylbenzene (13)	
Chloroform (7)	Methyl tert-butyl ether (5)	
VOCs where a Significant Difference was found between samples collected with the Dialysis sampler, PDB sampler, and Low-Flow Purging (at $p<0.05$)[1]		
sec-Butylbenzene (7)	p-Isopropyltoluene (13)	n-Butylbenzene (9)
[1] Number of comparisons for each compound above the minimum detection limit.		

The three compounds that showed a significant difference, sec-butylbenzene, n-butylbenzene, and p-isopropyltoluene, were all less-volatile aromatic VOCs and all were detected only at low concentrations (<10 μg/L) in this study. In addition, the number of field comparison data points where all three sampling techniques had above minimum detection limit concentrations was small; 1, 3 and 8 for sec-butylbenzene, n-butylbenzene, and p-isopropyltoluene, respectively. These compounds previously were found to have the poorest correlation coefficients between the diffusion samplers and the low-flow purging technique.

4.3.2.2.4 Multi-factor ANOVA on Ranks for VOC Results. A multi-factor ANOVA on ranked data was run for each of the three VOCs, sec-butylbenzene, n-butylbenzene, and p-isopropyltoluene that showed a significant difference between sampling techniques. The ANOVA included the variables of sampling technique (dialysis, PDB, low-flow), site (Lakehurst, Port Hueneme, West Trenton), and date (2 dates for Lakehurst, 1 for Port Hueneme and 1 for West Trenton). This analysis was completed to determine if these other factors could have caused the differences observed. The results are given in Table 4-5.

Table 4-5. Results Of Multi-Factor ANOVA On Ranks For Three Volatile Organic Compounds [n, number of comparisons; SD, significantly different; NSD, not significantly different; at p<0.05, at 95% confidence level; LF, low-flow purging; D, dialysis sampler; PDB, polyethylene diffusion bag sampler]

Compound	**n**	**Sampling Date** SD/NSD at p<0.05	**Sampling Site** SD/NSD at p<0.05	**Sampling Technique** SD/NSD at p<0.05	**Tukey Test** results for Significant Differences
n-Butylbenzene	9	NSD	NSD	SD	LF > D = PDB
p-Isopropyltoluene	13	NSD	NSD	SD	LF > D = PDB
sec-Butylbenzene	7	NSD	SD	SD	LF > D = PDB

The multi-factor ANOVA on ranks showed that the differences in the field comparison data for these three VOCs noted by the Kruskal-Wallis test were not due to sampling date (for all three VOCs) or sampling site (for 2 of the three VOCs). All three VOCs were still found to exhibit significant differences between sampling techniques. The multiple comparison test indicated for all three compounds, the dialysis sampler and PDB sampler recovered approximately equal concentrations and that both were significantly less than the concentrations recovered by low-flow purging.

This was statistical confirmation of the phenomena seen in the 1:1 plots for these compounds. For example, the plots for n-butylbenzene showed good agreement between the dialysis and PDB sampler results (Figure 4-7) with only one point above the laboratory reporting level. However, the plot of dialysis sampler versus low-flow purging (Figure 4-8) showed poor agreement for the majority of comparison points which were all below the laboratory reporting level for n-butylbenzene. All results in the yellow region of the graph indicated that n-butylbenzene is recovered in higher concentrations with the low-flow purge pump than with the dialysis sampler. The reason for this finding was most likely because the pump drew in low concentrations of this VOC during the purging process that were not present in the open interval at the depth the diffusion samplers were suspended prior to purging. This was the case for both s-butylbenzene and p-isopropyltoluene also. Thus, even though the statistical testing indicated significant differences between the sampling techniques, these VOCs probably may be sampled effectively with dialysis samplers, particularly at concentrations above the laboratory reporting level.

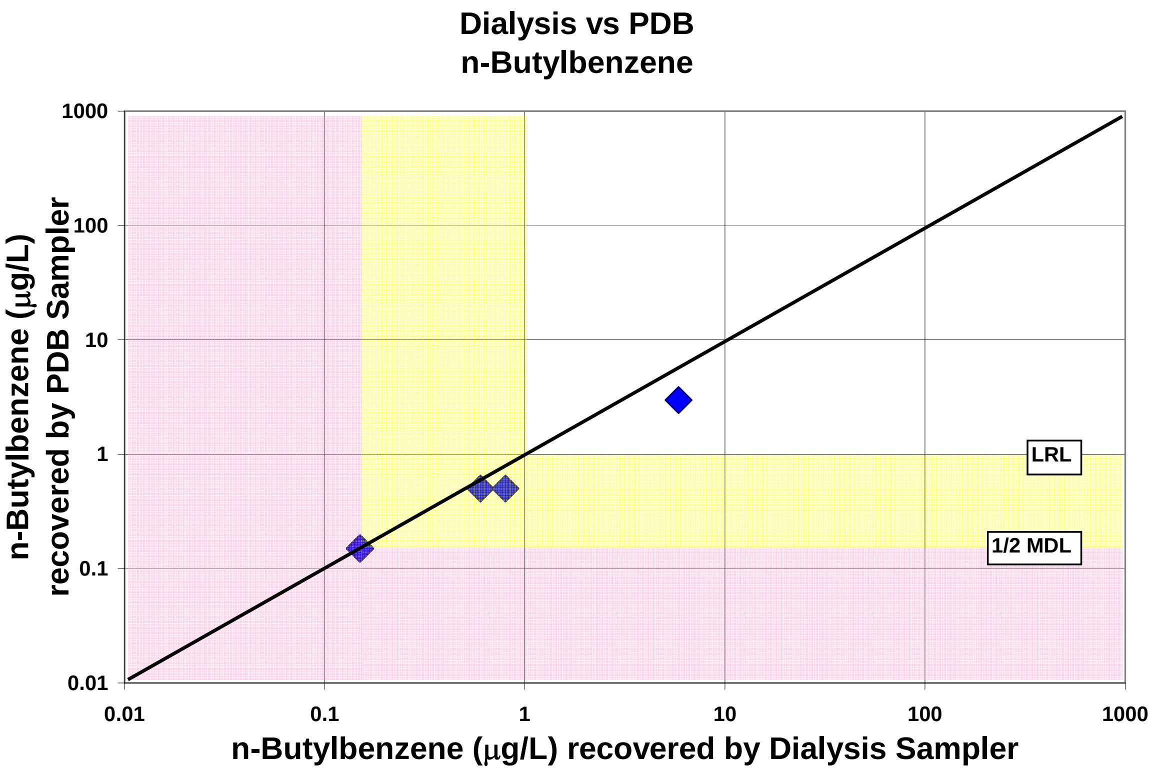


Figure 4-7. Dialysis Sampler Versus Polyethylene Diffusion Bag (PDB) Sampler Results For n-Butylbenzene

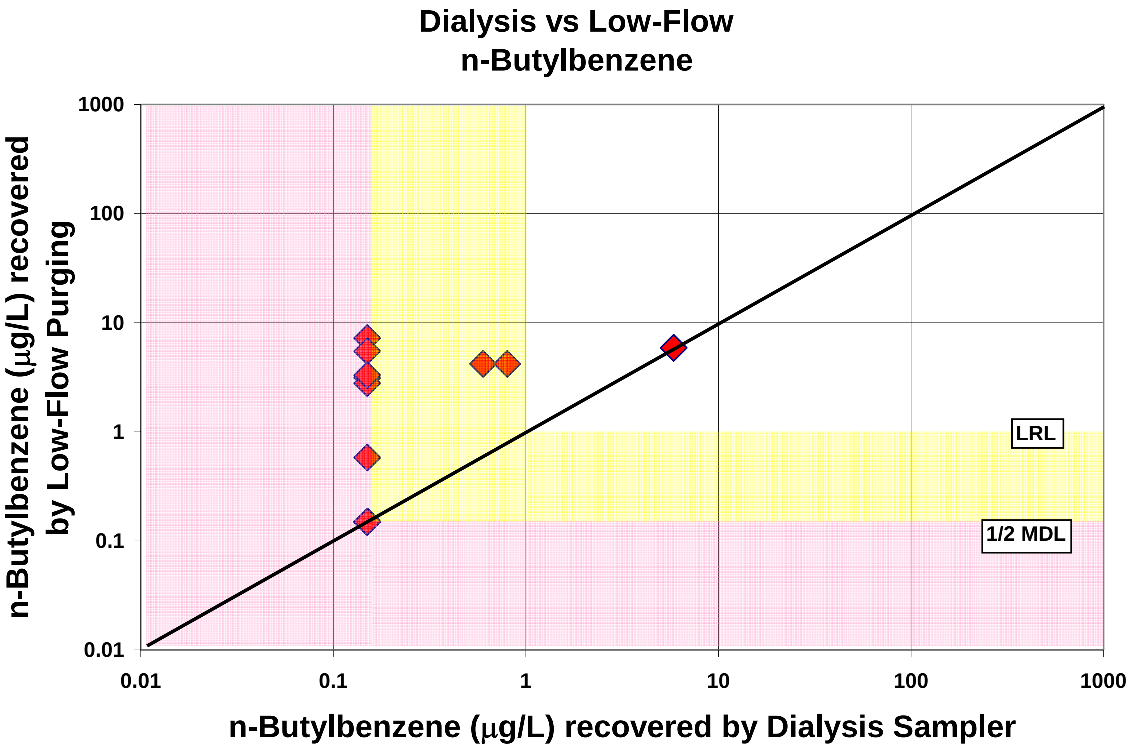


Figure 4-8. Dialysis Sampler Versus Low-Flow Purging Results For n-Butylbenzene

4.3.2.3 Concentration Ranges Measured for VOCs

Because it is useful to know the concentration ranges over which dialysis samplers can function, the concentrations ranges for the VOCs measured by the dialysis samplers in this demonstration study are given in Table 4-6. For many VOCs these ranges were wide and encompassed most of the concentrations that would be found in ground water wells. However, the wells sampled in this study were not highly contaminated with all VOCs, so the full concentration range of use for some compounds could not be determined.

Table 4-6. Ranges Of Concentrations Measured Using Dialysis Samplers For VOCs

VOCs Detected	Concentration range measured		
	Low	High	Units
1,1,1-Trichloroethane	0.2	11	µg/L
1,1-Dichloroethene	0.2	47	µg/L
1,2,4-Trimethylbenzene	4.0	346	µg/L
1,3,5-Trimethylbenzene	7.0	28	µg/L
Benzene	0.3	5120	µg/L
cis-1,2-Dichloroethene	0.4	18600	µg/L
Chloroform	0.5	2	µg/L
Dichlorodifluoromethane	0.6	70	µg/L
Ethylbenzene	0.4	976	µg/L
Isopropylbenzene	0.7	41	µg/L
m,p-Xylene	1.5	940	µg/L
Methyl tert-butyl ether	3.0	8030	µg/L
Naphthalene	10.0	130	µg/L
n-Butylbenzene	0.6	6	µg/L
n-Propylbenzene	0.6	78	µg/L
o-Xylene	0.9	244	µg/L
p-Isopropyltoluene	0.3	4	µg/L
sec-Butylbenzene	2.0	2	µg/L
Styrene	0.4	2	µg/L
tert-Butylbenzene	0.4	2	µg/L
Trichloroethene	0.7	24600	µg/L
Toluene	0.7	361	µg/L
trans-1,2-Dichloroethene	0.3	82	µg/L
Vinyl chloride	0.3	1280	µg/L

4.3.3 Evaluation of Field Comparison Results for Inorganic and Selected Organic Constituents

Thirty different non-VOC water-quality constituents were found above their detection limits in wells in the field comparison studies. This group of constituents included inorganic parameters (all the major cations and anions, many trace elements, silica, and total dissolved solids), and three organic constituents (dissolved organic carbon, methane, and ethene). All of these parameters were compared only between dialysis samplers and low-flow purging, because PDB samplers could not collect samples for most of these chemical constituents.

4.3.3.1 Graphical Analysis of Inorganics and Selected Organic Constituents

The results for the 30 inorganic and selected organic constituents found at above-detection-limit concentrations at least four times during the field comparison portion of the study were evaluated graphically using 1:1 correspondence plots. Ideally, if both the dialysis sampler and low-flow purging collected a constituent 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 constituents 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 Appendix A. Selected plots will also be presented in this section for the sake of illustrating common findings.

Similar to the plots made for VOCs, the inorganics and selected organic constituents field comparison data typically varied from the detection limit of a compound to up to 3 to 4 orders of magnitude greater, so all plots were shown as log-log plots. These plots also were divided into three parts: a white region that included all data points where both the sampling techniques being compared had concentrations above the laboratory reporting level for the compound being plotted; a yellow region that included all points where the concentrations for one or both of the sampling techniques were less than the laboratory reporting level but still above one half the minimum detection limit; and a rose-colored region that included concentrations that were less than one half the minimum-detection limit

4.3.3.1.1 Major Cations and Anions, Silica, and Total Dissolved Solids. Calcium and chloride are examples of a major cation and anion that were sampled in this demonstration. The 1:1 plots of these two inorganics are shown in Figures 4-9 and 4-10. Both constituents showed excellent agreement between concentrations obtained using both sampling techniques in the 1 to 1000 mg/L range in concentration. The data points were closely grouped on or near the 1:1 correspondence line indicating that these inorganics were sampled equally by both the dialysis sampler and low-flow purging. At concentrations above the laboratory reporting level, similar results were found for magnesium, sodium, potassium, alkalinity, fluoride, nitrate, bromide, silica, and total dissolved solids (Appendix A). Data comparison points for sulfate were also primarily close to the 1:1 line, but had a few more points above the line, indicating that low-flow purging recovered slightly higher concentrations than dialysis samplers in some instances (Appendix A).

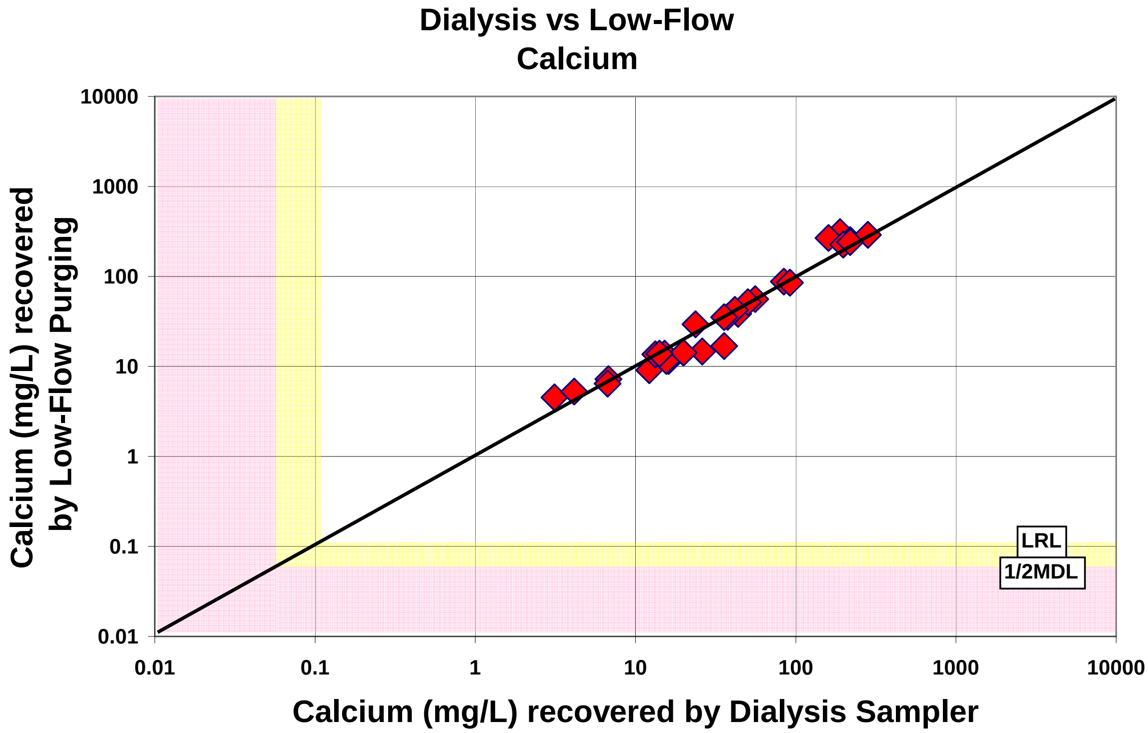


Figure 4-9. Dialysis Sampler Versus Low-Flow Purging Results For Calcium

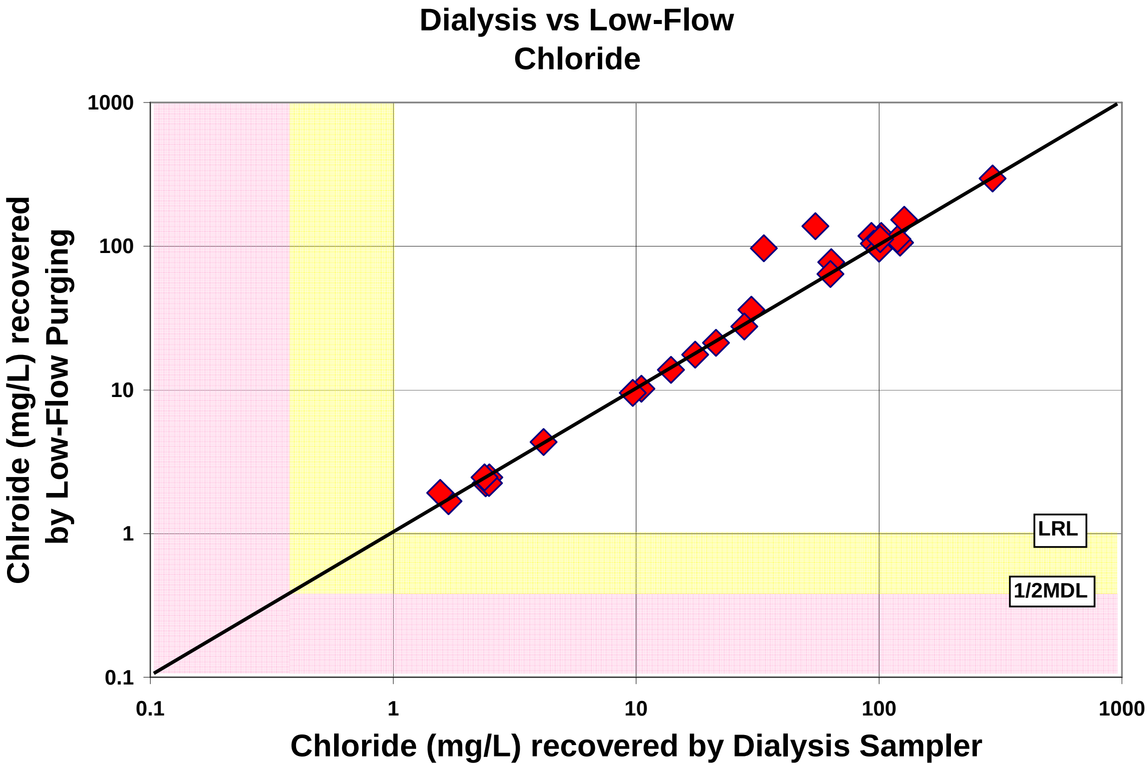


Figure 4-10. Dialysis Sampler Versus Low-Flow Purging Results For Chloride

Most major cations and anions also exhibited distributions close to the 1:1 line at concentrations below the laboratory reporting level. At low concentrations, bromide and nitrate were more often higher in the low-flow purge sample than in the corresponding dialysis sample (Appendix A). This may have been due to the same phenomenon observed for some of the aromatic VOCs, in that low concentrations of these two constituents were drawn into the well by pumping that were not present in the well screen when the dialysis sampler was deployed.

4.3.3.1.2 Trace Elements. Arsenic and manganese were examples of trace elements detected in this demonstration that appeared to be recovered approximately equally by both sampling techniques in this demonstration (Figures 4-11 and 4-12). Although having fewer data comparison points, plots for barium, cadmium, chromium, lead, molybdenum, nickel, selenium, vanadium, and zinc were similarly distributed, particularly at concentrations above the laboratory reporting level for each element (Appendix A). At concentrations below the laboratory reporting level, a few elements, cadmium and nickel, were more often higher in the low-flow purge sample than in the corresponding dialysis sample. The purge pump may be drawing water containing these elements into the well that were not there when the dialysis sampler was deployed. Increased nickel may be due to contamination from the purge pump's stainless-steel materials of construction (Wilde et al. 1998). Also, at low concentrations, a few elements, aluminum and zinc, were more often higher in the dialysis sampler than in the low-flow purge sample. These two elements were found in low concentrations in both trip blanks and dialysis sampler equipment blanks.

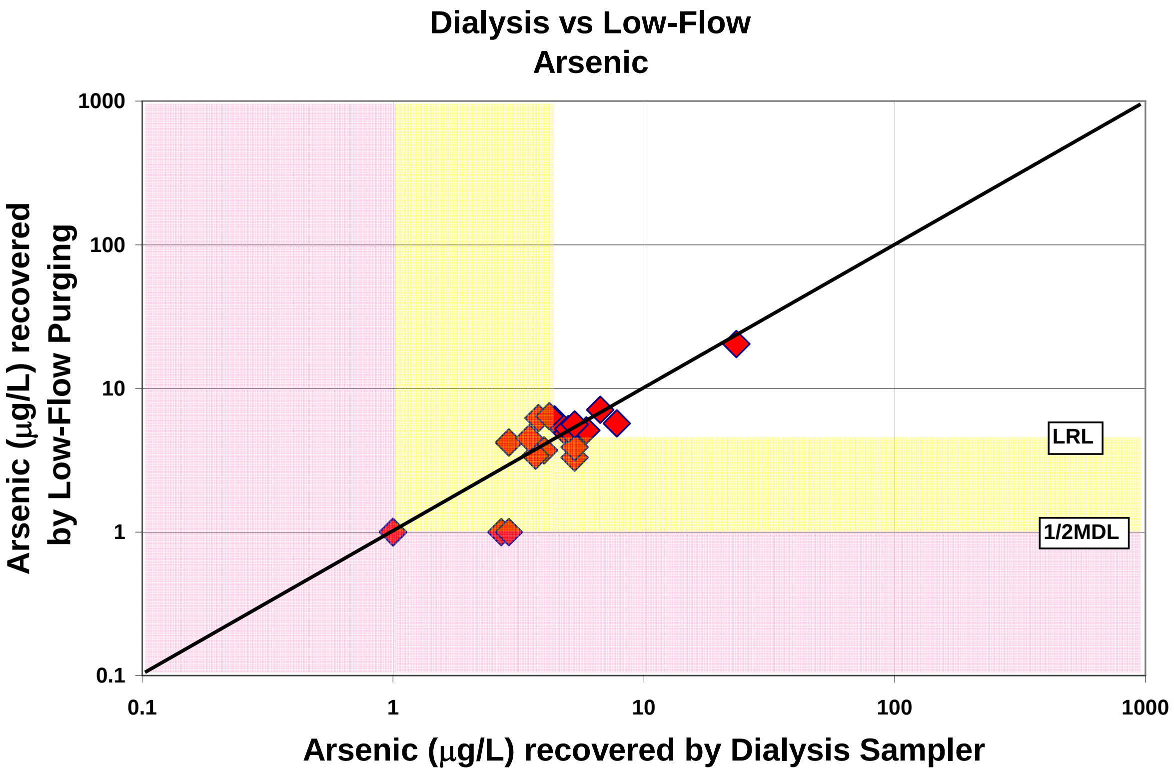


Figure 4-11. Dialysis Sampler Versus Low-Flow Purging Results For Arsenic

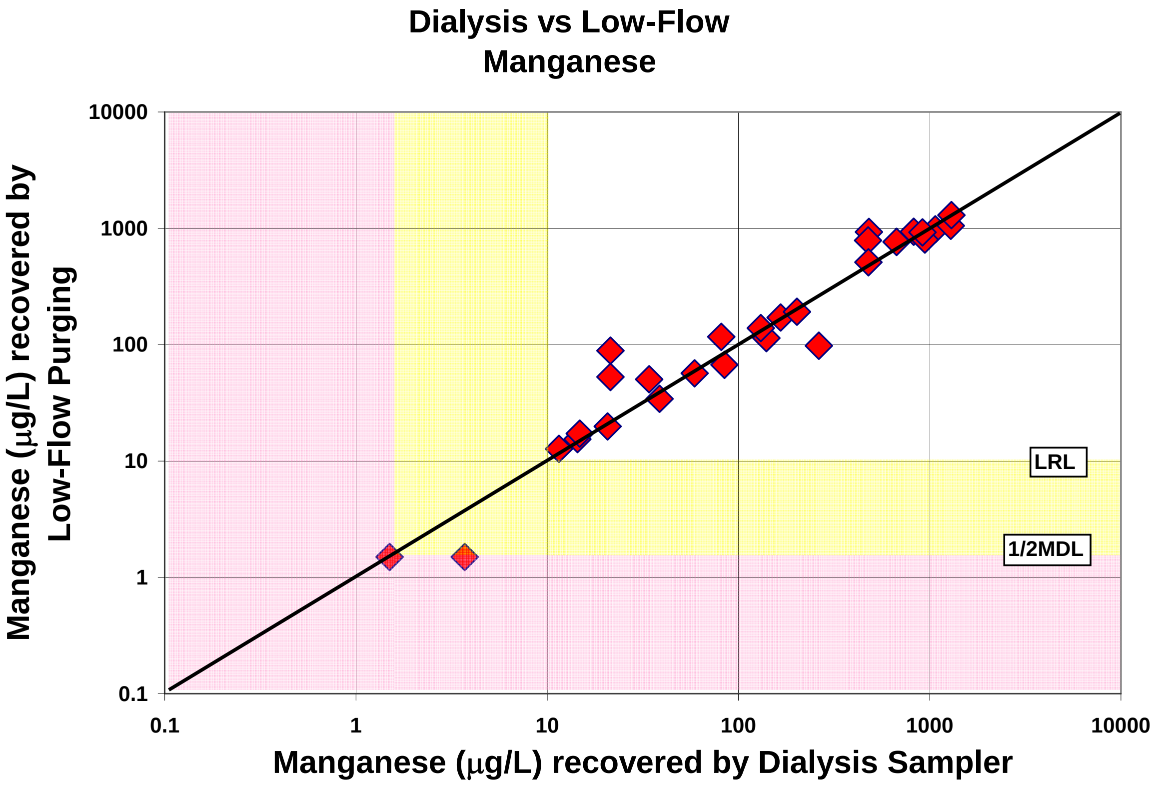


Figure 4-12. Dialysis Sampler Versus Low-Flow Purging Results For Manganese

The distribution of comparison points for iron was not as consistent as most other trace elements (Figure 4-13). Although most points were near the 1:1 line, a few more were found below the line than above, implying that iron was more often higher in the dialysis samplers than in low-flow purge samples. One possible explanation for this observation is that pumped samples became oxygenated to a degree during pumping, altering the iron redox chemistry of the samples, and decreasing their dissolved iron content. Similar results have been observed in pumped wells compared to peeper diffusion samples by Lorah et al. (2004). Another possible explanation may be that iron concentrations were affected by the dissolved oxygen content of the water in the well compared to the water used to fill the dialysis sampler. For example, if a sampler is filled with oxygenated water and then deployed in an anoxic well, dissolved iron may diffuse into the sampler from the well water, react with the oxygen in the sampler, and precipitate out as ferric oxide or ferric hydroxide. Once precipitated out, these iron precipitates may take a longer period of time to re-dissolve and re-equilibrate once the water in the sampler goes anoxic. If the deployment period is short, iron precipitates inside the diffusion sampler may be present when sampling takes place, resulting in higher iron concentrations inside the dialysis sampler than in the subsequent low-flow purge samples. No precipitation of ferric oxide or ferric hydroxide was observed in any of the dialysis samplers used in any of the field comparisons in this study. This phenomenon has only been observed in nylon-screen diffusion samplers by Vroblesky and Pravecek (2002). Precautions were taken in this study to fill the samplers with anoxic water and to try to keep them anoxic up until the time they were deployed in any anoxic wells. However, it was difficult to maintain deoxygenated conditions during transport to the field, so some re-oxygenation may have taken place to cause the few higher iron concentrations seen in the dialysis sampler.

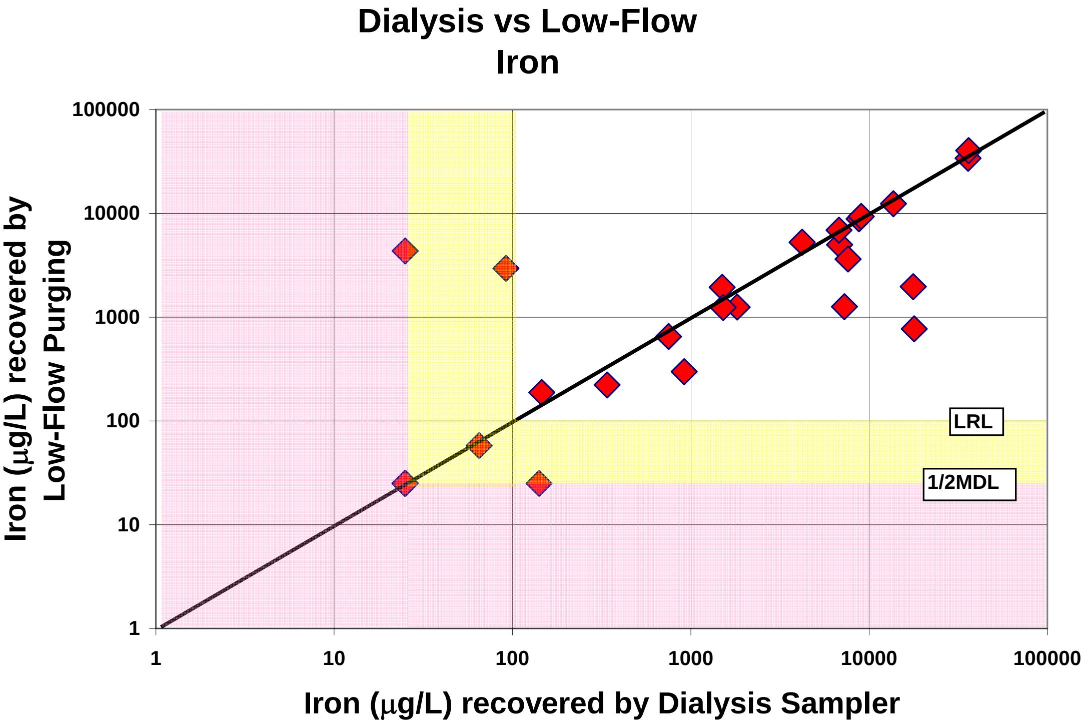


Figure 4-13. Dialysis Sampler Versus Low-Flow Purging Results For Iron

4.3.3.1.3 Dissolved Gases and Sulfide. Carbon dioxide, methane, and ethene were dissolved gases detected in wells in this study that appeared to be recovered equally by both sampling techniques (Figures A-74 through A-76). Dissolved organic carbon was recovered equally to slightly better by the dialysis sampler than low-flow purging (Figure A-78). Sulfide comparison points fell mostly below the 1:1 correspondence line (Figure 4-14) indicating sulfide was usually recovered in higher concentrations by the dialysis samplers than by low-flow purging. The explanation for this latter finding may be similar to the possible explanations given above for iron since sulfide is also a redox active constituent.

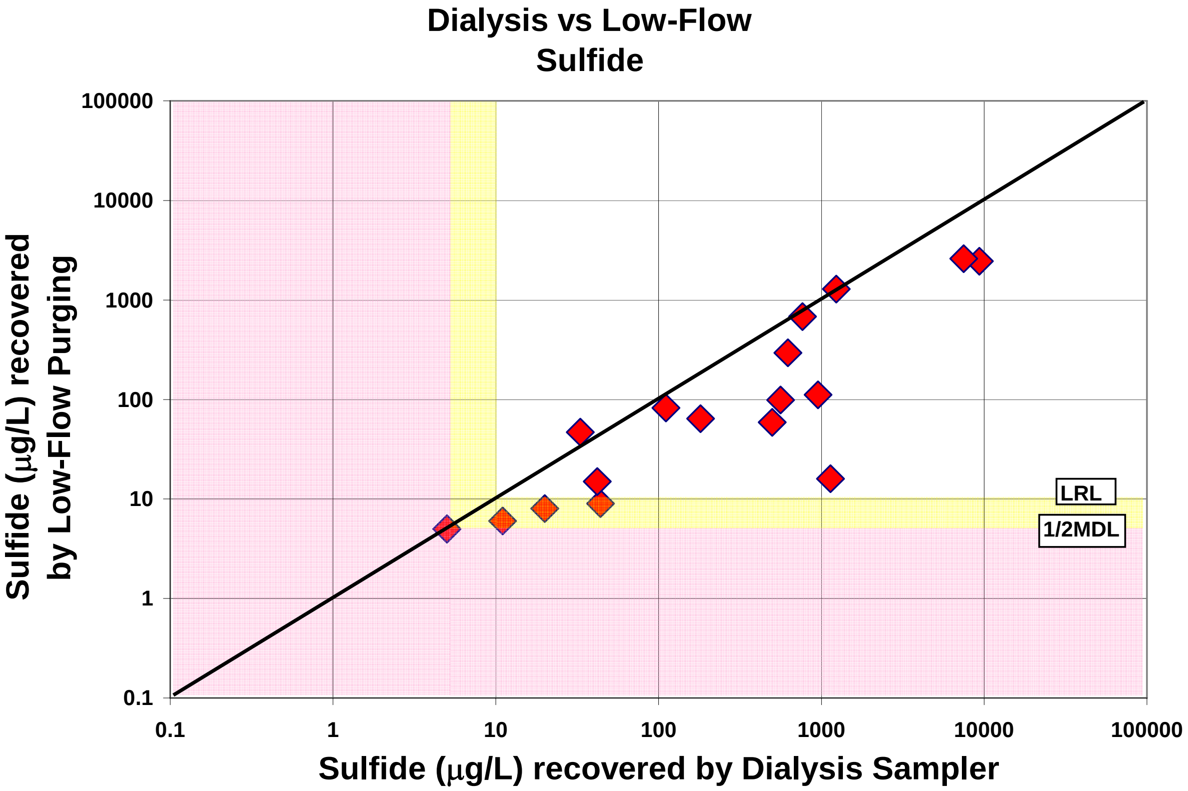


Figure 4-14. Dialysis Sampler Versus Low-Flow Purging Results For Sulfide

4.3.3.2 Statistical Analysis of Inorganic and Selected Organic Constituent Results

4.3.3.2.1 Correlation Analysis of Results. Pearson's correlation coefficients (S-Plus, 2002) were calculated for all field comparison results between the dialysis sampler and low-flow purging for all inorganic and selected organic constituents. The results are given in Table 4-6. All correlations between concentrations sampled with the dialysis samplers and concentrations sampled with low-flow purging were strongly positive. For 29 of the 30 constituents listed in Table 4-7, correlations coefficients exceeded 0.50. Only lead (0.49) had a correlation coefficient slightly below 0.50.

Table 4-7. Correlation Of Sampling Techniques By Inorganic and Selected Organic Constituents [Dialysis, dialysis sampler; LF, low-flow purging; vs., versus; n, number of comparisons correlated: r, Pearson's correlation coefficient; LSRE, least-squares regression equation; yellow shading highlights r values less than 0.50]

		Dialysis vs. LF	
Compound	**n**	**r**	**LSRE**
Aluminum	22	0.71	y=1.01x+12
Arsenic	18	0.94	y=0.83x+0.74
Barium	25	0.82	y=0.35x+39
Bicarbonate/Alkalinity	27	0.97	y=0.82x+12
Bromide	8	0.94	y=0.73x+0.60
Cadmium	5	1.00	y=1.03x+0.35
Calcium	28	0.97	y=1.23x-5.9
Carbon dioxide	28	0.90	y=0.67x+5.6
Chloride	28	0.95	y=1.01x+7.4
Chromium	5	0.98	y=0.98x+1.1
Dissolved organic carbon	27	0.89	y=0.85x-1.1
Ethene	9	0.74	y=0.74x+0.03
Fluoride	16	0.81	y=0.56x+0.15
Iron	23	0.88	y=0.87x-548
Lead	14	0.49	y=0.49x+5.6
Magnesium	28	0.99	y=0.99x-0.07
Manganese	27	0.95	y=0.96x+34
Methane	21	0.72	y=0.38x+191
Molybdenum	11	0.91	y=0.74x+10
Nickel	11	0.59	y=0.55x+3.6
Nitrate	11	0.88	y=0.79x+0.98
Potassium	28	0.99	y=0.93x-0.03
Selenium	8	0.99	y=0.97x+0.35
Silica	28	0.87	y=0.74x+4.1
Sodium	28	0.97	y=0.87x+10
Sulfate	25	0.82	y=1.06x+43
Sulfide	16	0.94	y=0.29x+70
Total dissolved solids	27	0.97	y=1.05x+37
Vanadium	7	0.65	y=0.51x+1.9
Zinc	18	0.50	y=0.43x+8.5

The least-squares regression equation for each correlation listed in Table 4-7 can also be used as an indicator of how well the two distributions being compared match. If the two distributions match exactly, the slope should be 1 and the intercept should be 0. Regression slopes between 1.75 and 0.25 were found for all 24 constituents comparing the recoveries of the dialysis samplers and low-flow purging, indicating there was fairly good agreement for most constituents.

4.3.3.2.2 Normality Testing Results. The distributions of concentration data from all 30 inorganic and selected organic parameters detected in wells from the field comparison study were tested to determine if they were normal. Identical with the VOC distribution testing, 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). Parameter concentrations from comparisons where at least one sampling technique had an above detection value were included in this analysis. Initially, only 4 of the 30 constituents were found to be normally distributed. A log-transformation was applied and the distributions retested. This resulted in a small improvement in that 11 of the 30 constituents were found to be normally distributed. Because the majority of results were still not normally distributed, non-parametric statistical tests were used to compare the inorganic and selected organic constituent data collected using different sampling techniques.

4.3.3.2.3 Wilcoxon Signed Rank Test on Inorganic and Selected Organic Constituent Results. Inorganic and selected organic constituent 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 4-8 below. For 24 of 30 constituents, no significant difference was found between samples collected with the dialysis sampler and low-flow purging. Thus, although some constituents seemed to be recovered better with one sampling technique or the other on the 1:1 correspondence plots, these differences mostly turned out not to be significant statistically. These results indicated that in most cases, dialysis samplers were able to collect inorganic and organic constituents as accurately as low-flow purging over a range of concentrations.

Table 4-8. Statistical Comparison Of Inorganic and Selected Organic Constituent Concentrations By The Dialysis Sampler And Low-Flow Purging Using The Wilcoxon Signed Rank Test [(p<0.05); the 95% confidence level]

Constituents where No Significant Difference was found between samples collected with the Dialysis sampler and Low-Flow Purging (at p<0.05)		
Aluminum (22)[1]	**Chloride (28)**	**Selenium (8)**
Arsenic (18)	**Chromium (5)**	**Silica (28)**
Barium (25)	**Fluoride (16)**	**Sodium (28)**
Bicarbonate/Alkalinity (27)	**Iron (23)**	**Sulfate (25)**
Bromide (8)	**Lead (14)**	**Vanadium (7)**
Cadmium (5)	**Magnesium (28)**	**Zinc (18)**
Calcium (28)	**Manganese (27)**	**Methane (21)**
Carbon dioxide (28)	**Molybdenum (11)**	**Ethene (9)**
Constituents where a Significant Difference was found between samples collected with the Dialysis sampler and Low-Flow Purging (at p<0.05)		
Dissolved organic carbon (27)	**Nitrate (11)**	**Nickel (11)**
Total dissolved solids (27)	**Potassium (28)**	**Sulfide (16)**

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

The six constituents that showed a significant difference in this test, dissolved organic carbon, total dissolved solids, potassium, nitrate, nickel, and sulfide, varied widely in their chemical characteristics. Some were cations, some anions; some were organic, some inorganic; some were present in very low concentrations, and some were present in very high concentrations. The number of comparisons for each ranged from 11 to 28. Correlations between sampling techniques for these constituents were all positive and ranged from 0.59 to 0.99 (Table 4-7).

4.3.3.2.4 Multi-factor ANOVA on Ranks for Inorganic and Selected Organic Constituents. A multi-factor ANOVA on ranked data was run for each of the six constituents that the Wilcoxon test showed a significant difference for between sampling techniques, dissolved organic carbon, total dissolved solids, nitrate, potassium, nickel, and sulfide. The ANOVA included the variables of sampling technique (dialysis, PDB, low-flow), site (Lakehurst, Port Hueneme, West Trenton), and date (2 dates for Lakehurst, 1 for Port Hueneme and 1 for West Trenton). This analysis was completed to determine if these other factors could have caused the observed differences. The results are given in Table 4-9.

Table 4-9. Results Of Multi-Factor ANOVA On Ranks For Six Constituents
[n, number of comparisons; SD/NSD, significantly different/not significantly different; at p<0.05, at 95% confidence level; PH, Port Hueneme/Point Mugu; L, Lakehurst; WT, West Trenton; LF, low-flow purging; D, dialysis sampler; pink shading highlights significant differences found]

Constituent	**n**	**Sampling Date** SD/NSD at p<0.05	**Sampling Site** SD/NSD at p<0.05	**Sampling Technique** SD/NSD at p<0.05	**Tukey Test** results for Significant Differences
Dissolved organic carbon	27	NSD	SD	NSD	PH > L > WT
Total dissolved solids	27	NSD	SD	NSD	PH > L > WT
Potassium	28	NSD	SD	NSD	PH > L > WT
Nitrate	11	NSD	NSD	NSD	
Nickel	11	NSD	NSD	SD	LF > D
Sulfide	16	NSD	SD	SD	PH > L> WT D > LF

The multi-factor ANOVA on ranks showed that the differences in the field comparison data for these six constituents were not due to sampling date. Four constituents, dissolved organic carbon, total dissolved solids, potassium, and sulfide were found to be significantly different due to differences in concentrations present at the three sites. In all cases, the Port Hueneme/Point Mugu site had significantly higher concentrations of these four constituents than the Lakehurst site which in turn had significantly higher concentrations than the West Trenton site. The ANOVA on ranks also showed that DOC, TDS, and potassium were not significantly different due to the sampling techniques used to collect the samples.

The ANOVA on ranks failed to find any significant difference due to sampling site or confirm any significant differences due to sampling technique for nitrate. This contrasted with the results of the Wilcoxon test which showed a significant difference between sampling techniques. The reason for this disagreement may be the result of the decreased number of degrees of freedom and therefore the decreased power of the ANOVA on ranks to determine significant differences between the factors tested. The original difference noted by the Wilcoxon test between nitrate concentrations recovered by dialysis samplers and low-flow purging may be due to differences between the nitrate results obtained above and below the laboratory reporting level. Of the 11 comparisons of nitrate concentrations, 6 of these comparisons had low concentrations below the laboratory reporting level and in most of these comparisons the nitrate concentrations did not agree well between the two sampling methods (figure A-59). In the 5 field comparisons where nitrate concentrations were above the laboratory reporting level for both sampling techniques, the results agreed very closely between the two sampling methods. Based on these observations and the disagreement between the statistical tests, it was concluded that at concentrations above the reporting level, there was no difference in nitrate concentrations recovered by the dialysis sampler and low-flow purging. However, at concentrations below the reporting level, there may be a difference in nitrate concentrations recovered by the two sampling methods. The conclusion that nitrate concentrations above the detection limit can be effectively sampled by the dialysis sampler is supported by the results of another field comparison study by Harter and Talozi (2004) which found that nitrate was sampled equally well by a dialysis sampler and a purging technique.

The significant differences between sampling techniques noted by the Wilcoxon test were confirmed by the multi-factor ANOVA on ranks for nickel and sulfide. Nickel was recovered in higher concentrations by low-flow purging than the dialysis sampler. Sulfide was recovered in higher concentrations by the dialysis sampler than by low-flow purging. These findings also confirmed statistically the phenomena observed on the 1:1 plots for these two inorganic constituents.

One reason nickel was recovered in higher concentrations by low-flow purging may be because the low-flow purging pump was made with 316 stainless-steel components that contain iron, manganese, chromium, nickel, and molybdenum. Desorption or release of trace amounts of nickel from the pump has been seen in previous studies (Wilde et al. 1998). However, none of the other metals showed a similar difference between sampling techniques. In 10 of the 11 comparisons for nickel, the field data occurred at concentrations below the laboratory reporting level. The one field comparison where nickel was at the laboratory reporting level for both sampling methods, the results agreed very closely. Since the statistical testing was based only on low-concentration data, no final conclusions should be made regarding the ability of dialysis samplers to collect accurate samples for nickel. Nickel did readily diffuse through the regenerated cellulose membrane in the bench-scale testing conducted as part of this study.

The reason sulfide was recovered in higher concentrations by the dialysis sampler is not readily apparent. Results of analysis of dialysis sampler field equipment blanks were all below minimum detection levels (<10 μg/L), indicating that sulfide was not leaching from the membrane. The recovery of higher dissolved sulfide concentrations by the dialysis samplers than by low-flow purging may be due to losses of this volatile redox-active constituent under the purging process. Active pumping conditions present in a well during the purging process may induce volatilization of hydrogen sulfide gas or may produce more oxygenated conditions which can result in conversion of sulfide to sulfate in low-flow purge samples. Another possible explanation for higher sulfide concentrations in samples from the dialysis sampler than in samples from low-flow purging is that sulfate-reducing bacteria may attach to the regenerated cellulose membrane during the period of equilibration in a well. If conditions are right, when the sulfate-reducing bacteria produce sulfide in the immediate vicinity of the dialysis membrane, the sulfide concentration that equilibrates inside the sampler may be artificially high when compared to a subsequent purged sample. If this is happening, lower sulfate concentrations should be found in dialysis samplers in wells where this occurred. However, lower sulfate concentrations were not found in dialysis samples where higher sulfide concentrations were measured. Microbial analysis or scanning electron microscope photos of the regenerated cellulose membrane samplers after removal from a well may be needed to shed light on this possible explanation.

4.3.3.3 Concentration Ranges Measured for Inorganic and Selected Organic Constituents

Because it is useful to know the concentration ranges over which dialysis samplers can function, the concentrations ranges for the constituents measured by the dialysis samplers in this demonstration study are given in Table 4-10. For many constituents, these ranges do encompass the concentrations that many of these chemical parameters would usually be found at in ground-water wells. However, the wells sampled in this study were not highly contaminated with some trace elements, so the full concentration range of use for dialysis samplers for these elements was not determined.

Table 4-10. Ranges of Concentrations Measured Using Dialysis Samplers For Inorganic and Selected Organic Constituents

Inorganics Detected	Concentration Range Measured		
	Low	High	Units
Aluminum	11	150	µg/L
Alkalinity/Bicarbonate (as $CaCO_3$)	13	879	mg/L
Arsenic	3	23	µg/L
Barium	10	706	µg/L
Bromide	0.4	3.8	mg/L
Calcium	3	282	mg/L
Cadmium	0.3	29	µg/L
Methane	1	4200	µg/L
Chloride	2	293	mg/L
Carbon dioxide	1	88	mg/L
Chromium	5	11	µg/L
Dissolved organic carbon	0.3	51	mg/L
Ethene	0.1	0.6	µg/L
Fluoride	0.1	1.1	mg/L
Iron	65	36200	µg/L
Potassium	0.3	30	mg/L
Magnesium	0.2	100	mg/L
Manganese	4	1300	µg/L
Molybdenum	4	58	µg/L
Sodium	1	364	mg/L
Nickel	3	10	µg/L
Nitrate-N	0.3	5.3	mg/L
Lead	0.3	35	µg/L
Sulfide	11	9350	µg/L
Selenium	2	10	µg/L
Silica	3	49	mg/L
Sulfate	1	879	mg/L
Total dissolved solids	40	2320	mg/L
Vanadium	3	6	µg/L
Zinc	2	1420	µg/L

4.4 Discussion of Field Comparison Results

4.4.1 Comparison of Results to Previous Studies

Most previous studies involving dialysis samplers have shown similar results to those in this demonstration but usually with far fewer sample comparisons. The results of this study compared well with those of Imbrigiotta et al. (2002) who found dialysis samplers recovered concentrations of calcium, chloride, alkalinity, iron, and several chlorinated VOCs from nine fractured rock wells at the NAWC site in West Trenton, NJ, that were not statistically different from samples collected with a low-flow purging method and a modified conventional purging method. As in this study, dialysis samplers gave accurate results for dissolved iron but with lower precision.

The findings of this study agreed with those of Vroblesky et al. (2002) who found dialysis samplers deployed in three wells at the Naval Air Station Fort Worth Joint Reserve Base recovered concentrations of arsenic, calcium, chloride, ferrous iron, manganese, and sulfate that were the same as concentrations recovered by low-flow purging and nylon-screen diffusion samplers. Vroblesky and Pravecek (2002) found similar results to this study when they compared the use of dialysis samplers in 13 wells at Hickam AFB in Hawaii and found they recovered concentrations of chloride, iron, sulfate, and aromatic VOCs equal to those recovered by low-flow purging. Both of these reports did point out that sampling redox-active constituents, such as iron, was sometimes problematic. They found if anaerobic wells were sampled with nylon-screened diffusion samplers filled with aerobic water, iron concentrations were frequently overestimated compared to low-flow purge samples. They postulated that dissolved iron diffusing into the samplers combined with the dissolved oxygen present in the water inside to form an iron oxide precipitate. They reasoned that if the diffusion sampler was sampled before this precipitate re-dissolved, this iron would be included in the sample and result in higher iron concentrations in the diffusion samplers than with low-flow purging. Though this phenomenon was not observed in any dialysis samplers by Vroblesky and Pravecek (2002), to avoid this potential problem, the dialysis samplers used in this study were filled with nitrogen-sparged deionized water and stored in the same between the time of construction and deployment. This seemed to be effective because most iron comparisons in this demonstration agreed fairly well (Figure 4-13). However, even with taking this precaution, a few comparison points in this study were found to have higher iron concentrations in the sample from the dialysis sampler than in the corresponding low-flow purge sample (Figure 4-13). It is possible that in these few cases, the water inside the dialysis sampler became re-oxygenated before the sampler was deployed.

The results of this study did not agree with those of Vroblesky et al. (2003) who found dialysis samplers consistently recovered lower concentrations of TCE and PCE in 5 wells at Andersen AFB in Guam than both PDB samplers and low-flow purging. The results of this demonstration showed excellent agreement in the concentrations of all chlorinated VOCs detected between samples collected with dialysis samplers and PDB samplers and dialysis samplers and low-flow purging. Vroblesky et al. (2003) speculated that the reason their results did not agree may have been due to the fact that the ground water on Guam was very low in oxidizable organic carbon and that the regenerated-cellulose membrane may itself have been used as a carbon source by bacteria in wells to create localized conditions around the bags that were more conducive to TCE and PCE biodegradation. At all three sites sampled in this demonstration, dissolved organic carbon was present in readily detectable concentrations so this possible problem was not encountered.

This demonstration agreed well with the results of Harter and Talozi (2004) who found that nitrate and specific conductance equilibrated within 1 to 4 days at 21 ^{o}C in 43 wells and gave comparable results to a conventional purging technique. This study showed good agreement between above reporting level nitrate and total dissolved solids concentrations collected by dialysis samplers and low-flow purging (Figures A-59 and A79).

The results of this study partially agreed with the findings of Parsons (2005) which compared a number of different diffusion samplers, grab samplers, and purging methods that was conducted in 20 wells at McClellan AFB, Sacramento, California. Dialysis samplers, PDB samplers, rigid porous polyethylene samplers, polysulfone samplers, a downhole thief sampler, a disposable polyethylene point-source bailer, low-flow purging, and conventional purging were all compared in their ability to sample for anions, trace metals, hexavalent chromium, 1, 4-dioxane, and VOCs. Results of the McClellan AFB study reported that regenerated-cellulose dialysis samplers recovered concentrations of VOCs, anions, 1,4-dioxane, and hexavalent chromium as well as or better than low-flow purging. These findings for anions and VOCs agreed with the findings of this demonstration. However, the McClellan AFB study also found dialysis samplers recovered lower concentrations of VOCs than PDB samplers. These findings were in direct contrast to those of this demonstration where VOC concentrations recovered by dialysis samplers and PDB samplers agreed extremely well for all compounds detected. The reason for the different results is not immediately apparent. The McClellan AFB study did not report which specific VOCs or what VOC concentrations were detected. It is possible that the concentrations being compared were between the reporting level and the minimum detection limit where small absolute differences can produce large percentage differences that can adversely affect statistical evaluations.

The results of this demonstration disagreed with the findings of the McClellan AFB report for trace metals in that Parsons (2005) concluded that dialysis samplers generally recovered lower concentrations of trace metals than low-flow purging, the disposable bailer, and the porous polyethylene sampler in their tests. The results of this demonstration found most all trace elements tested were sampled about equally with dialysis samplers and low-flow purging. Once again, it was impossible to evaluate the results from the study by Parsons (2005) because the specific metals compared or the metals concentrations found with each of the samplers were not provided. This “lumping” of trace metals was done to increase the power of the statistical techniques used but it may have inadvertently led to concluding small differences were significant. One possible reason for different concentrations being recovered by dialysis samplers and low-flow purging was that there was a 7 to 10 day lag time between when the samples were collected with each of these samplers due to the experimental design of the McClellan AFB study. Additionally, no vertical profiling was done prior to the multi-sampler deployments in the test wells at McClellan AFB, so differences in recovery of metals between diffusion samplers and purging methods may be due to the diffusion samplers not being deployed at the depth of highest mass influx. Overall, the results for most of the trace metals detected using dialysis samplers in the current demonstration agreed very well with the low-flow purging results. This was probably in large part because of the use of proper deployment depths as determined by both chemical and hydraulic vertical profiling of each well.

4.4.2 Deployment Considerations

4.4.2.1 Deployment Considerations for Diffusion Samplers in General

4.4.2.1.1 Basic Sampling Considerations. All diffusion samplers, including dialysis and PDB samplers, require two trips to the field to collect a sample, one to deploy the samplers and one to retrieve the samplers. This may or may not be problematic depending on the travel distance to the site. All diffusion samplers require some field work prior to their initial deployment to conduct chemical and hydraulic vertical profiling to determine the depth at which the sampler will be suspended in each well. Vertical profiling is discussed in more detail in Section 4.4.2.1.3 below. Diffusion samplers can easily be deployed by one person and sampled by two persons. Considerations in deploying diffusion samplers include that the sampler 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 ground-water sample.

4.4.2.1.2 Sampler Volume and Length. The volume of water contained in a diffusion 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. In fact, this minimum volume should be increased by 10-20% to account for volume used to rinse bottles or losses caused by sampling difficulties in the field. Planning for a small amount of extra water volume in the diffusion sampler can only result in the minor problem of having to dispose of a few milliliters of purge water, whereas if the volume is too small, the problem may involve sacrificing certain analyses because minimum volume requirements cannot be met.

The maximum volume that a diffusion sampler can contain is that enclosed in a 5-ft long sampler of the diameter that will fit down the well casing. This is in keeping with the desire to have a diffusion sampler not represent more than 5 ft of an open interval (ITRC, 2004). The maximum length of a diffusion sampler should never be longer than the open interval of a well or the length of the zone of highest mass flux present in the open interval.

4.4.2.1.3 Sampler Depth and Vertical Profiling. The proper functioning of diffusion samplers depends on their ability to equilibrate with chemical concentrations in ground water flowing naturally through the open interval of a well. The depth of deployment of a diffusion sampler is therefore crucial to collecting a representative sample. The depth of deployment should not be arbitrary. The diffusion sampler should be placed at a depth where the highest mass flux passes through the open interval of each well (ITRC, 2004). This means the variation in ground-water flow and any stratification of concentrations of contaminants should be determined over the length of the open interval prior to deployment of a diffusion sampler. Vertical profiling by preferably both hydraulic and chemical methods is recommended to obtain this information.

The only exception to the vertical profiling requirement is if the open interval of a well is short (<5 ft). With short open intervals, diffusion samplers can be positioned in the center of the screen. For wells with larger open intervals (>5 ft) vertical profiling should be done to determine the optimal depth for deployment (ITRC, 2004). This entails some extra work prior to the first time a well is sampled with diffusion samplers but should not need to be repeated before subsequent sampling events.

Hydraulic vertical profiling is usually done using either a closely spaced packer/pump setup or a borehole flow meter. The packer/pump method involves packing off and test pumping small portions of the open interval to determine if there are zones of higher or lower transmissivity over the length of the open interval. The zone with the highest ground water input to the well should be determined. This procedure works well in unconsolidated sand-and-gravel wells where most of the ground-water flow through the open interval is horizontal. A borehole flow meter measures vertical flow in the open interval by following the movement of a heat pulse generated by the instrument. This procedure works well in fractured-bedrock wells where ground-water flow is primarily vertical, in that it enters the open interval through one fracture and leaves through another fracture at a different depth. The zone over which most of the vertical flow occurs should be determined.

Chemical vertical profiling is usually accomplished by equilibrating, sampling, and analyzing small closely spaced diffusion samplers which have been suspended over the length of the open interval of a well. The diffusion samplers should be sampled for a representative indicator parameter depending on the type of contamination present or chemical of concern at a particular site. Knowledge of what depth the chemicals of concern are highest in concentration must be determined. (For example, at the NAWC site, PDB samplers were spaced 3 to 5 ft apart over the 20 to 25 ft open intervals of the wells. These PDB samplers were sampled and analyzed only for chlorinated VOCs since this was the primary contamination present at this site.)

In addition to hydraulic and chemical vertical profiling information, some knowledge of the site geology, lithology, and past contamination history is also required to make an informed decision on the depth of deployment. Based on all these factors, positioning the diffusion sampler at the depth of the zone of highest mass flux of the contaminant of concern (ground water flow times concentration) in the open interval should result in collection of a sample that is most representative of the zone that most influences the quality of ground water from the well.

4.4.2.1.4 Comparison Sampling. After determining the optimal depth for diffusion sampler deployment, the results from a sample collected by this method may or may not match the results of a comparison sample collected at the same depth by a low-flow purging technique. The reason for this lies in the nature of their different sampling mechanisms. Diffusion samplers can only equilibrate with water that flows past them during the period of time and at the depth they are suspended in a well. On the other hand, purge pumps can draw water in over the entire open or screened interval of a well even at low-flow rates (Varlgen et al. 2006). Purge pumps can also draw water in from areas of the aquifer located laterally from the open interval that would not normally enter the open interval of a well under non-pumping conditions. Contamination entering a well screen at a specific depth can mix with uncontaminated water entering at another depth in the open interval during purging causing dilution of concentrations. 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).

4.4.2.2 Deployment Considerations for Dialysis Samplers in Particular

4.4.2.2.1 Regenerated Cellulose Dialysis Membrane Hydration. Dialysis samplers made with regenerated-cellulose dialysis membrane 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. The samplers can conveniently be kept wetted by sliding them into a LDPE sleeve knotted at one end, partially filled with deionized water, and then knotted or clamped at the other end. The LDPE tubing is very inexpensive and can be purchased in wall thicknesses strong enough to retain its integrity even when containing water and a dialysis sampler. The sealed LDPE sleeve only needs to be partially filled with water because the headspace in the sleeve will be saturated with water vapor to the extent necessary to keep the membrane hydrated. Alternatively, dialysis samplers can be submerged in a bucket or PVC tube filled with deionized water. All these methods of keeping a regenerated-cellulose membrane hydrated work and allow easy transport to the field site.

4.4.2.2.2 Contamination of Samplers by Sampler Construction Materials. Initial concerns over the potential contamination of regenerated cellulose membranes with trace metals and sulfides were determined to be unfounded based on the results of blanks analyzed during the bench-scale testing. No trace metals, sulfides, or VOCs were found to desorb in any of the tests using the manufacturer's pre-cleaned dialysis membranes. However, the results of equipment blanks from dialysis samplers used during all four field demonstrations showed consistent low concentrations of zinc. Since it did not originate from the regenerated-cellulose membranes, the zinc probably came from the galvanized fender washers that were used as weights in the samplers. The washers were double-bagged in sealed polyethylene bags, but many bags were found to have leaked and were filled with water upon retrieval from most wells. Stainless-steel or plastic-coated weights would probably alleviate this problem. Low concentrations of barium were found in two dialysis sampler equipment blanks but this element was also found in two deionized water trip blanks. This indicated the need for high-quality deionized water, free of the constituents of interest, to fill the dialysis samplers.

4.4.2.2.3 Volume Loss Due to the Dialysis Process. The process of dialysis through the regenerated cellulose membrane occurs in both directions simultaneously. At the same time the ions in well water are diffusing inward to equilibrate inside the sampler, the deionized water is slowly diffusing outward, essentially to try and dilute the aquifer to deionized water. Previous studies had pointed out this loss of sampler volume during the equilibration period in wells with high ionic strength ground waters (Vroblesky et al. 2002; Vroblesky and Pravecek, 2002; Vroblesky et al. 2003). The volume lost was determined in these studies to be severe enough to warrant the insertion of a rigid support inside the regenerated cellulose membrane to limit the collapse of the sampler to a set volume. Wells sampled in this demonstration in the coastal plain and bedrock aquifers of New Jersey were not particularly high in dissolved solids (<500 mg/L), so there was no concern of excessive volume loss when sampling these wells. However, wells sampled at Port Hueneme/Point Mugu, California near the Pacific Ocean were much higher in TDS (up to 2,300 mg/L), so this was of concern at this site.

The volume/weight-loss phenomenon for dialysis samplers was tested at all three sites in the field demonstration. All samplers were constructed without internal rigid supports and weighed prior to shipment or transport to the field sites. Samplers were then weighed in the field immediately after retrieval from a well. The weight differences for 28 different dialysis samplers were measured in this study. Assuming the density of water was 1 g/mL, the weight loss was expressed as a loss of volume per unit time. The average volume loss measured in this demonstration was 2.7% per week. The volume loss only in the high dissolved solids wells at the Port Hueneme/Point Mugu site averaged 2.8% per week and ranged from 0 to 7% per week. From these findings, it was concluded that the volume loss due to dialysis appeared to be small even for wells with dissolved solids concentrations as high as 2,300 mg/L. The <3% volume loss per week was not considered a limitation for dialysis samplers, since one to two week deployment periods were sufficient for all of the parameters measured in this demonstration.

4.4.2.2.4 Effect of Biodegradation on Dialysis Sampler Integrity. Previous studies pointed out regenerated cellulose dialysis membrane samplers became discolored or biofouled during equilibration in some wells (Vroblesky et al. 2002; Vroblesky and Pravecek, 2002; Vroblesky et al. 2003). Discoloration of the membrane was thought to be an indication that biodegradation of the dialysis membrane was occurring. The authors felt that if the membrane began to biodegrade, perforations might develop or the characteristics of the membrane might change to the extent that the passage of constituents would be affected, either positively or negatively. Vroblesky and coworkers allowed the dialysis samplers to equilibrate in shallow wells with warmer ground water temperatures (~21 ^{o}C) for extended equilibration periods ranging from 2 to 3 weeks. Despite the concerns about biodegradation, no perforations were noted in the dialysis samplers used in any of their studies. Leblanc (2004) suspected that bacterial action on regenerated cellulose dialysis samplers buried in lake-bottom sediments contributed to making the membranes more brittle and easily breakable. Many samplers in this study were lost prior to sample recovery and the author attributed it to biodegradation effects. This study allowed dialysis samplers to equilibrate with the pore water of lake sediments for 2 to 3 weeks.

To investigate this phenomenon, four identical dialysis samplers were constructed, weighed, and deployed in a well at the NAWC West Trenton, New Jersey site. The samplers were retrieved and weighed at approximately one week intervals, and then redeployed in the same well. Observations as to the extent of any discoloration and the appearance of any perforations were made each time the samplers were removed from the well. The average ground-water temperature during this test was ~15 ^{o}C. Discoloration was noted after one week but did not appear to increase with time. The first perforations were observed in one sampler after 4 weeks. Over the course of the 5th and 6th weeks, the other three samplers eventually developed perforations also. Based on these results, it could be concluded that dialysis samplers should last about 4 weeks in a well at ~15 ^{o}C before biodegradation would compromise the membrane. These findings imply that biodegradation should not be a significant limitation for dialysis samplers if one- to two-week deployments are used. Such deployments were sufficient for all the constituents measured in this demonstration. The reason the previous studies mentioned above experienced problems with biodegradation was probably because of their longer deployment times, warmer ground-water temperatures, and proximity to high bacteria populations, for example, samplers buried in lake sediments.

4.5 Summary of Field Comparison Findings

4.5.1 Conclusions

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

- Dialysis samplers made of regenerated cellulose dialysis membrane can be used to collect both organic and inorganic chemical constituents from ground water in wells.

- A one- to two-week deployment time was sufficient for equilibration of all chemical constituents monitored in the field comparisons.

- For most VOCs, the graphs comparing dialysis sampler results to PDB sampler results show a tight grouping of data points around the 1:1 line, indicating extremely good agreement between the sampling techniques. Graphs comparing dialysis sampler results to low-flow purging results show more scatter in the data points around the 1:1 line, indicating that the agreement, though still good, is not as strong as the agreement between diffusion sampling techniques.

- The correlation coefficients for most VOC concentrations were strongly positive between samples collected with dialysis samplers and PDB samplers and between samples collected with dialysis samplers and low-flow purging.

- Dialysis samplers recovered concentrations of all VOCs that were not statistically significantly different from concentrations recovered by PDB samplers.

- Dialysis samplers recovered concentrations of 21 of 24 VOCs that were not statistically significantly different from concentrations recovered by low-flow purging.

- For most inorganic and selected organic constituents, the graphs comparing dialysis sampler results to low-flow purging results show a tight grouping of data points around the 1:1 line, indicating extremely good agreement between the sampling techniques, particularly at concentrations above the laboratory reporting level.

- The correlation coefficients for most inorganic and organic constituents were strongly positive between dialysis samplers and low-flow purging.

- Dialysis samplers recovered concentrations of 28 of 30 inorganic and selected organic constituents that were not statistically significantly different due to sampling technique from concentrations recovered by low-flow purging.

- De-oxygenated deionized water should be used to fill and store dialysis samplers that will be deployed in anoxic wells to avoid altering the concentrations of redox active chemicals, such as iron and sulfide.

- Dialysis samplers can easily be deployed by one person and sampled by two persons. The basic considerations in deploying diffusion samplers include that they must be submerged below the air/water interface in a well and they must remain submerged and be allowed to equilibrate for an appropriate period of time for the chemicals of concern at a site,

- The size of a dialysis sampler must be carefully determined before sampler construction begins to be sure it will contain the necessary minimum sample volume for all analyses that will be run on a sample. The size of a dialysis sampler should not be longer than 5 ft or the length of the open interval of the well or the length of the zone of highest mass influx of the chemical of concern to the well.

- A dialysis sampler should be placed at a depth where the highest mass flux passes through the open interval of each well. This means the variation in ground-water flow and any stratification of concentrations of contaminants should be determined over the length of the open interval prior to deployment of a diffusion sampler. Vertical profiling by preferably both hydraulic and chemical methods should be conducted to obtain this information prior to the first deployment of a dialysis sampler in a well.

- Dialysis samplers made with regenerated cellulose dialysis membrane must be kept hydrated between the time they are constructed and deployed.

- Dialysis 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 (1-2 weeks) this loss can be taken into account when constructing the sampler and should not impact the use of these samplers.

- Dialysis samplers may biodegrade within 4 to 6 weeks in a well. If equilibration times for the chemicals of concern are short (1-2 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 ground-water temperatures and high microbial populations can accelerate biodegradation.

- Differences between chemical concentrations collected with dialysis samplers and low-flow purging may be due to the fact that the sampling techniques use different mechanisms to collect samples. Dialysis 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.

4.5.2 Criteria For Use of Dialysis Samplers

The use of dialysis samplers would be advantageous over low-flow purging to sample wells in the following situations:

1. where it would be difficult or impossible to bring in a pump and its power source, (wells in remote wilderness areas, wells inside buildings),
2. where normal sampling activities would be extremely hazardous or inconvenient, (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, (residential areas near military bases),
4. where collection, transport, and treatment of purge water would be costly, difficult, or undesirable due to safety concerns, (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 they are completed in, (incorrect screen size and filter pack), and
6. at sites where large numbers of long-term monitoring wells must be sampled for both inorganics and VOCs.

Dialysis samplers should not be used in the following situations:

1. where "total" or unfiltered samples must be collected,
2. small diameter wells that require a large sample volume (>1 liter), or
3. wells that must be sampled for mercury, silver, and tin.

5.0 COST ASSESSMENT

5.1 Cost Reporting

One of the objectives of this demonstration was to evaluate the cost savings produced by using diffusion samplers instead of traditional low-flow purging techniques. The costs for collecting samples with the dialysis sampler and low-flow purging have been estimated based on the costs experienced in both the laboratory and field portions of this project. Costs for collecting samples (VOCs only) with PDB samplers have also been estimated and compared. Table 5-1 delineates the cost tracking categories considered in this cost comparison. A detailed tracking of costs will be reported in the Cost and Performance Report.

Table 5-1. Cost Tracking

Cost Category	Sub-Category	Details
Start-Up Costs	Site characterization	Must obtain information on well construction, recent water chemistry, recent contaminant concentrations
	Vertical profiling - chemical	Must be done once prior to diffusion sampling or low-flow purging
	Vertical profiling – hydraulic/geophysical	Must be done once prior to diffusion sampling or low-flow purging
Capital Costs – Dialysis Membrane Diffusion Samplers	Dialysis sampler construction materials	Membrane, mesh, rope, stopcock, clamps, weights
	Dialysis sampler construction	Lab personnel time
	Dialysis sampler transport containers	Polyethylene lay-flat tubing or PVC tube filled with deionized water
Capital Costs – Low-flow Purging	Variable-speed submersible pump	Rental of pump and control box
	Pump discharge tubing	Teflon-lined polyethylene tubing
	Generator and extension cord	Rental of generator
	Pump cleaning stand	
	Pump cleaning supplies	DI water, liquinox, methanol
	Cartridge filters for field filtration	In-line 0.45 μ capsule filters
Capital Costs – Polyethylene Diffusion Bag (PDB) Sampler	PDB sampler construction materials	Membrane, mesh, rope, stopcock, weights, heat-sealer
	PDB sampler construction	Lab personnel time
	PDB sampler transport containers	Clean cooler or plastic bag
Operating Costs – Direct Environmental Activity Costs	Dialysis sampler - deployment	Field personnel time
	Dialysis sampler – retrieval and sampling	Field personnel time
	Dialysis sampler – purge water disposal	Field personnel time
	PDB sampler – deployment	Field personnel time
	PDB sampler – retrieval and sampling	Field personnel time
	PDB sampler – purge water disposal	Field personnel time
	Low-flow purging – stabilization and sampling	Field personnel time
	Low-flow purging - filtration	Field personnel time
	Low-flow purging – cleaning pump and tubing	Field personnel time
	Low-flow purging – fuel for generator	Field personnel time
	Low-flow purging – Purge-water disposal	Field personnel time
	Low-flow purging – pump maintenance	Field personnel time

This comparison was performed with the following assumptions:

- Vertical profiling and site characterization are needed for both diffusion membrane samplers and low-flow purge pumps in order to determine the proper sampling depth in a well,
- The low-flow purging will require field filtration of samples whereas the diffusion samplers will not, and
- The analytical costs should be the same for all sampling techniques.

5.2 Cost Analysis

The primary cost comparison has been conducted between the cost of constructing and using dialysis samplers, constructing and using PDB samplers, and renting and using the equipment needed to conduct low-flow purging to sample a well. Cost comparisons were made on both a per sample basis and on a per site basis.

5.2.1 Cost Basis

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 35 ft below land surface, and an average sampling depth of 30 ft below land surface.
- The minimum required volume of ground water for at typical suite of VOC and inorganic analyses was assumed to be 1.7 L, the volume contained in one dialysis sampler 2.5 inches in diameter by 2 ft in length.
- The minimum required volume of ground water for a typical VOC analysis was assumed to be 150 mL, the volume contained in one PDB sampler 1.25 inches in diameter by 1 ft in length.
- Both the dialysis samplers and the PDB samplers were constructed by laboratory personnel, not purchase commercially.
- During sampling, less than 0.025 L of purge water was produced using either type diffusion sampler, while approximately 40 L (10 gallons) of purge water was produced during each low-flow purge sampling.

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 semi-annually for a period of 10 years.

5.2.2 Cost Drivers

The cost drivers were:

- The difference in cost of renting the low-flow pumping equipment versus purchasing diffusion sampler construction materials,
- The amount of time involved in pumping to stabilize field parameters prior to sample collection versus deployment and retrieval of the diffusion samplers prior to sample collection,
- The life cycle period for the cost comparison was considered to be 10 years.

5.2.3 Cost Comparison

The costs of constructing, deploying, and sampling using the three sampling technologies evaluated in this project were estimated as follows:

Dialysis Sampler

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

Membrane ($3.50/ft)(2 ft)	$7.00
Protective mesh ($0.75/ft)(3 ft)	2.25
PVC supports ($0.25 ea)(2/bag)	0.50
Weights ($0.10/wt)(10 wts/bag)	4.00
Rope ($0.10/ft)(40 ft)	4.00
Stopcock ($2.00)(1/bag)	2.00
Miscellaneous (clamp, ties, etc)	0.50
Storage bag ($0.06/ft)(3 ft)	0.18
Total materials costs per sampler	**$20.43**

Note: This constructs a 2.5-in diameter by 2-ft long sampler suitable for use in a 4-in diameter well. Smaller dialysis membrane (1.25-in diameter) can be purchased to make samplers that can be used in a 2-inch diameter well. The smaller diameter dialysis membrane costs essentially the same per unit length as the larger size but holds less volume.

The time for laboratory personnel to construct one dialysis 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 the weights and sealing the weights in a small polyethylene bag, assembling the pieces, filling the bag 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. The sampler was inserted into a thicker-walled larger diameter polyethylene sleeve storage bag filled with water and knotted at both ends.

Labor Costs for construction and field sampling were both estimated separately**.** It required approximately 45 minutes for one person to construct a dialysis sampler. At a labor rate of $50/hour/person, the construction labor cost would be $37.50. To deploy a single sampler it took one person 10 minutes. To recover, and collect a single sample from a well it took two persons approximately 10 minutes. At a labor rate of $50/hour/person, the field labor cost would be approximately $25. Therefore, the total labor costs would be $63 per sample.

The total cost (labor and materials) required to collect a single sample via the dialysis sampler would be approximately $83. When disposal costs of the purge water are included to the costs ($0.50/gallon), the total cost for sampling and disposal remains at approximately $83.

PDB Sampler

Material costs for a 1.25-in diameter by 1-ft long polyethylene diffusion bag are as follows:

LDPE membrane ($0.06/ft)(1 ft)	$0.06
Protective mesh (0.75.ft)(1.5 ft)	1.13
Weights ($0.10/wt)(10 wts/bag)	4.00
Rope ($0.10/ft)(40 ft)	4.00
Total material costs per sampler	**$9.19**

Note: Because PDB samplers can only be used to collect samples for VOCs, which require a volume of at most 150 mL, a 1.25-in by 1-ft long PDB sampler is usually sufficient for any well. The time for laboratory personnel to construct one PDB sampler was 30 minutes. This included, cutting the membrane, cutting the mesh, heat sealing one end, filling the membrane with deionized water, heat sealing the other end, cleaning and installing the weights in one end of the mesh, installing the filled LDPE membrane into the mesh, and closing the mesh at both ends.

Labor Costs for both construction and field sampling were estimated**.** It requires approximately 30 minutes for one person to construct a single PDB sampler. At a labor rate of $50/hour/person, the construction cost would be $25. To deploy a single sampler it took one person 10 minutes. To recover and collect a single sample from a well using a PDB sampler it took two persons approximately 10 minutes. At a labor rate of $50/hour/person, the field sampling labor cost would be approximately $25. Therefore, the total labor cost per sample would be $50.

The total cost (labor and materials) required to collect a single sample via the PDB sampler would be approximately $59. When disposal costs of the purge water are included to the costs ($0.50/gallon), the total cost for sampling and disposal remains at approximately $59.

Low-Flow Pump

Material costs for a submersible pump capable of pumping approximately 25 ft of head were used in the low-flow purge 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 many years of experience in field sampling, it was realistically estimated that 15 samples could be collected per week (3 samples/day x 5 days). 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 capsule filter was used in line to collect dissolved samples.

Pump Rental ($150/week)	$10.00
Tubing ($1.00/foot) (40 feet)	40.00
Generator Rental ($180/week)	12.00
Controller ($225/week)	15.00
Decontamination solutions	5.00
Fuel for generator (5 gal x $2.50/gal)	12.50
Capsule filter ($25 each)	25.00
Total material costs per sample	**$119.50**

Labor Costs in the field 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) in order to collect a single sample from a well using the low-flow purge technique. This time included cleaning the pump, setting the pump in the well at the appropriate depth, achieving parameter stabilization, collection of the samples, sample filtration, and removal of the pump from the well. At a labor rate of $50/hour/person, the total labor cost would be (1.6 hours x $50/hour/person x 2 persons) or approximately $160.

The total cost (labor and materials) required to collect a single sample with the low-flow purge technique would be approximately $280. When disposal costs of the purge water are added to the costs ($0.50/gal x 10 gal/well), the total cost for sampling and disposal increases to approximately $285.

Table 5-2 summarizes the cost comparison of materials, construction labor, and field labor costs of each of the sampling technologies evaluated in this project.

Table 5-2. Comparison of Material Costs, Construction Labor Costs, and Field Sampling Labor Costs for Dialysis Samplers, PDB Samplers, and Low-Flow Purging

Costs	**Dialysis Sampler**	**PDB Sampler**	**Low-Flow Purging**
Materials Costs/Sample	$20	$9	$120
Construction Labor Costs/Sample	$38	$25	---
Field Sampling Labor Costs/Sample	$25	$25	$160
Total Labor Costs/Sample	$63	$50	$160
Purge Water Disposal	$0	$0	$5
Total Costs/Sample	$83	$59	$285

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

5.2.4 Life-Cycle Costs

Table 5-3 summarizes the life-cycle costs of the three sampling technologies evaluated in this project when used monitor a typical site over the period of 10 years.

Table 5-3. Comparison of Sampling Costs Over a Ten Year Period for Dialysis Samplers, PDB Samplers, and Low-Flow Purging

	Dialysis Sampler	**PDB Sampler***	**Low-Flow Purging**
Sampling Cost/Sample	$83	$59	$285
Samples(Wells)/Site	50	50	50
Site Field Sampling Costs per Sampling Event	$4,150	$2,950	$14,250
Sampling Events per 10-year Period	20	20	20
Total Field Sampling Costs	$83,000	$59,000	$285,000
Total Field Sampling Cost Savings per Site over Low-Flow Purging	$202,000	$226,000	---
*PDB sampler collects VOC samples only.			

6.0 IMPLEMENTATION ISSUES

6.1 Environmental Permit Checklist

No permits were required to be obtained to conduct this Demonstration Plan.

6.2 Other Regulatory Issues

Both the PI and co-PI 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 dialysis samplers and to get feedback on their concerns about the use of the technology.

6.3 End-User Issues

State regulators, environmental consultants, and the military can all be identified as end users of the results of this Demonstration Plan. As an example, New Jersey Department of Environmental Protection (NJDEP) site managers at the NAWC West Trenton, New Jersey site have approved the use of dialysis samplers as the sole means of sampling 25 wells at the site for long-term monitoring of inorganics and VOCs. NJDEP approval came about only because the U.S. Navy and the USGS conducted comparison sampling of dialysis samplers and low-flow purging at the site and found the comparison was favorable in these 25 wells. The U.S. Navy is currently planning further comparison sampling in 15-20 additional wells. Based on the results of this comparison, NJDEP may approve the use of dialysis samplers as the sole sampling technique in additional wells at the NAWC site. The driving force behind the US Navy's support for the implementation of this technology is the cost savings in the long-term monitoring plan.

Because there are currently no commercially available dialysis samplers of the type being tested in this demonstration, the samplers were custom built by USGS for all demonstration sites. One of the final products of this Demonstration Plan will be a User's Guide/Technical Protocol on the construction and proper use of regenerated cellulose dialysis membrane diffusion samplers. This information should be instrumental in encouraging the commercialization of this technology.

The technology transfer of the results of this project will be accomplished in several ways after the conclusion of this demonstration. As members of the ITRC Diffusion Sampler Team the PI and co-PI will have the final report available on the ITRC Diffusion Sampler Team website. The Dialysis Sampler User's Guide/Technical Protocol will be published as an ESTCP report. As members of the ITRC Diffusion Sampler Team the PI and co-PI have written part of an ITRC Technical/Regulatory Guidance Document that included the findings of this study on dialysis samplers. The ITRC Tech/Reg has been published by the ITRC and is available on the ITRC Diffusion Sampler Team website. Technology transfer will also be accomplished through NFESC by including the results of this demonstration on its website, in the RPM newsletter, and in a Tech Data Sheet. The results will also be included on the Federal Remediation Technologies Roundtable website. The results of this demonstration will also be disseminated by giving presentations at conferences such as, the Navy Cleanup Conference, the USGS-DODEC conference, and the annual ESTCP-SERDP conference.

6.4 Lessons Learned

Most state-regulators will want to see a side-by-side comparison of dialysis 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. If the comparison results do not agree between the sampling techniques, the state regulators will be reluctant to allow replacement of the current sampling technique with dialysis samplers. A large part of gaining acceptance of dialysis samplers at a site is educating the state regulators on how the samplers work and why the dialysis samplers may be giving valid results that do not agree exactly with the current sampling technique being used at the site. Publications on dialysis sampling such as this final report and reports written by the ITRC Diffusion Sampler Team will go a long way towards helping with this education process.

The fact that dialysis samplers are not currently commercially available is a stumbling block to having these samplers tested at more sites. We contacted one manufacturer about commercializing the dialysis sampler that was initially enthusiastic. However, they were also developing another passive sampler, so they have not moved forward as quickly on the dialysis sampler. The lesson from this is that researchers should contact several potential manufacturers during ESTCP testing to spur on the process of commercialization more quickly.

7.0 REFERENCES

Britt, S.L. 2005. *Testing the in-well horizontal laminar flow assumption with a sand-tank well model.* Ground Water Monitoring and Remediation. 25 (3): 73-81.

Ehlke, T.A., Imbrigiotta, T.E., and Dale, J.M. 2004. *Laboratory comparison of polyethylene and dialysis membrane diffusion samplers*. Ground Water Monitoring and Remediation. 24 (1): 53-59.

Gibs, J, Brown, G.A, Turner, K.S., MacLeod, C.L., Jelinski, J.C., and Koehnlein, S.A. 1993. *Effects of small-scale vertical variations in well-screen inflow rates and concentrations of organic compounds on the collection of representative ground-water quality samples*. Ground Water. 35 (2): 201-208.

Gibs, J., Z. Szabo, T. Ivahnenko, F.N. Wilde. 2000. *Change in field turbidity and trace element concentrations during well purging.* Ground Water. 38 (4): 577-588.

Harter, T. and S. Talozi. 2004. *A simple, inexpensive dialysis sampler for small diameter monitoring wells.* Ground Water Monitoring and Remediation. 24 (4):97-105.

Imbrigiotta, T.E., Ehlke, T.A., Lacombe, P.J., and Dale, J.M. 2002. *Comparison of dialysis membrane diffusion samplers and two purging methods in bedrock wells*. In A.R. Gavaskar and A.S.C. Chen (Eds.), Remediation of Chlorinated and Recalcitrant Compounds. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California. May 2002.

Interstate Technology and Regulatory Council. 2004. *Technical and regulatory guidance for using polyethylene diffusion bag samplers to monitor volatile organic compounds in ground water.* ITRC Technical/Regulatory Guidelines Report. February 2004. 24 p.

LeBlanc, D.R. 2003. *Diffusion and drive-point sampling to detect ordnance-related compounds in shallow ground water beneath Snake Pond, Cape Cod, Massachusetts, 2001-2002.* U.S. Geological Survey Water-Resources Investigations Report 03-4133. 20 p.

Lorah, M.M., Burris, D.R., and Dyer, L.J. 2004. *Natural attenuation of chlorinated solvent ground-water plumes discharging to wetlands*. U.S. Geological Survey Scientific Investigations Report 2004-5220. 33 p.

Magaritz, M., Wells, M., Amiel, A.J., and Ronen, D. 1989. *Application of a multi-layer sampler based on the dialysis cell technique for the study of trace metals in ground water*. Applied Geochemistry. 4: 617-624.

National Environmental Methods Index. 2002. *Environmental methods comparison.* http://www.nemi.gov.

Parker, L.V. and Mulherin, N.D. 2006. *Preliminary studies of alternative passive diffusion devices for sampling explosives.* In Proceedings for the 2006 North American Environmental Field Conference and Exposition, Tampa, Florida, January 10-12, 2006. 11 p.

Parsons. 2005. *Results report for the demonstration of no-purge groundwater sampling devices at former McClellan Air force Base, California.* Contract No. F44650-99-D-0005. October 2005. 400 p.

Puls, R.W., and Barcelona, M.J. 1996. *Ground water issue: Low-flow (minimal draw-down) ground-water sampling procedures*. U.S. Environmental Protection Agency Report EPA/540/S-95/504, R.S. Kerr Environmental Research Center, Ada, Oklahoma.

Reilly, T.E. and Gibs, J. 1993. Effects of physical and chemical heterogeneity on water-quality samples obtained from wells. Ground Water. 31 (5): 805-813.

Ronen, D., Magaritz, M., and Levy, I. 1987. *An in situ multilevel sampler for preventive monitoring and study of hydrochemical profiles in aquifers*. Ground Water Monitoring Review. 7(4): 69-74.

S-PLUS. 2002. *S-PLUS 6.1 for Windows, Professional Edition, Release 1.* Insightful Corporation, Seattle, Washington. Revison Date May 23, 2002.

U.S. Environmental Protection Agency. 2003. *SW-846 Online, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. http://www.epa.gov/epaoswer/hazwaste/test/main.htm.

Varljen, M.D., Barcelona, M.J., Obereiner, J., and Kaminski, D. 2006. *Numerical simulations to assess the monitoring zone achieved during low-flow purging and sampling.* Ground Water Monitoring and Remediation. 26 (1): 44-52.

Vroblesky, D.A. 2001a. *Users guide for polyethylene-based passive diffusion bag samplers to obtain volatile organic compound concentrations in wells, Part 1: Deployment, recovery, data interpretation, and quality control and assurance*. U.S. Geological Survey Water-Resources Investigations Report 01-4060. 18 p.

Vroblesky, D.A. 2001b. *User's guide for polyethylene-based passive diffusion bag samplers to obtain volatile organic compound concentrations in wells. Part 2: Field Tests.* U.S. Geological Survey Water-Resources Investigations Report 01-4061. 120 p.

Vroblesky, D.A., Manish, Joshi, Morrell, Jeffrey, and Peterson, J.E. 2003. *Evaluation of passive diffusion bag samplers, dialysis samplers, and nylon-screen samplers in selected wells at Andersen Air Force Base, Guam, March-April 2002.* U.S. Geological Survey Water-Resources Investigations Report 03-4157. 29 p.

Vroblesky, D.A., Petkewich, M.D., and Campbell, T.R. 2002. *Field tests of diffusion samplers for inorganic constituents in wells and at a ground-water-discharge zone.* U.S. Geological Survey Water-Resources Investigations Report 02-4031. 24 p.

Vroblesky, D.A., and Pravecek, T. 2002. *Evaluation of passive diffusion bag and dialysis samplers in selected wells at Hickam Air Force Base, Hawaii, July 2001.* U.S. Geological Survey Water-Resources Investigations Report 02-4159. 28 p.

Wilde, F.D., Radtke, D.B., Gibs, J., and Iwatsubo, R.T., eds. 1998. *National field manual for collection of water-quality data: Chapter A2. Selection of equipment for water sampling.* U.S. Geological Survey Techniques of Water-Resources Investigations Book 9. 82 p.

8.0 POINTS OF CONTACT

This project was a collaborative effort between the U.S. Navy, the U.S. Geological Survey, Battelle, and State agencies. The principal persons involved for each organization are as follows:

Table 8-1. Points of Contact

Point of Contact	Organization	Phone/FAX/email	Role
Joseph Trotsky	NFESC, 1100 23rd Avenue, Port Hueneme, CA 93043-4370	(805) 982-1258 (805) 982-4304 (FAX) joey.trotsky@navy.mil	Principal Investigator
Thomas Imbrigiotta	USGS, 810 Bear Tavern Rd, Suite 206 West Trenton, NJ 08628	(609) 771-3914 (609) 771-3915 (FAX) timbrig@usgs.gov	Co-Principal Investigator and Field QA officer
Matthew Place	Battelle, 505 King Avenue, Columbus, OH 43201	(614) 424-4531 (614) 424-3667 (FAX) place@batelle.org	Lab QA officer and Project staff
George Nicholas	NJDEP, PO Box 413, 401 East State St, 4th Floor West, Trenton, NJ 08625	(609) 984-6565 (609) 292-0848 (FAX) george.nicholas@dep.state.nj.us	Tech Transfer
Jeff Dale	US Navy, EFANE, 10 Industrial Highway, MS 82, code 1822, Lester, PA 19113	(610) 595-0567 ext 120 (610) 595-0555 (FAX) dalejm@navy.mil	Site Support and Tech Transfer

APPENDIX A. COMPARISON OF CONCENTRATIONS OF INORGANIC AND ORGANIC CONSTITUENTS RECOVERED BY DIFFERENT SAMPLING TECHNIQUES: 1:1 PLOTS

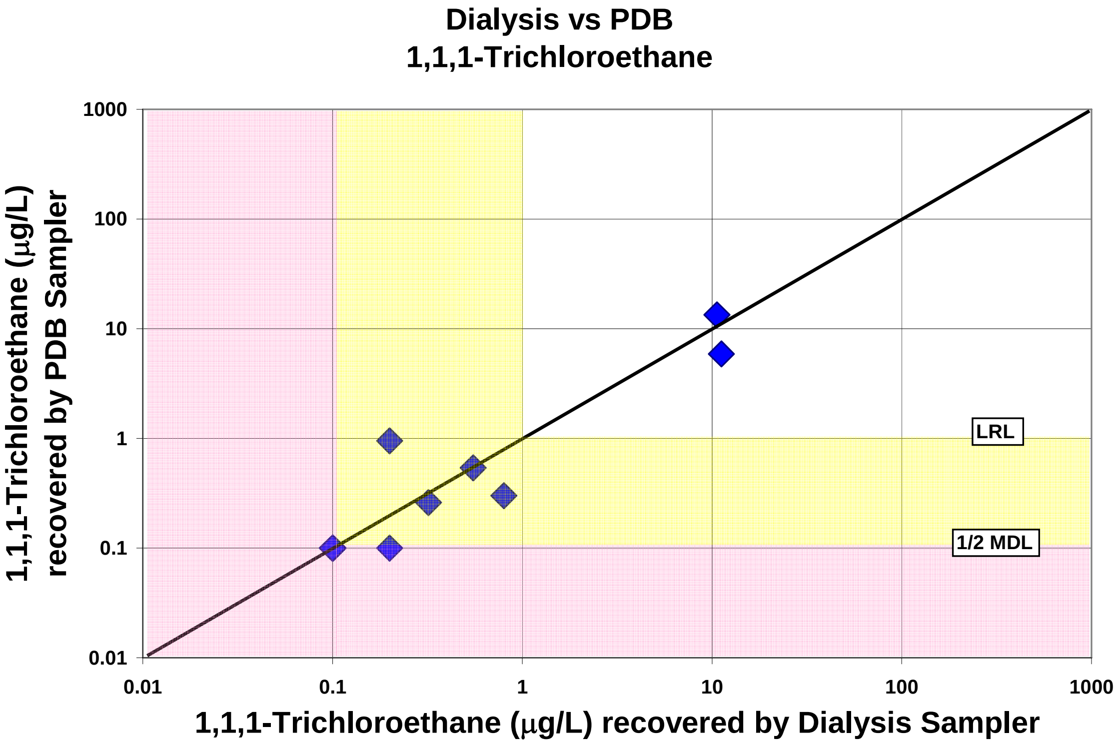


Figure A-1. Comparison of 1,1,1-trichloroethane concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

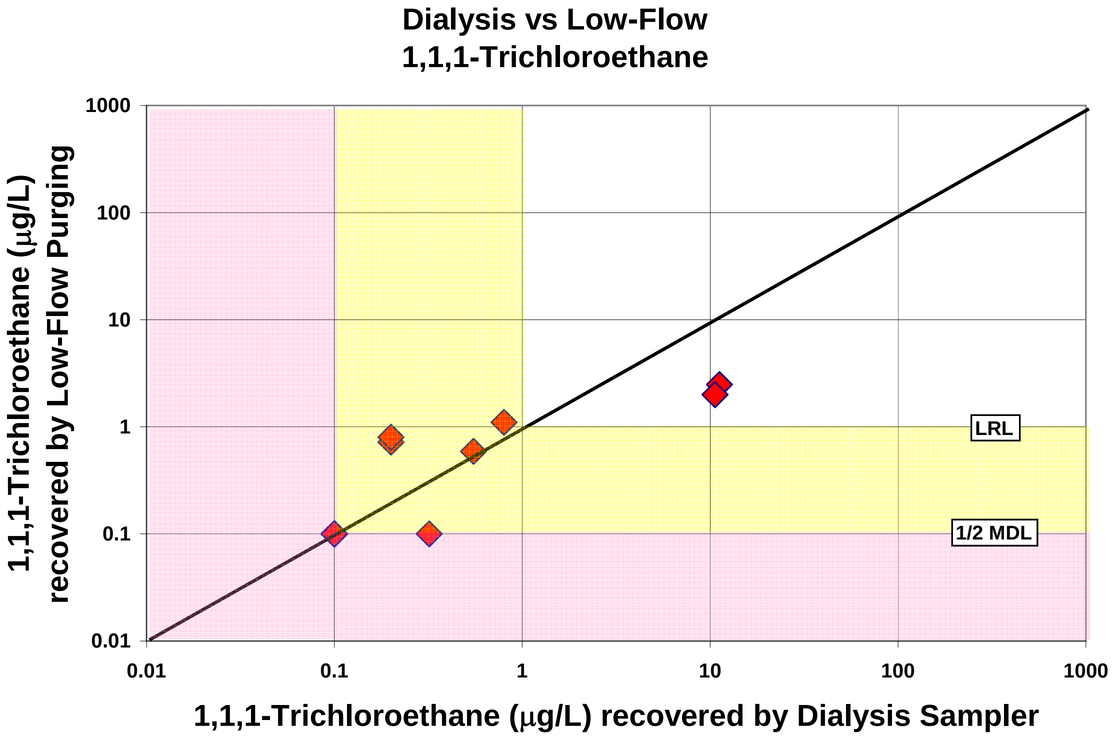


Figure A-2. Comparison of 1,1,1-trichloroethane concentrations recovered by the dialysis sampler and low-flow purging

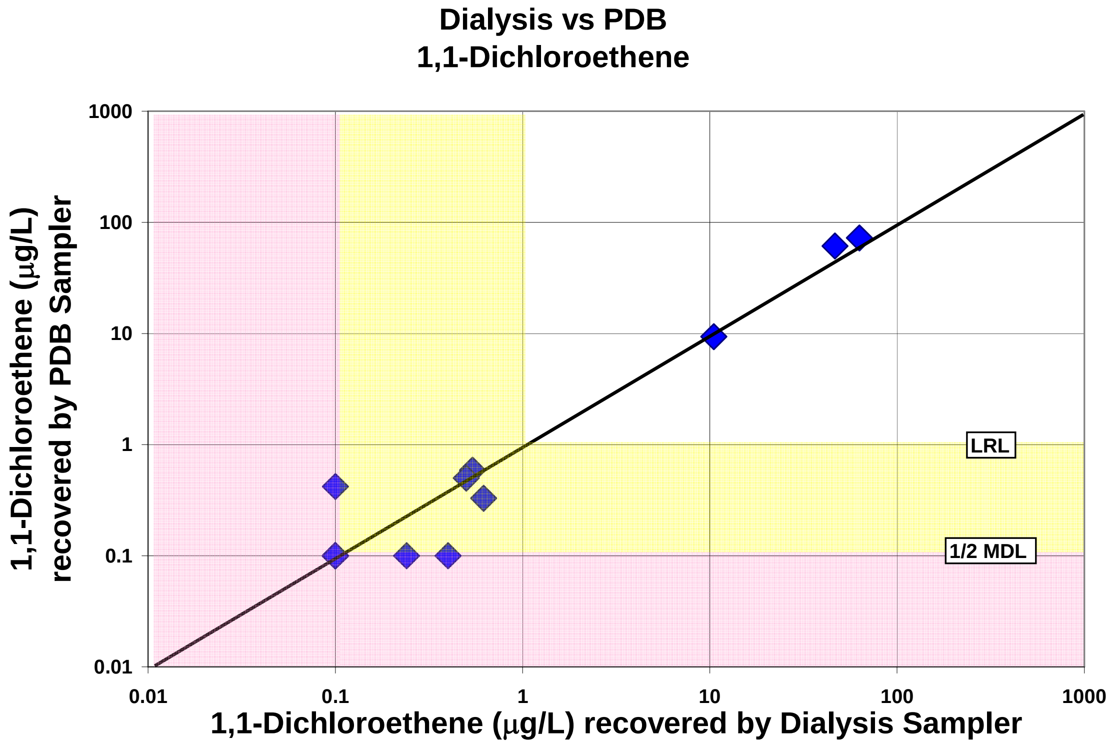


Figure A-3. Comparison of 1,1-dichloroethene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

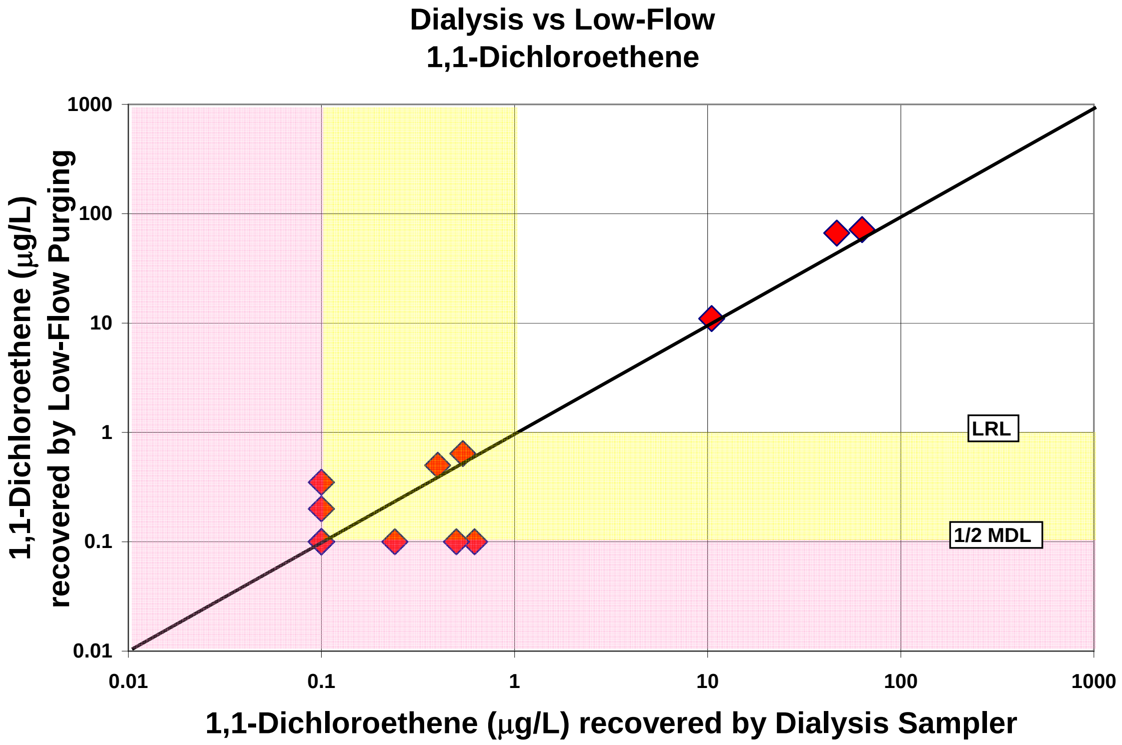


Figure A-4. Comparison of 1,1-dichloroethene concentrations recovered by the dialysis sampler and low-flow purging

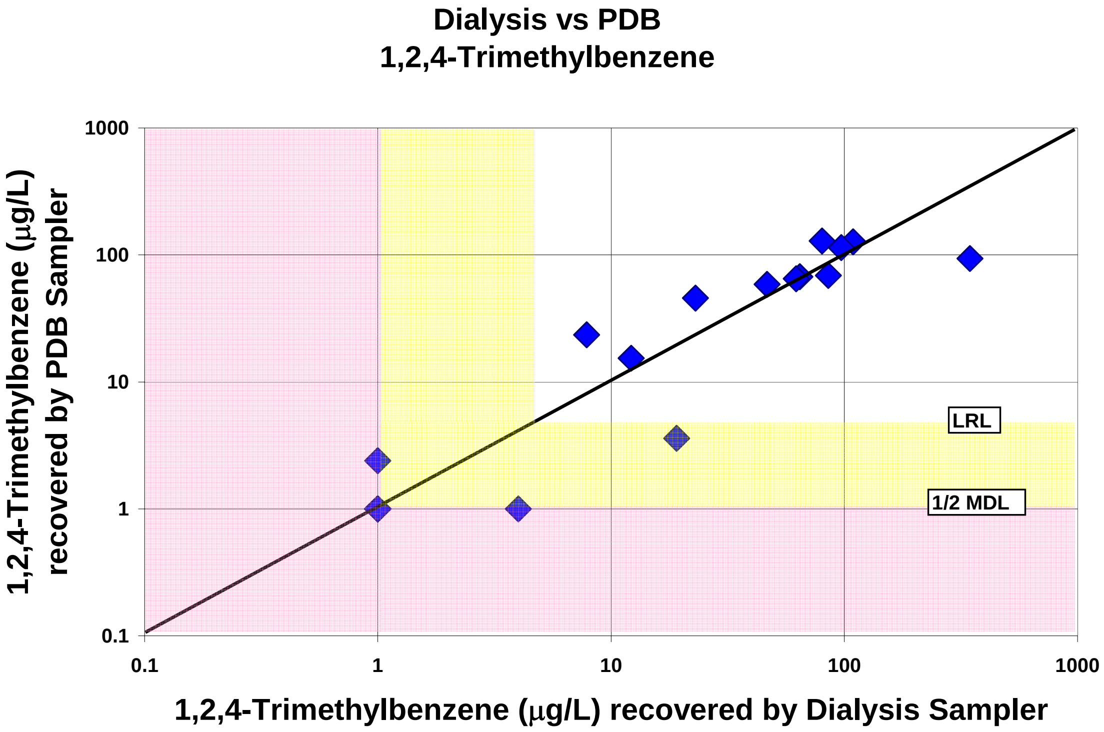


Figure A-5. Comparison of 1,2,4-trimethylbenzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

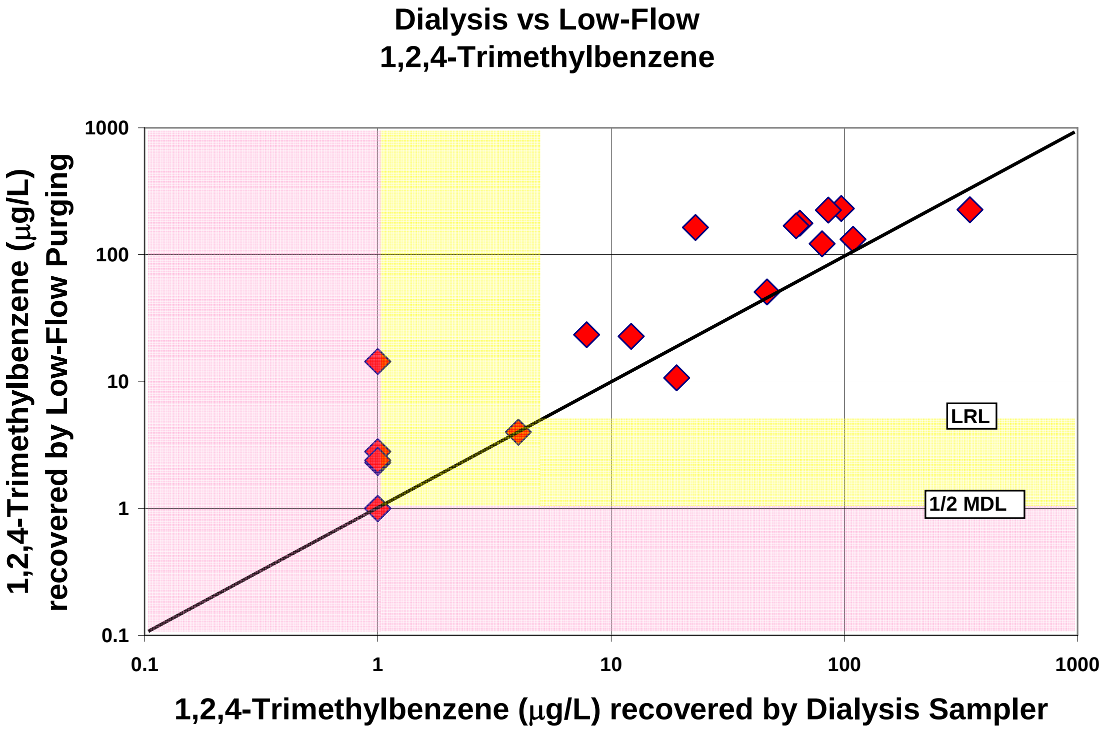


Figure A-6. Comparison of 1,2,4-trimethylbenzene concentrations recovered by the dialysis sampler and low-flow purging

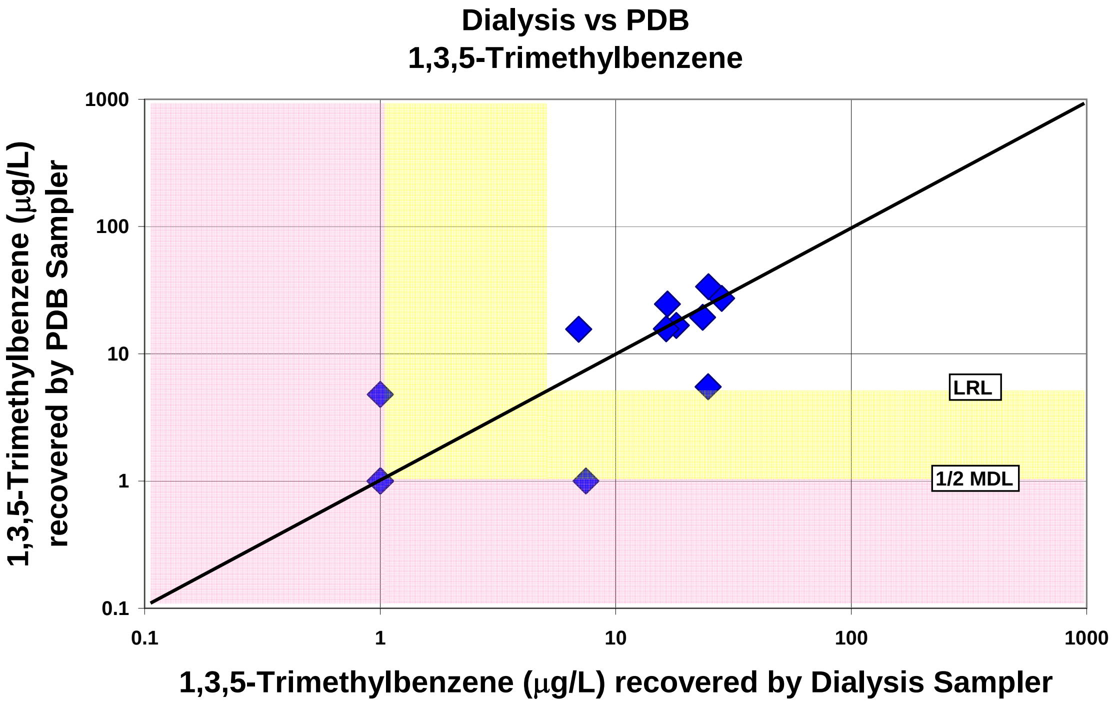


Figure A-7. Comparison of 1,3,5-trimethybenzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

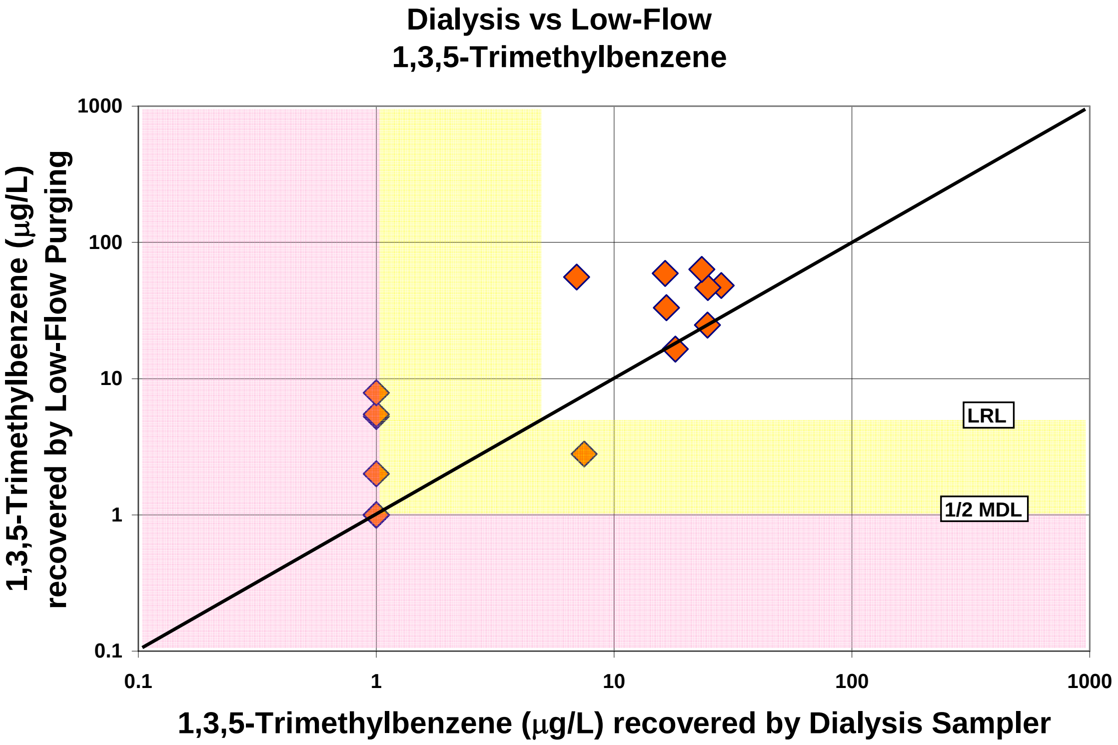


Figure A-8. Comparison of 1,3,5-trimethybenzene concentrations recovered by the dialysis sampler and low-flow purging

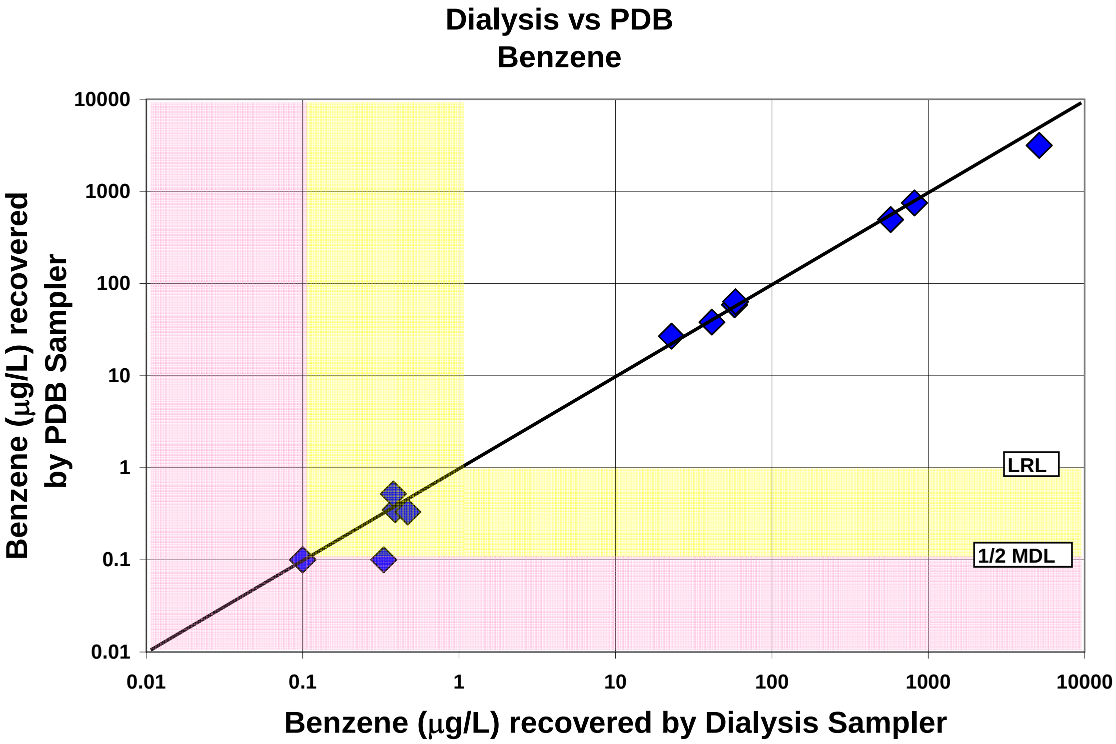


Figure A-9. Comparison of benzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

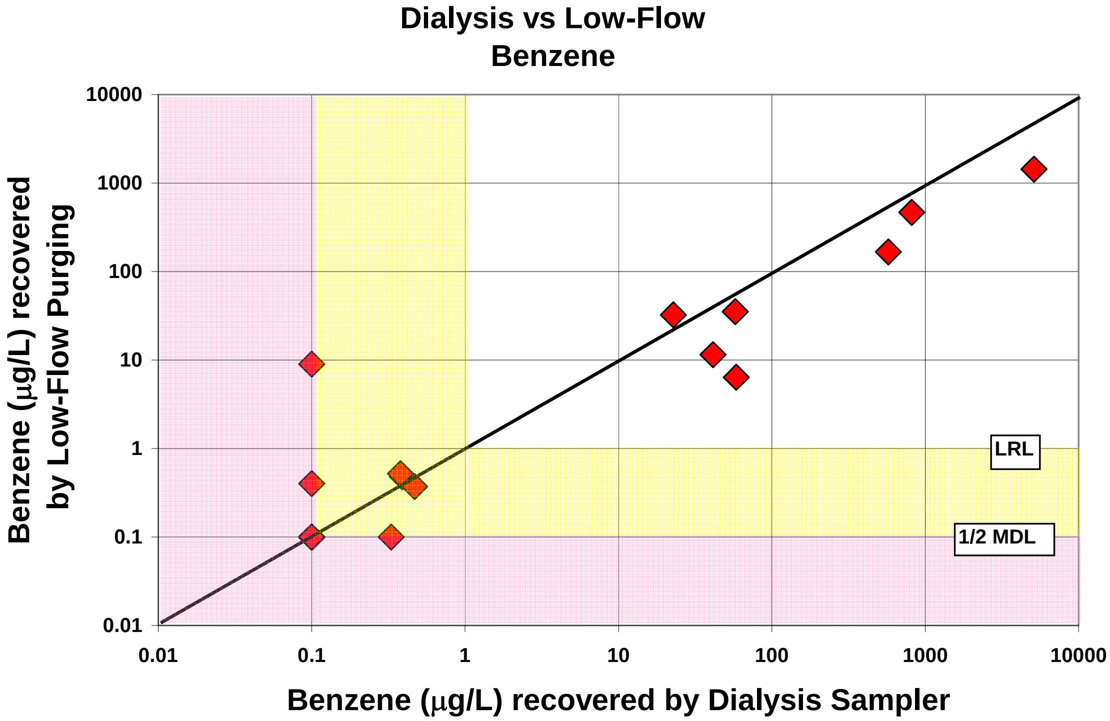


Figure A-10. Comparison of benzene concentrations recovered by the dialysis sampler and low-flow purging

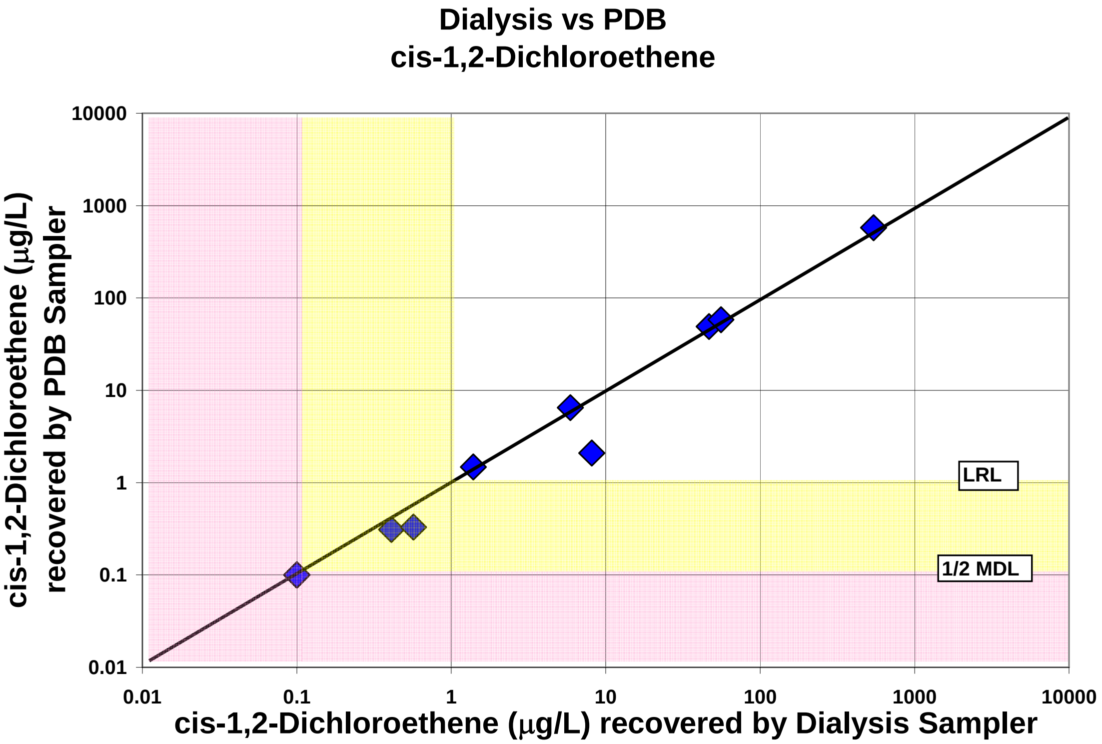


Figure A-11. Comparison of cis-1,2-dichloroethene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

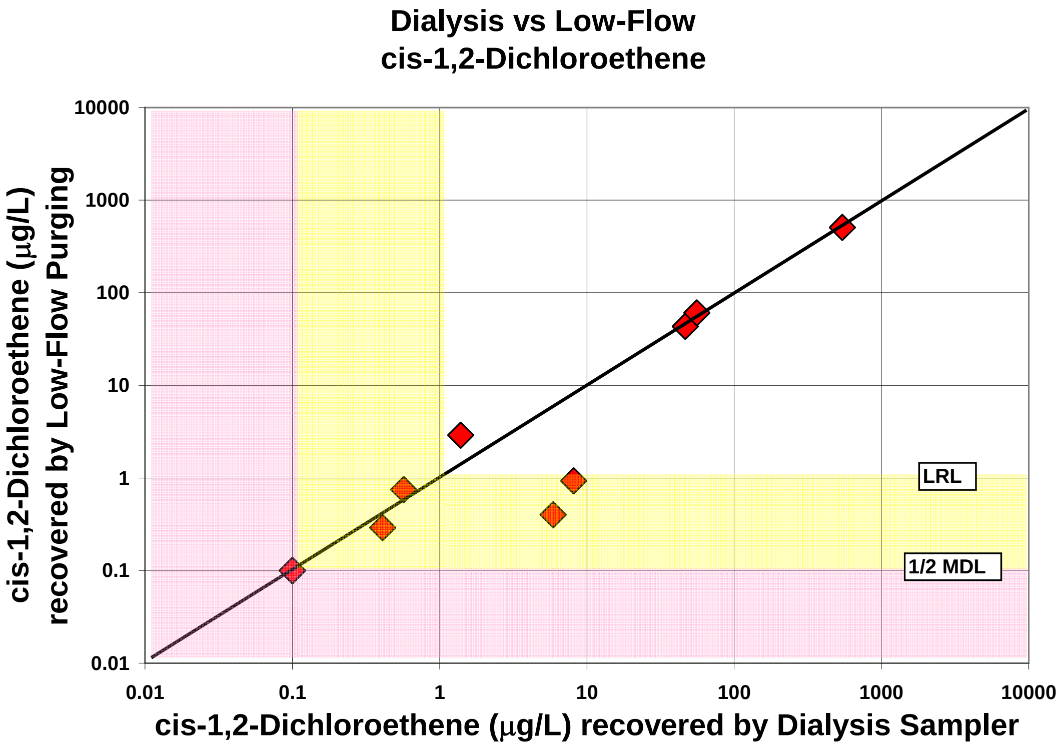


Figure A-12. Comparison of cis-1,2-dichloroethene concentrations recovered by the dialysis sampler and low-flow purging

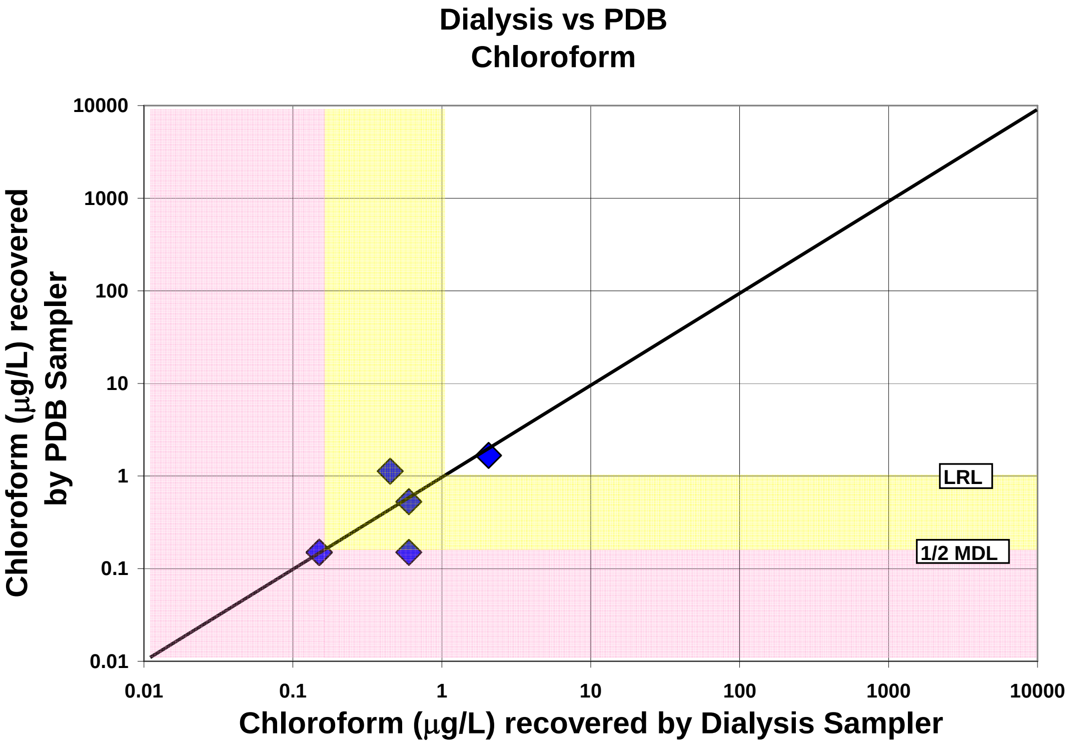


Figure A-13. Comparison of chloroform concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

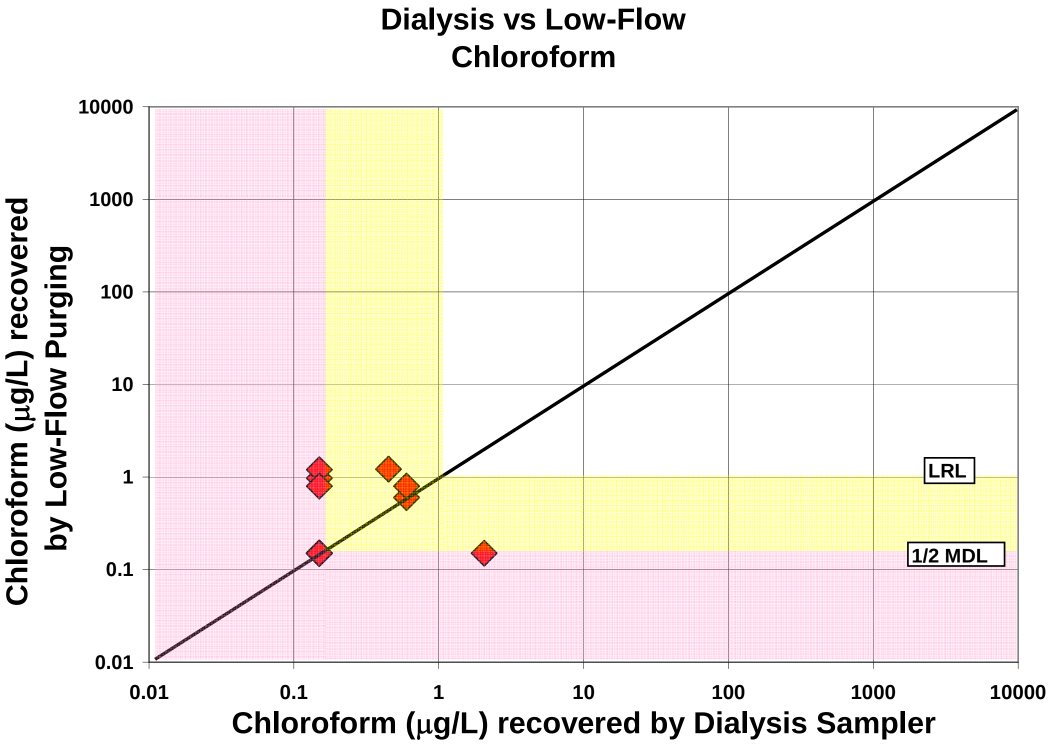


Figure A-14. Comparison of chloroform concentrations recovered by the dialysis sampler and low-flow purging

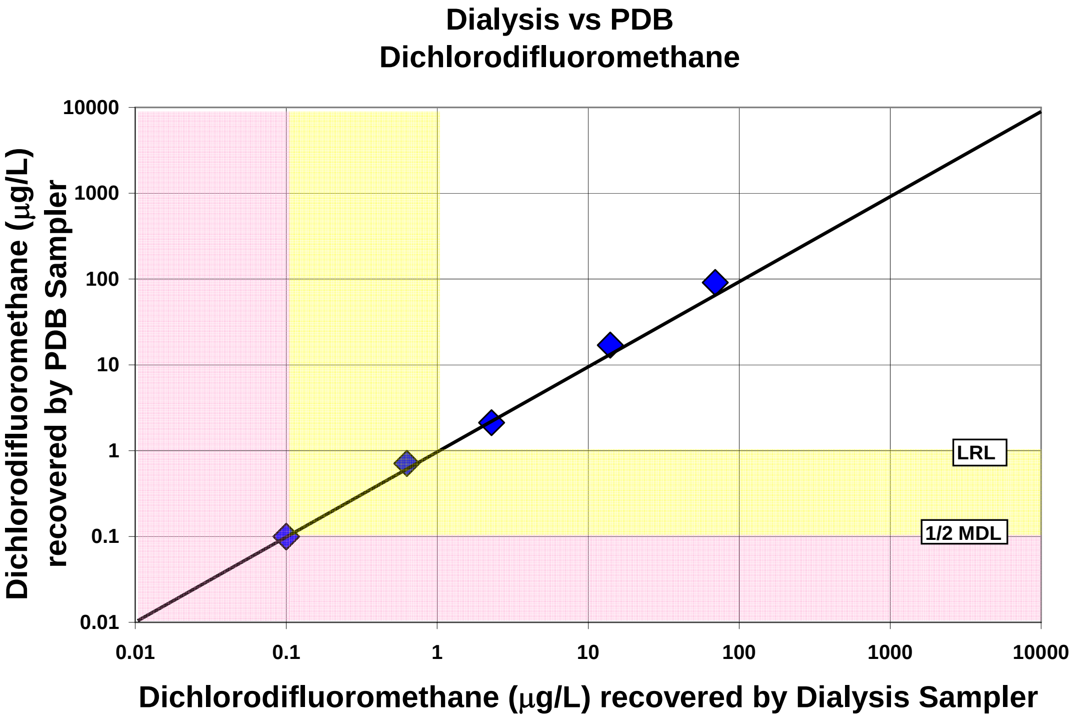


Figure A-15. Comparison of dichlorodifluoromethane concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

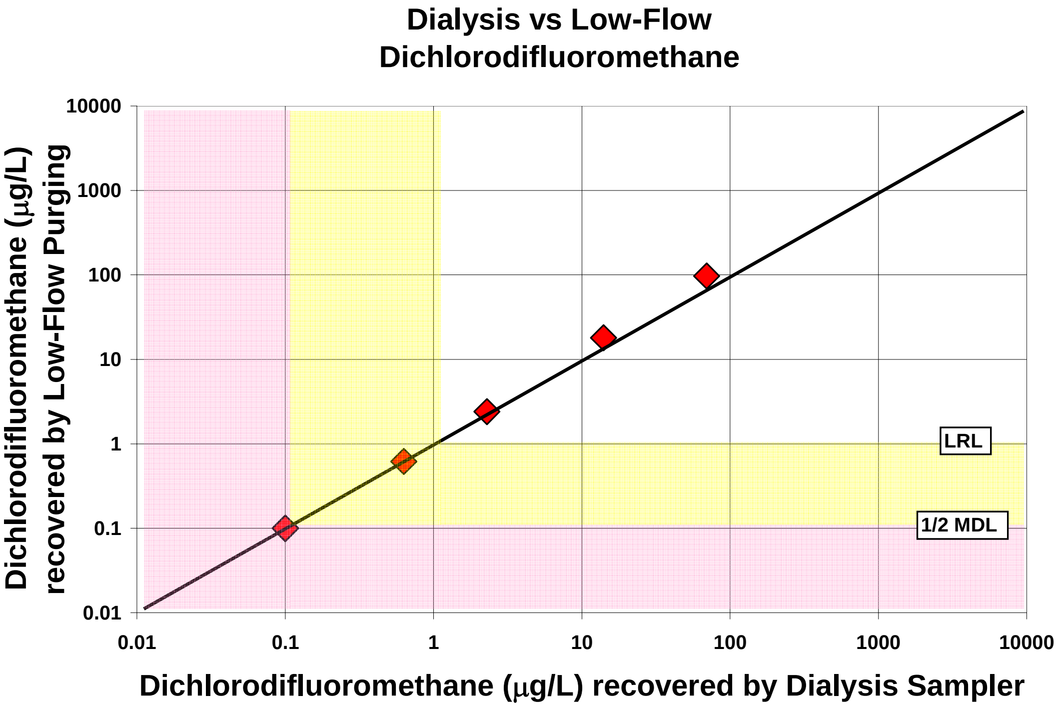


Figure A-16. Comparison of dichlorodifluoromethane concentrations recovered by the dialysis sampler and low-flow purging

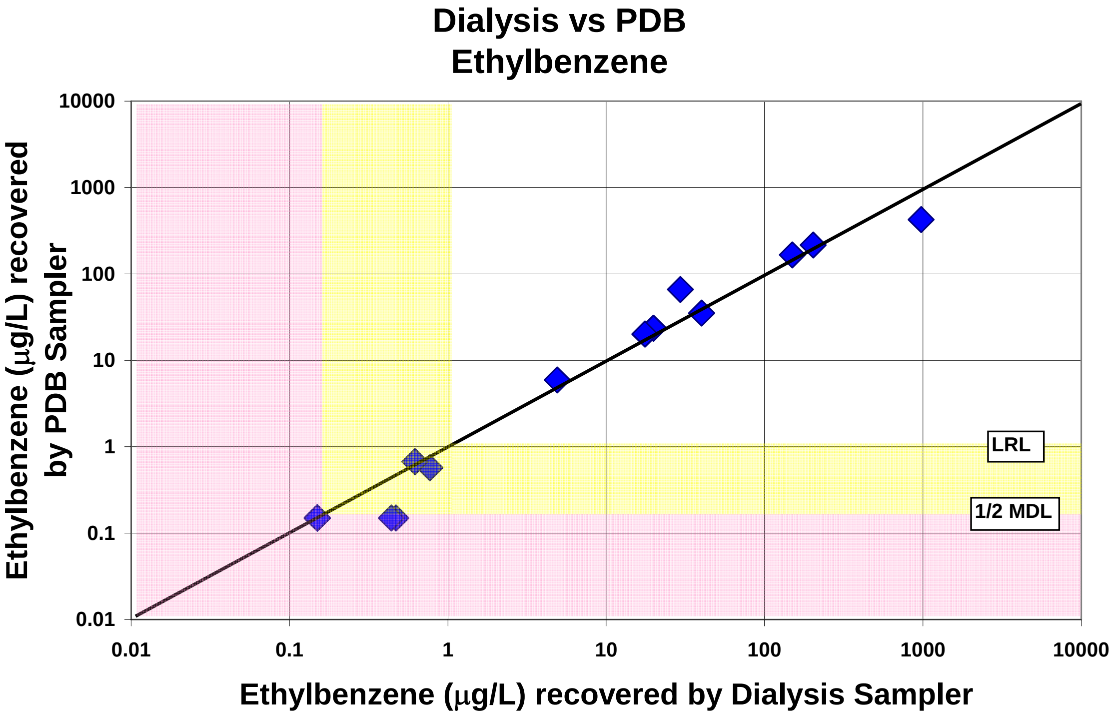


Figure A-17. Comparison of ethylbenzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

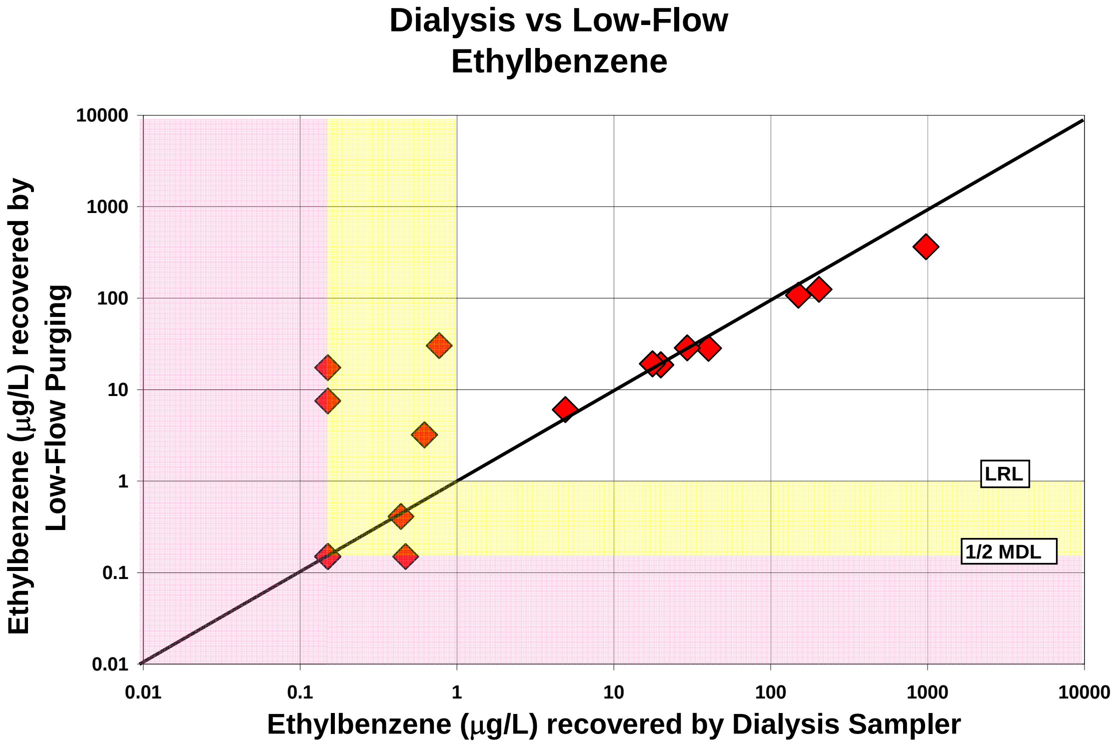


Figure A-18. Comparison of ethylbenzene concentrations recovered by the dialysis sampler and low-flow purging

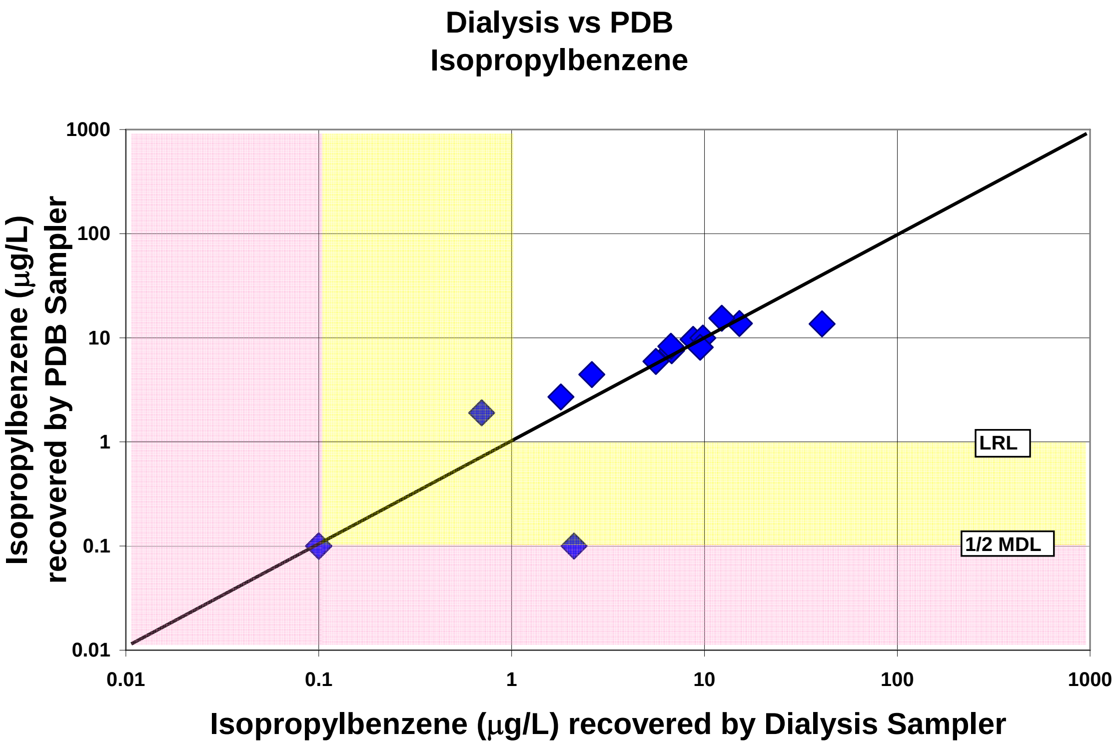


Figure A-19. Comparison of isopropylbenzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

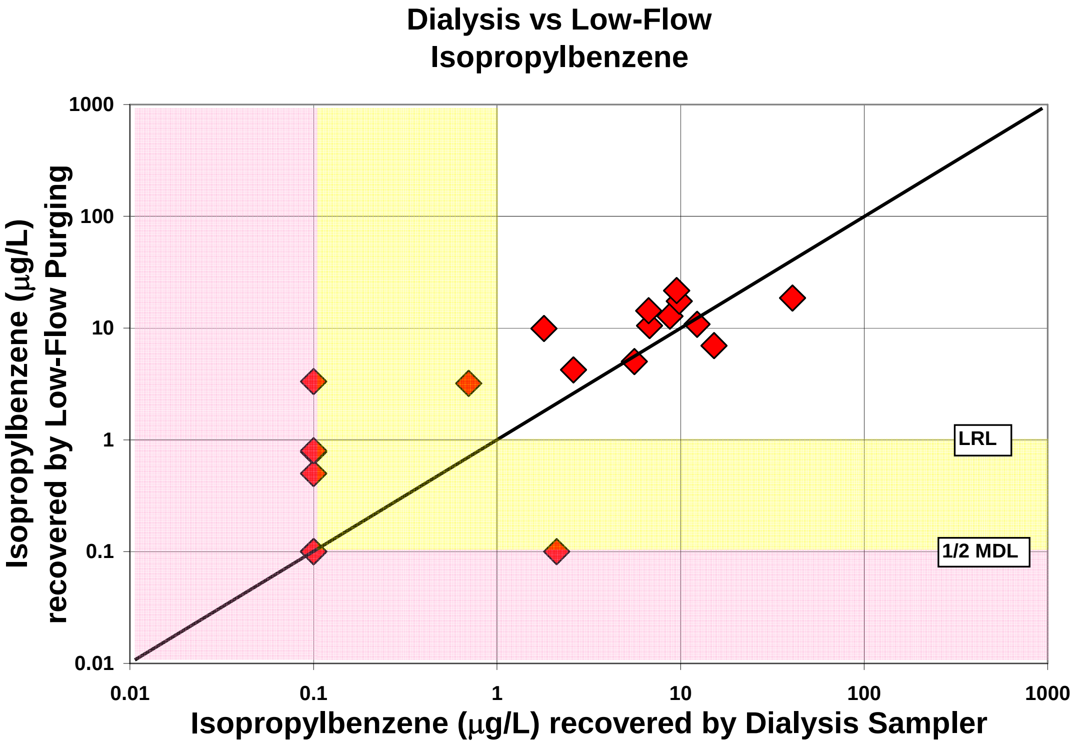


Figure A-20. Comparison of isopropylbenzene concentrations recovered by the dialysis sampler and low-flow purging

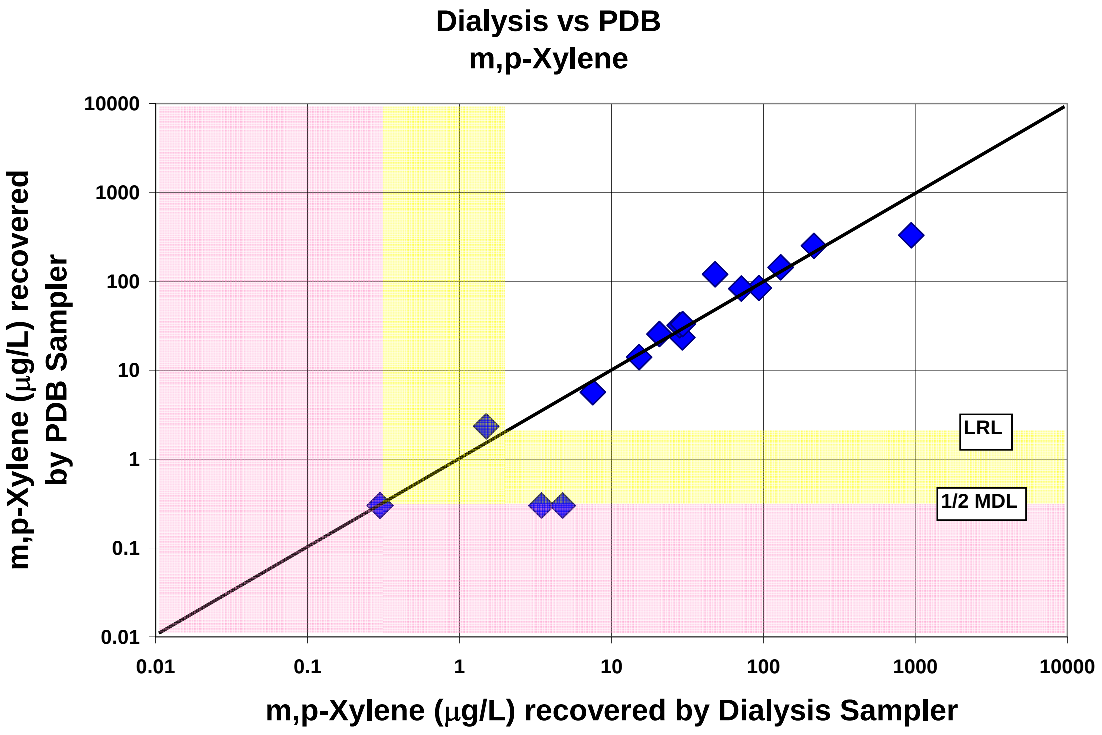


Figure A-21. Comparison of m,p-xylene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

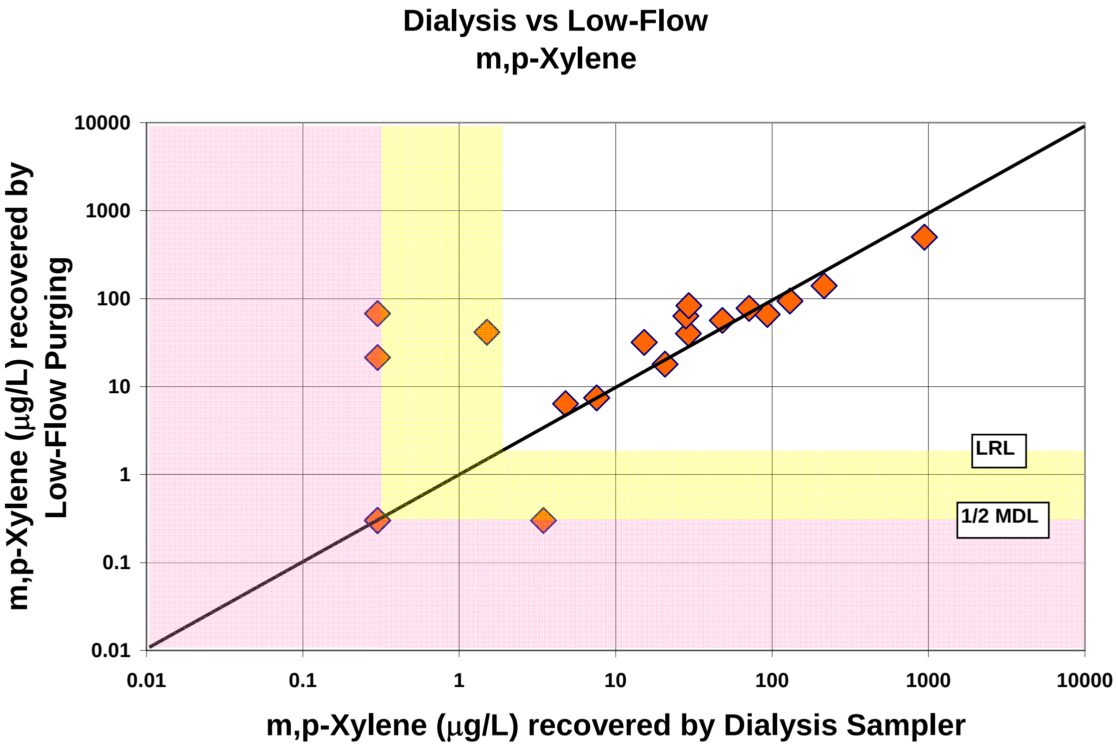


Figure A-22. Comparison of m,p-xylene concentrations recovered by the dialysis sampler and low-flow purging

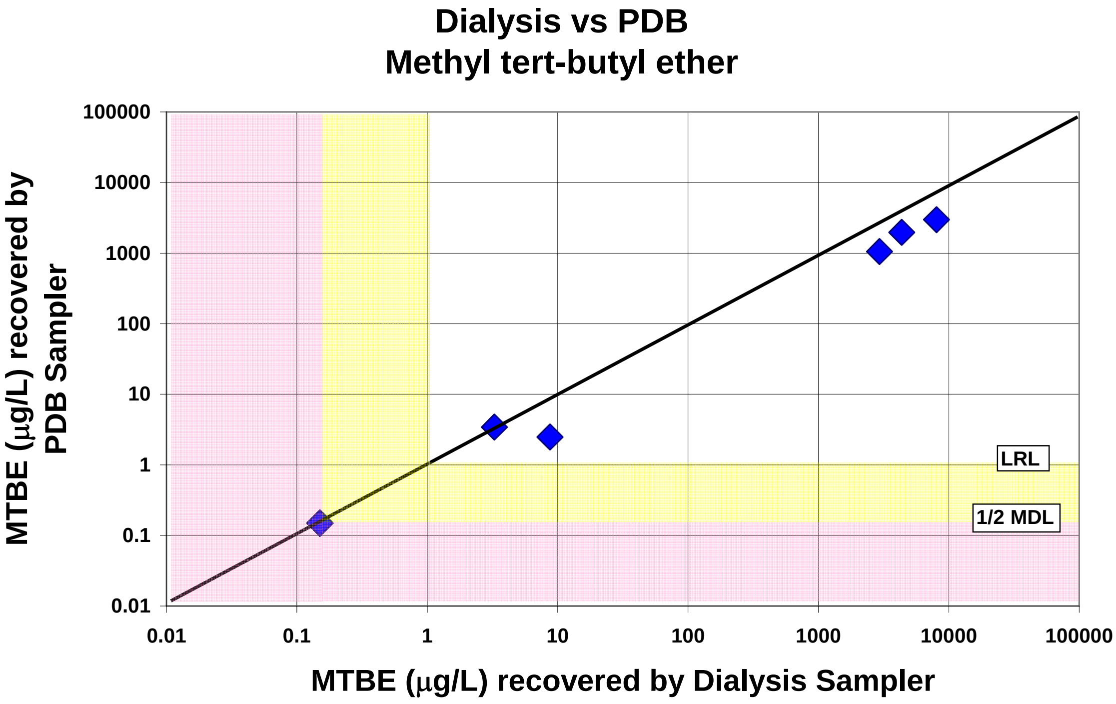


Figure A-23. Comparison of methyl-tert-butyl ether concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

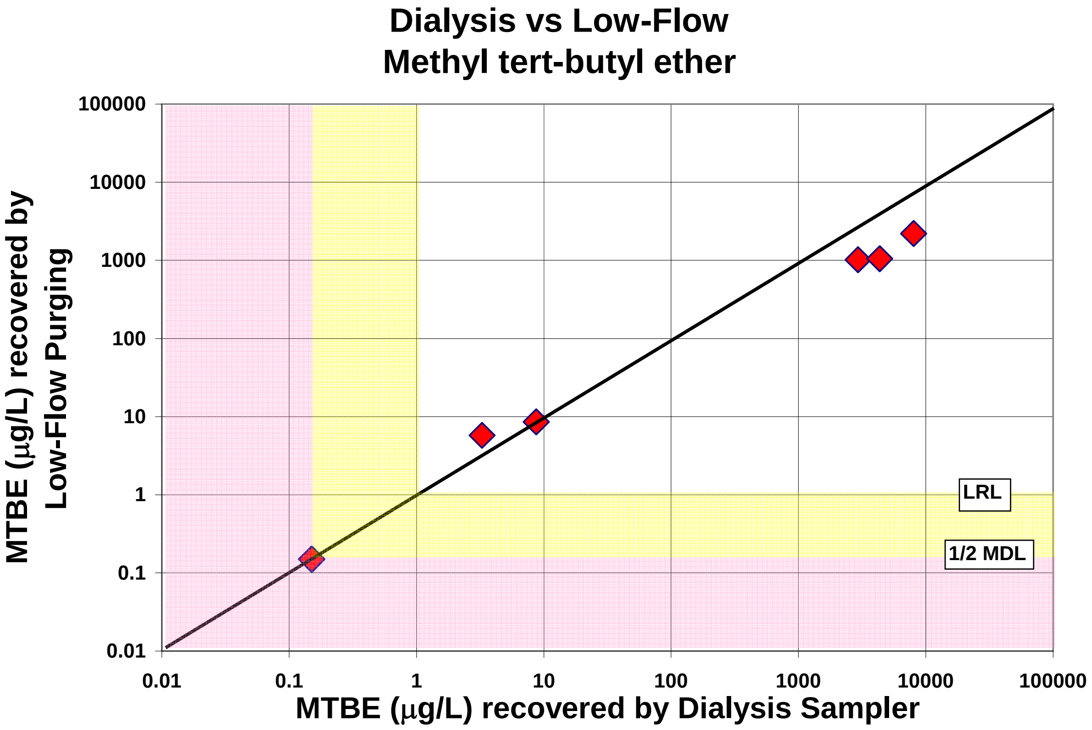


Figure A-24. Comparison of methyl-tert-butyl ether concentrations recovered by the dialysis sampler and low-flow purging

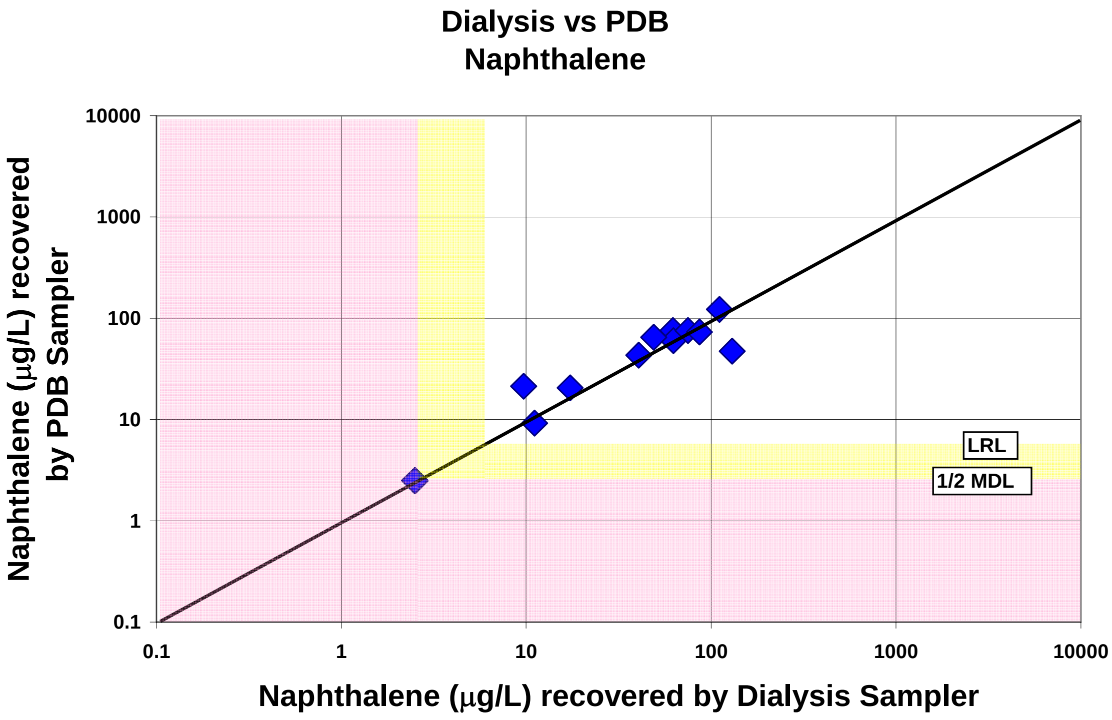


Figure A-25. Comparison of naphthalene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

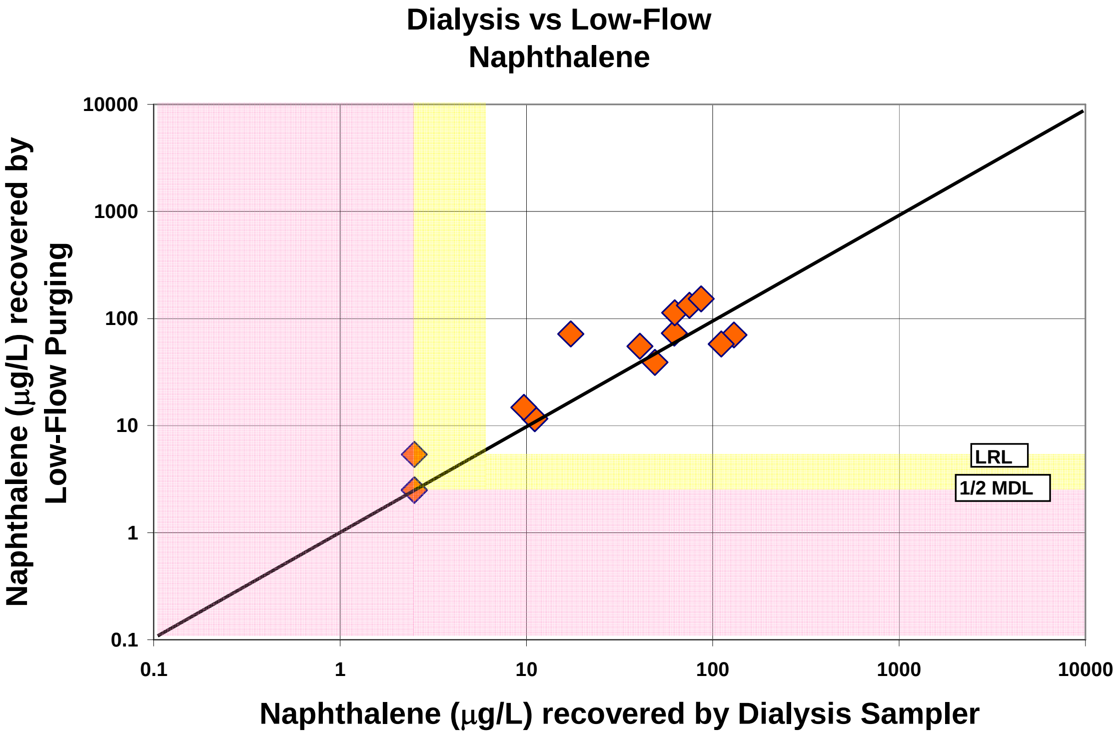


Figure A-26. Comparison of naphthalene concentrations recovered by the dialysis sampler and low-flow purging

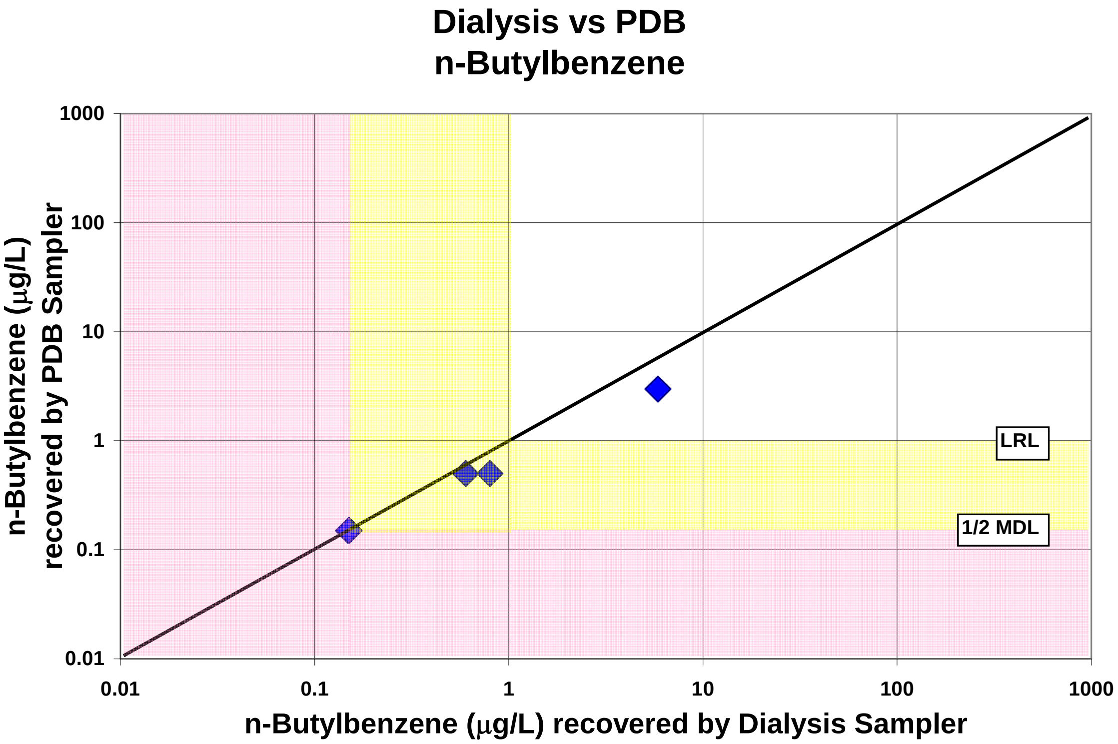


Figure A-27. Comparison of n-butylbenzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

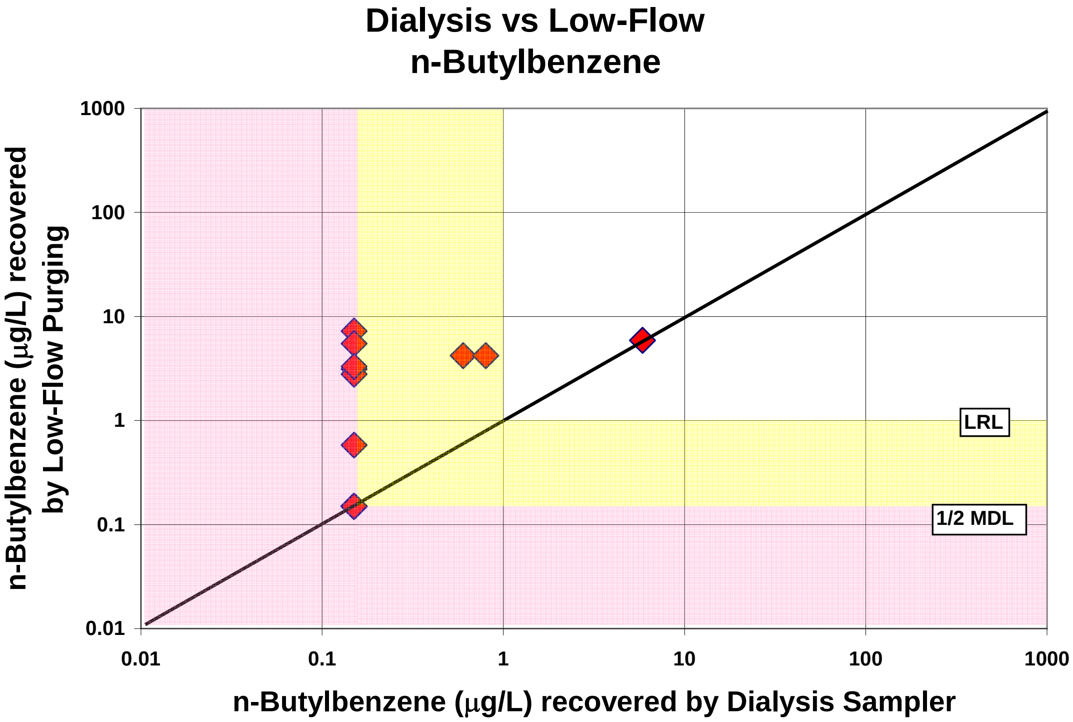


Figure A-28. Comparison of n-butylbenzene concentrations recovered by the dialysis sampler and low-flow purging

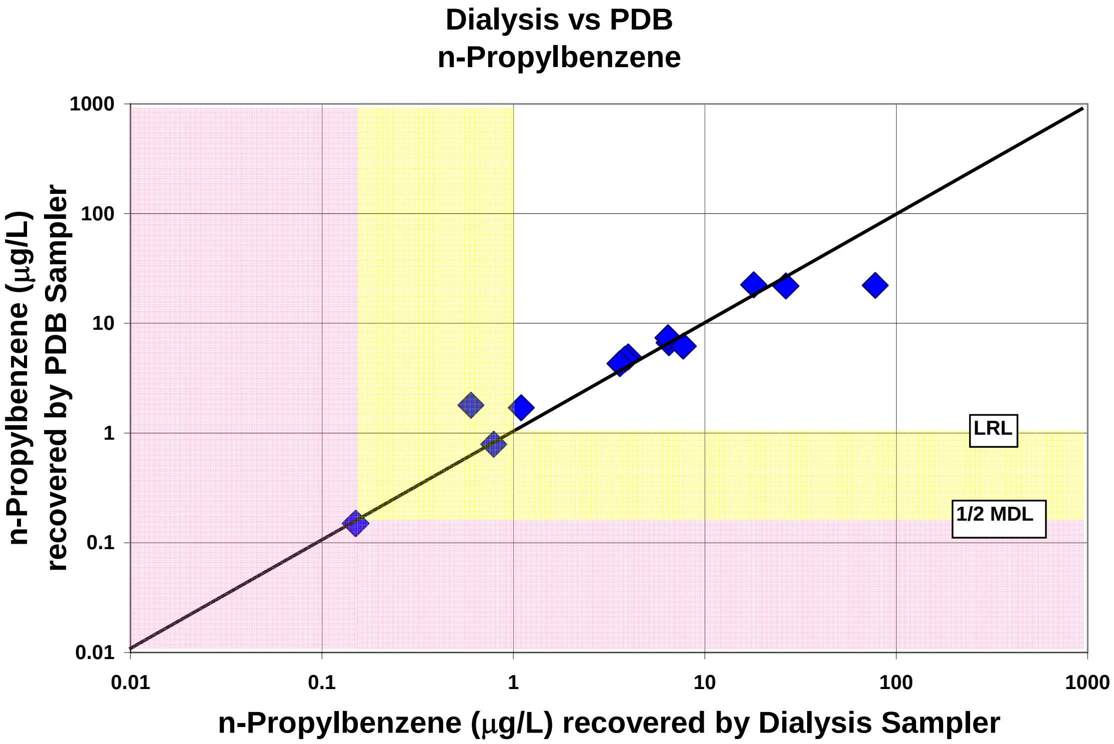


Figure A-29. Comparison of n-propylbenzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

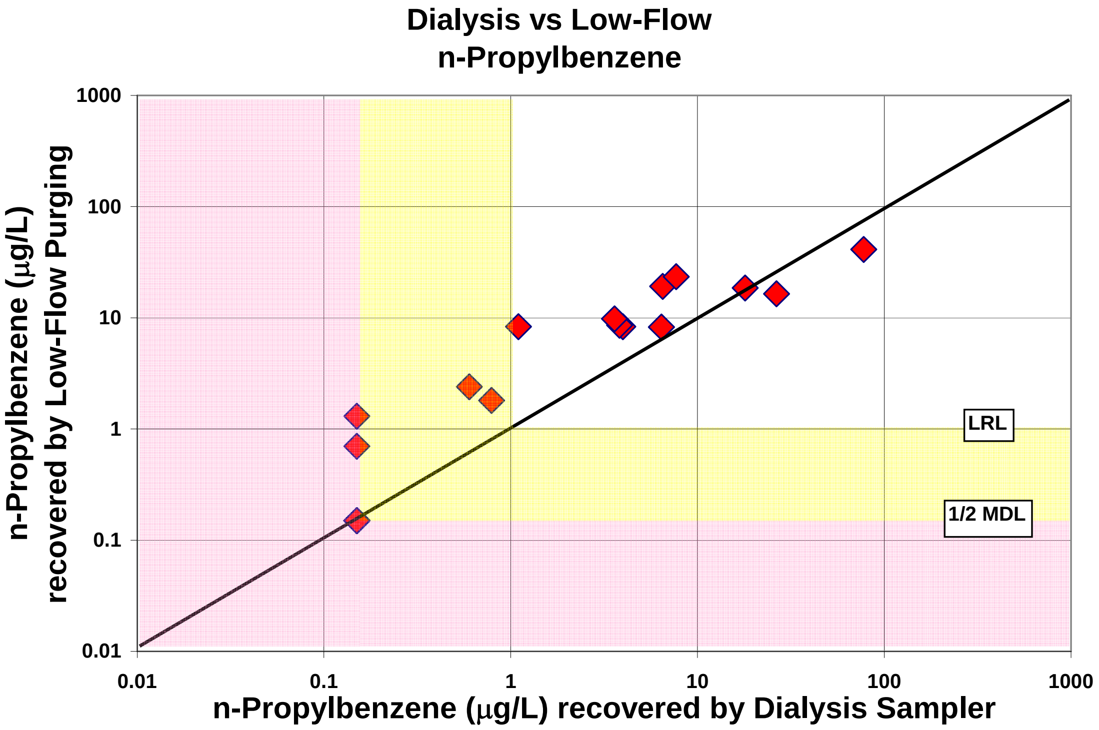


Figure A-30. Comparison of n-propylbenzene concentrations recovered by the dialysis sampler and low-flow purging

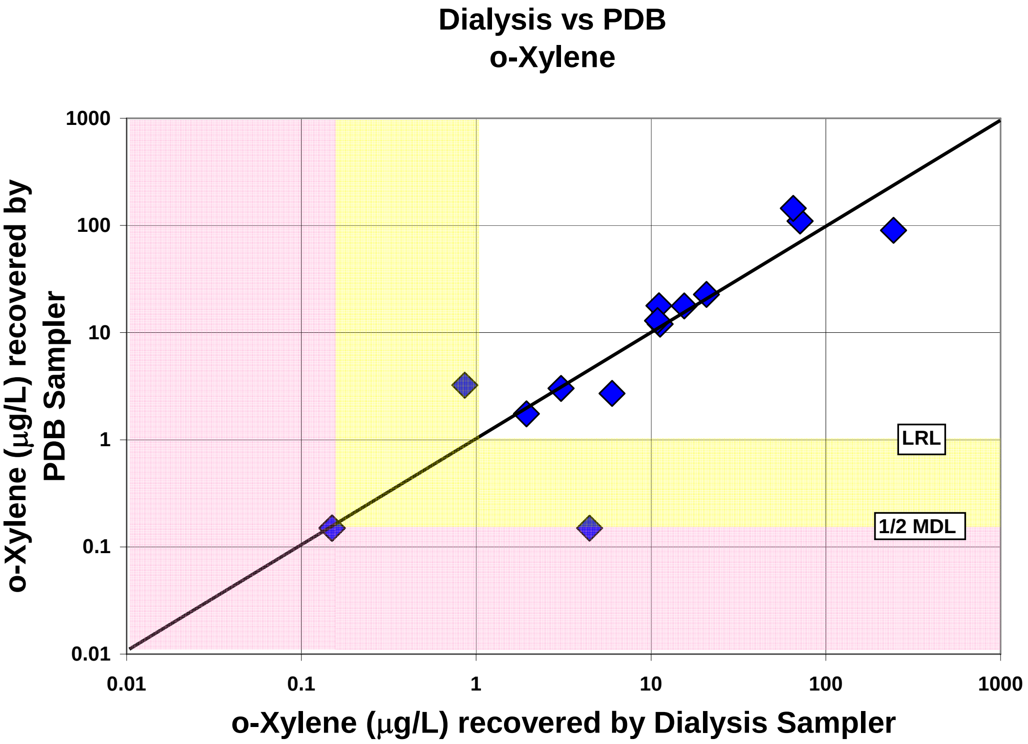


Figure A-31. Comparison of o-xylene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

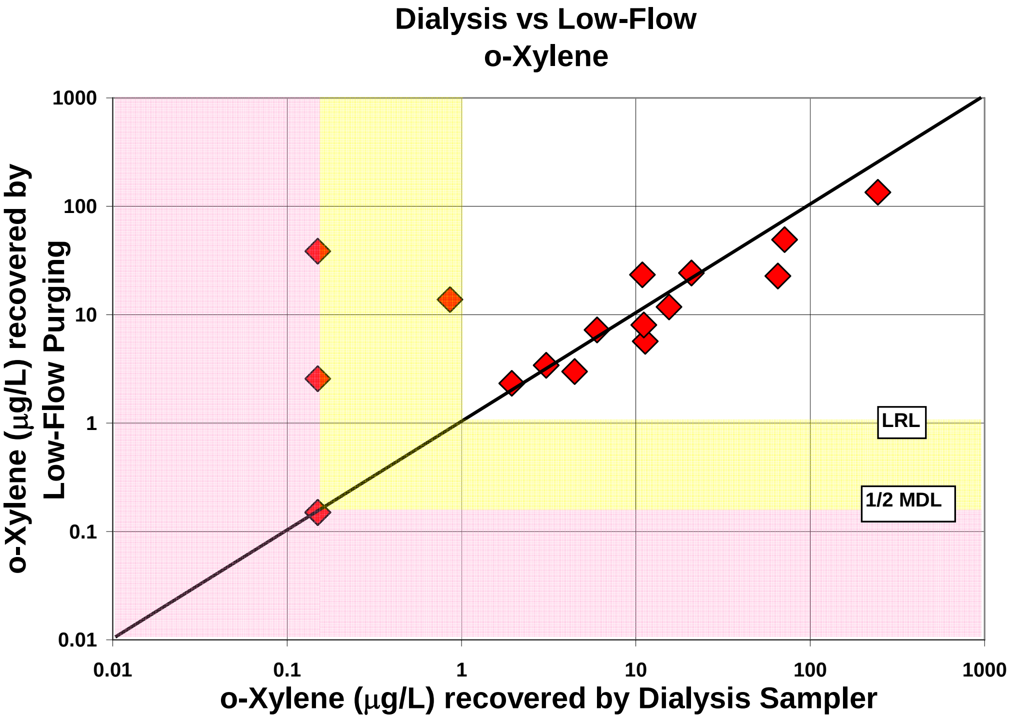


Figure A-32. Comparison of o-xylene concentrations recovered by the dialysis sampler and low-flow purging

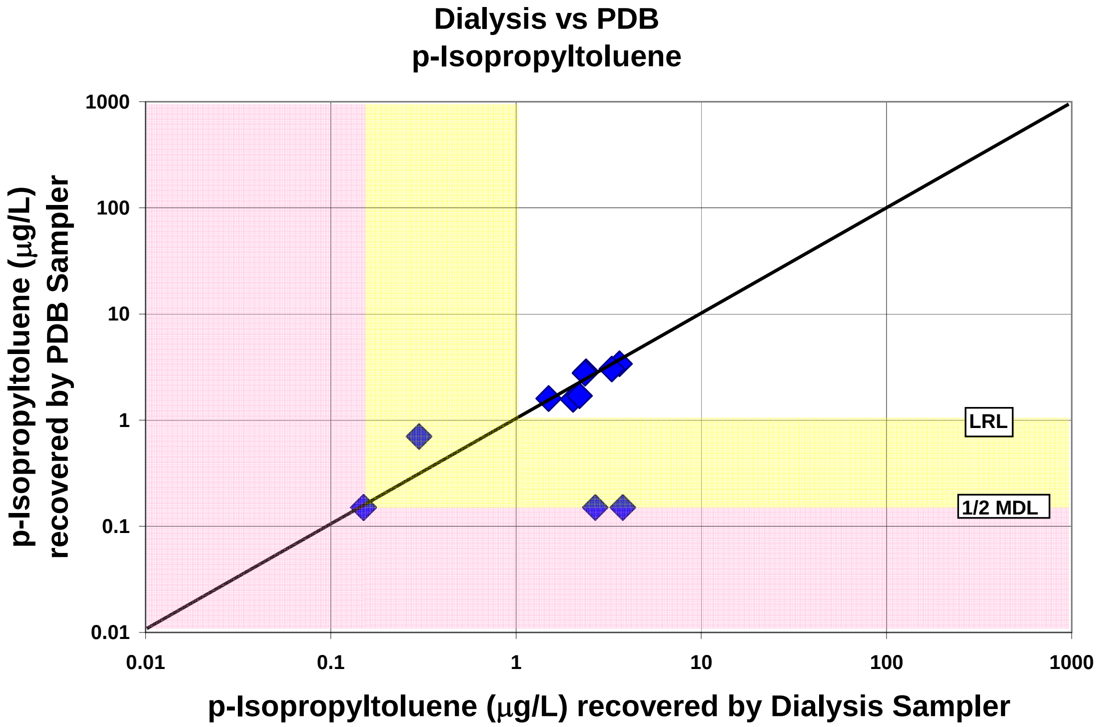


Figure A-33. Comparison of p-isopropyltoluene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

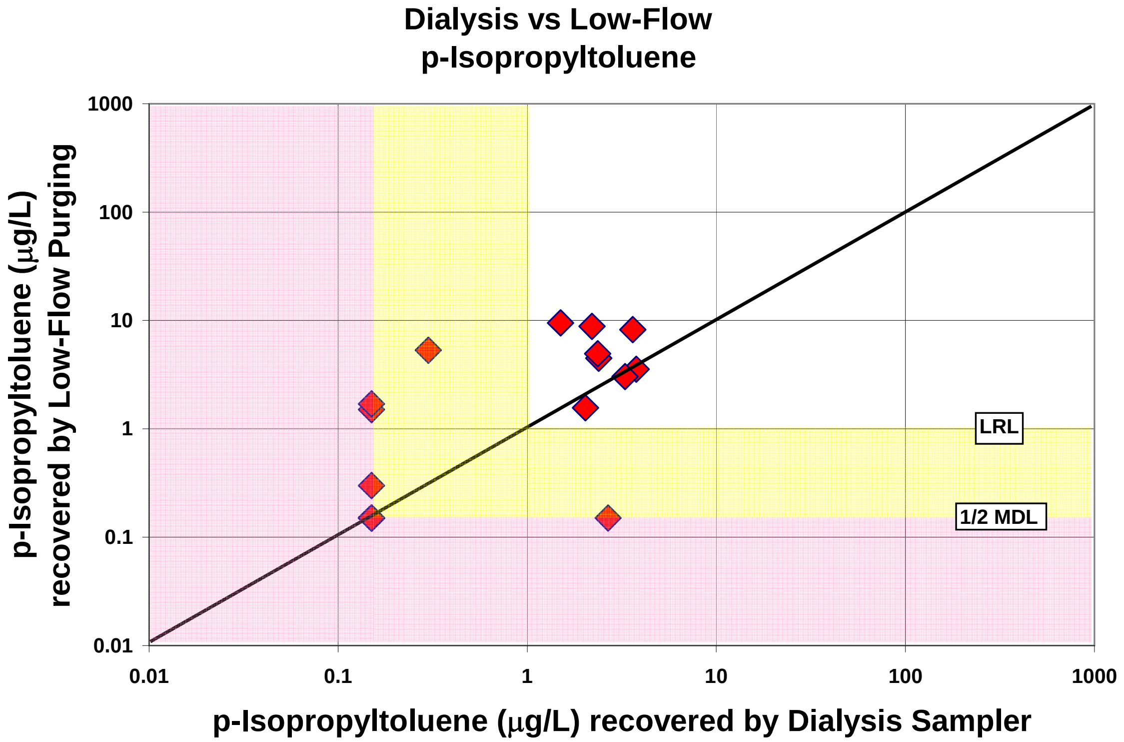


Figure A-34. Comparison of p-isopropyltoluene concentrations recovered by the dialysis sampler and low-flow purging

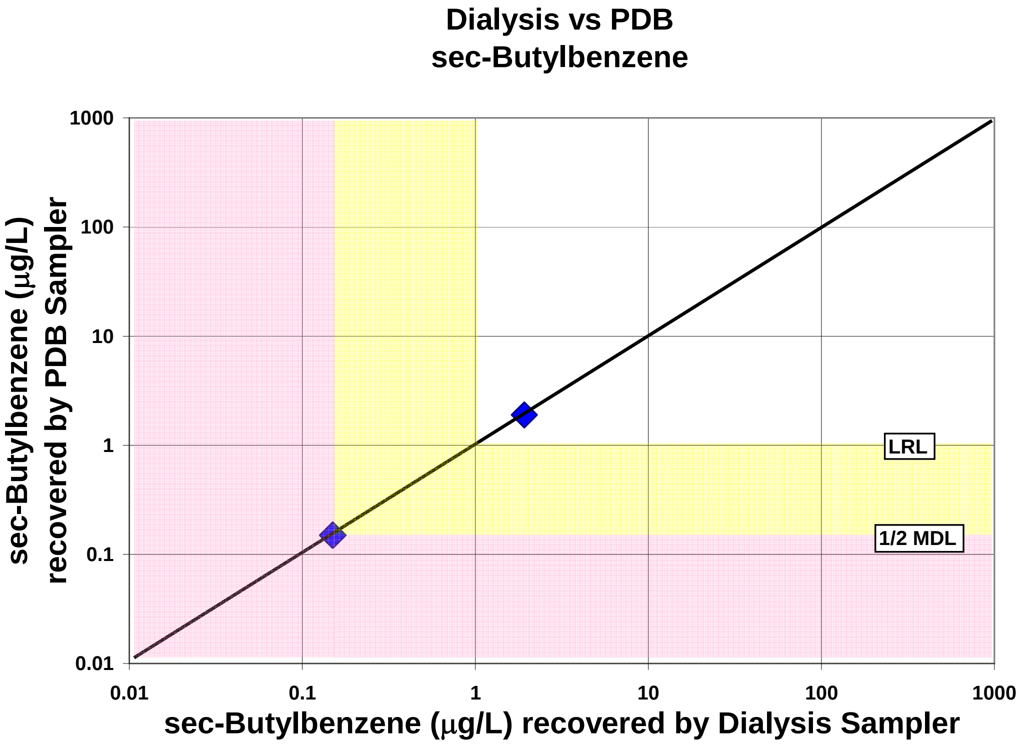


Figure A-35. Comparison of sec-butylbenzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

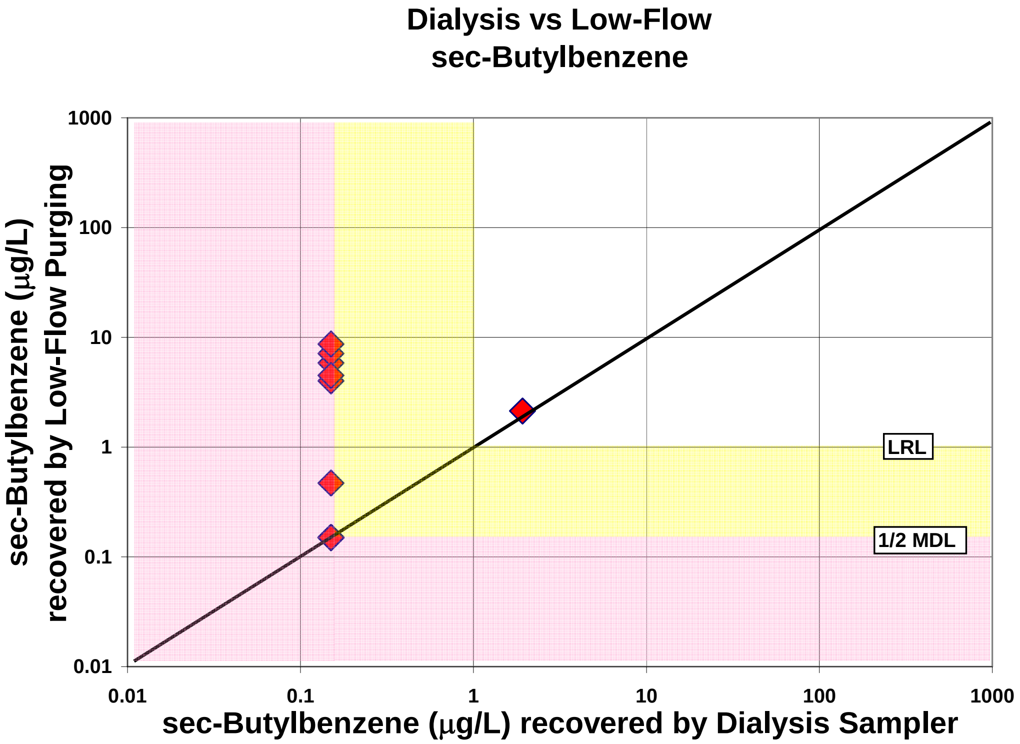


Figure A-36. Comparison of sec-butylbenzene concentrations recovered by the dialysis sampler and low-flow purging

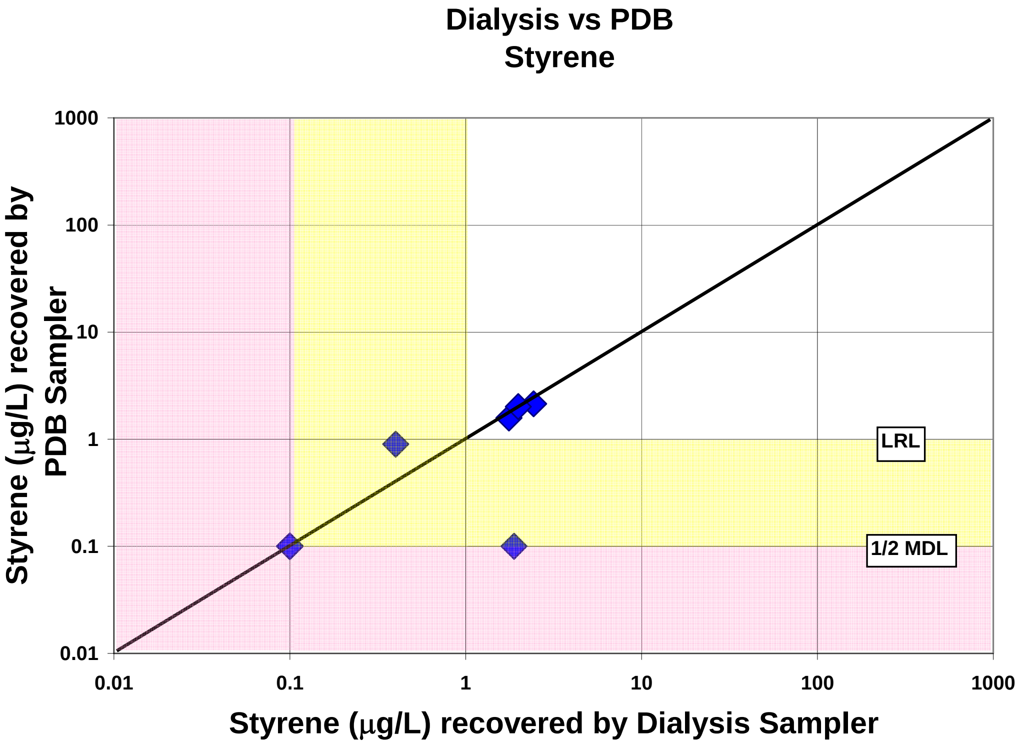


Figure A-37. Comparison of styrene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

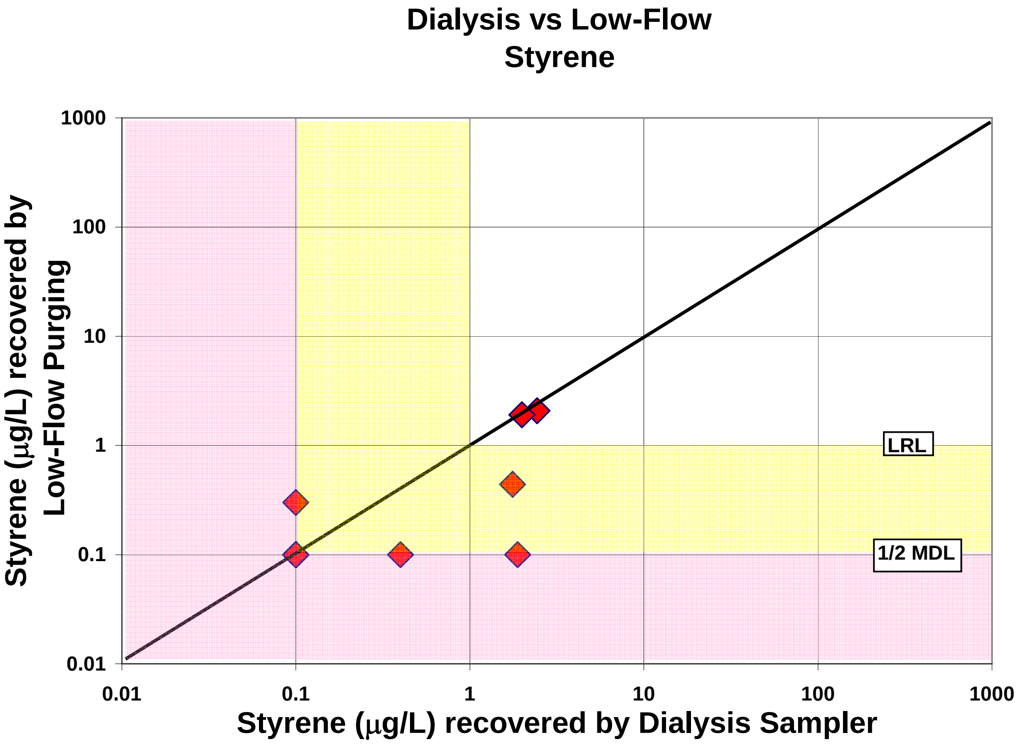


Figure A-38. Comparison of styrene concentrations recovered by the dialysis sampler and low-flow purging

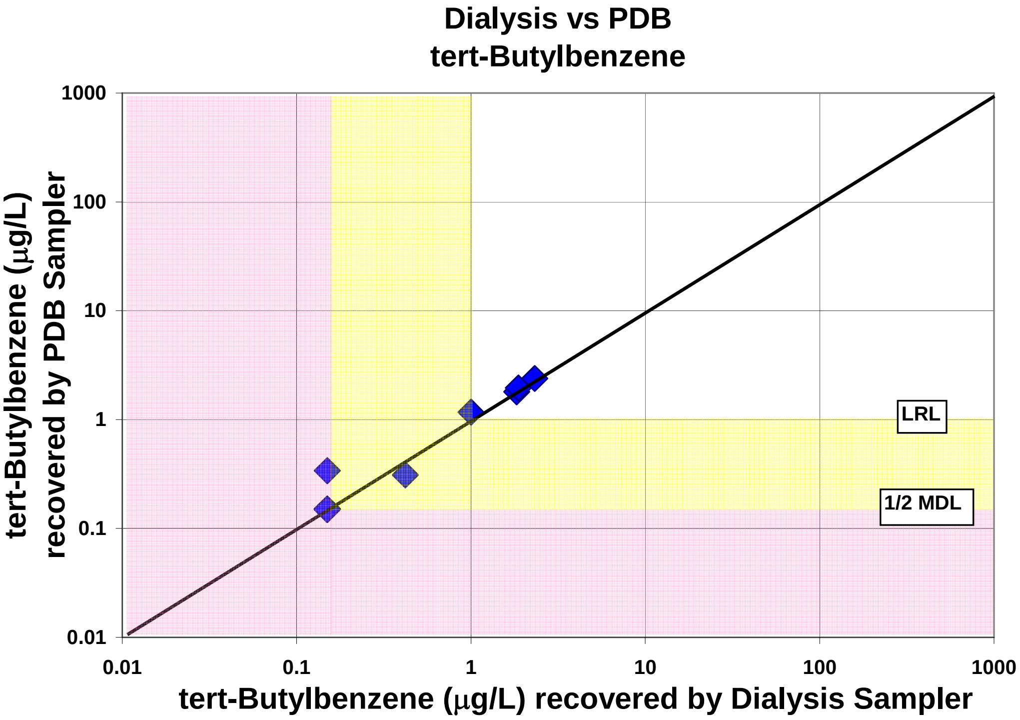


Figure A-39. Comparison of tert-butylbenzene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

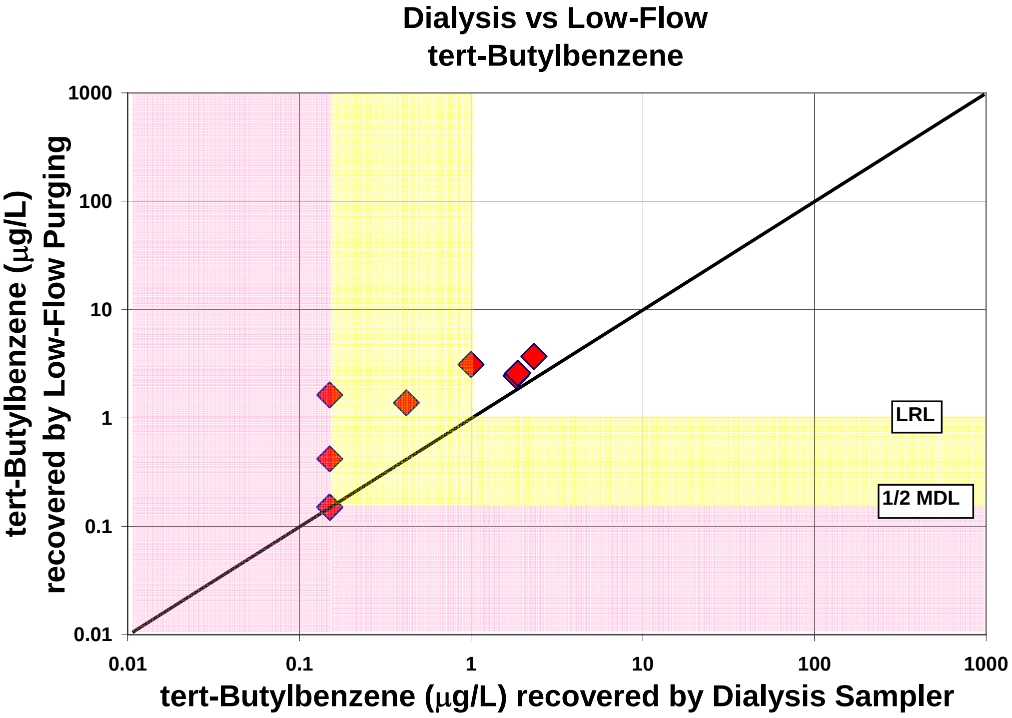


Figure A-40. Comparison of tert-butylbenzene concentrations recovered by the dialysis sampler and low-flow purging

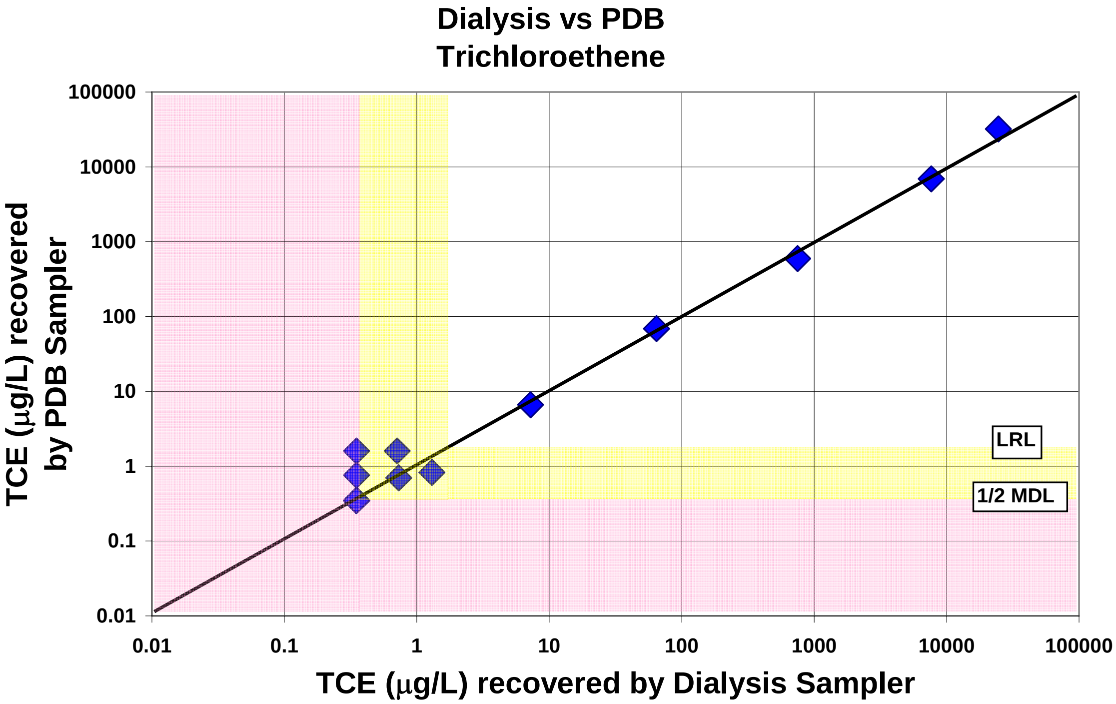


Figure A-41. Comparison of trichloroethene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

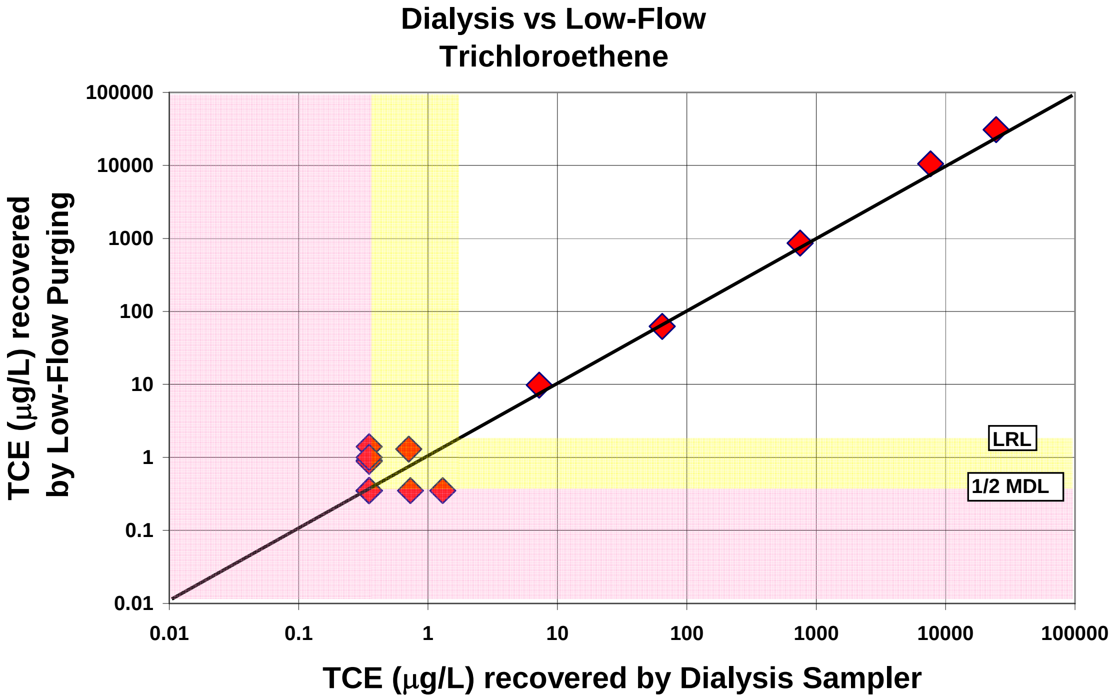


Figure A-42. Comparison of trichloroethene concentrations recovered by the dialysis sampler and low-flow purging

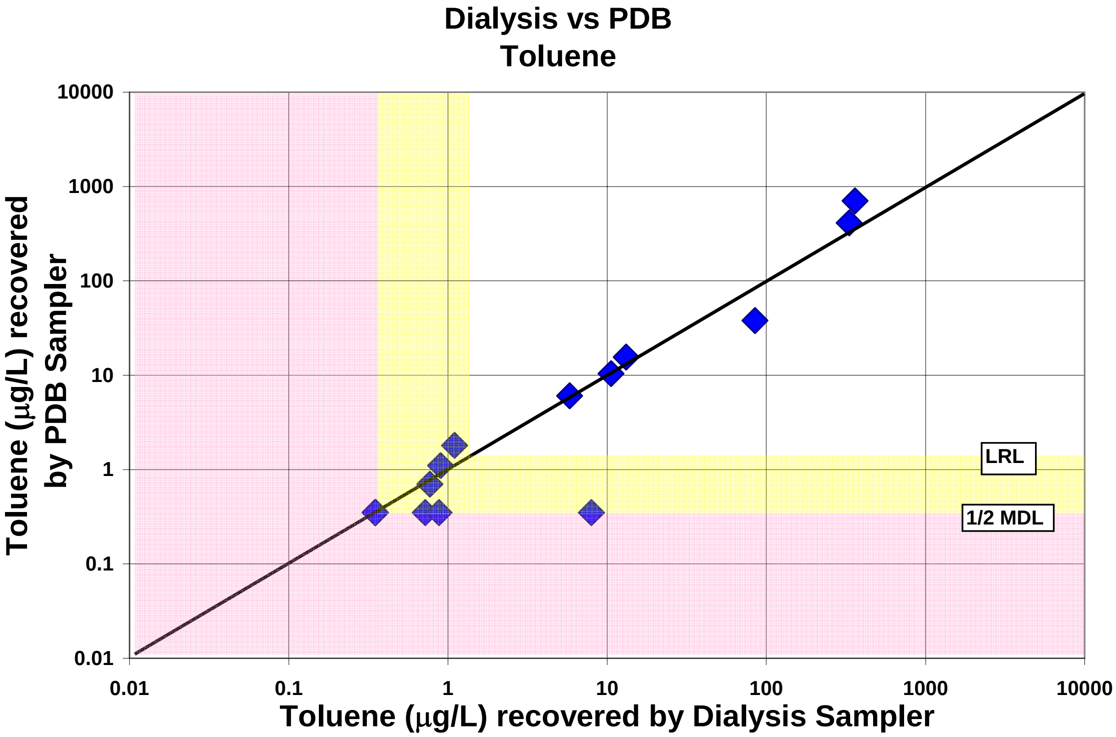


Figure A-43. Comparison of toluene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

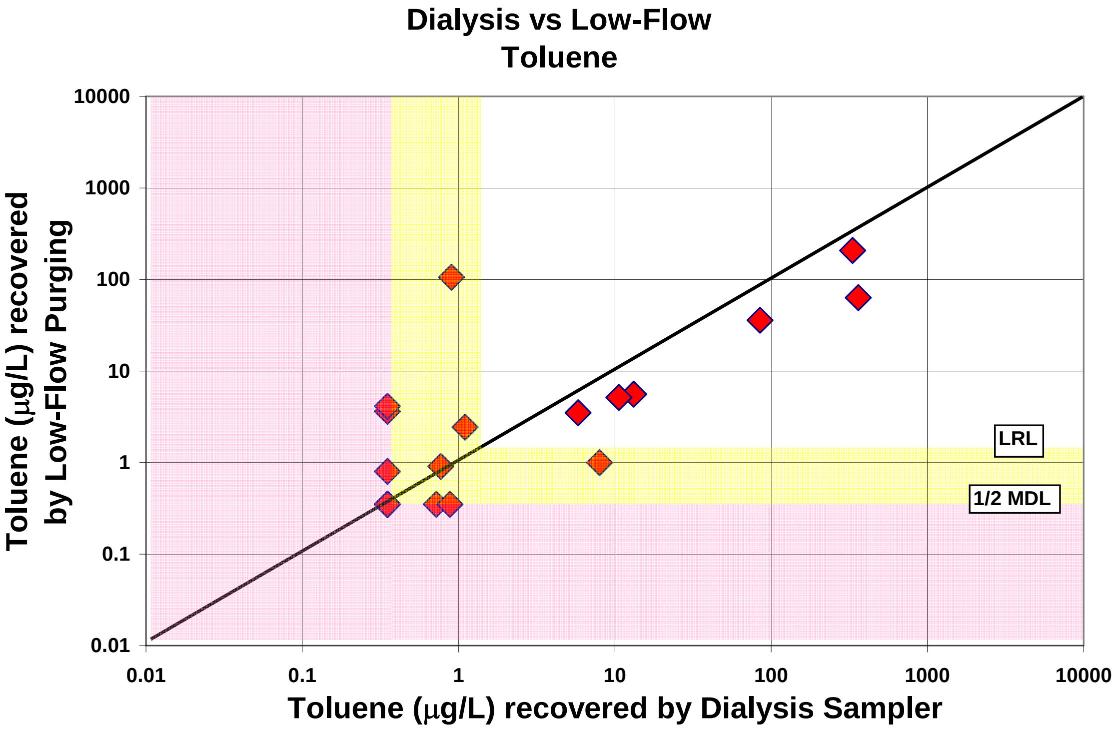


Figure A-44. Comparison of toluene concentrations recovered by the dialysis sampler and low-flow purging.

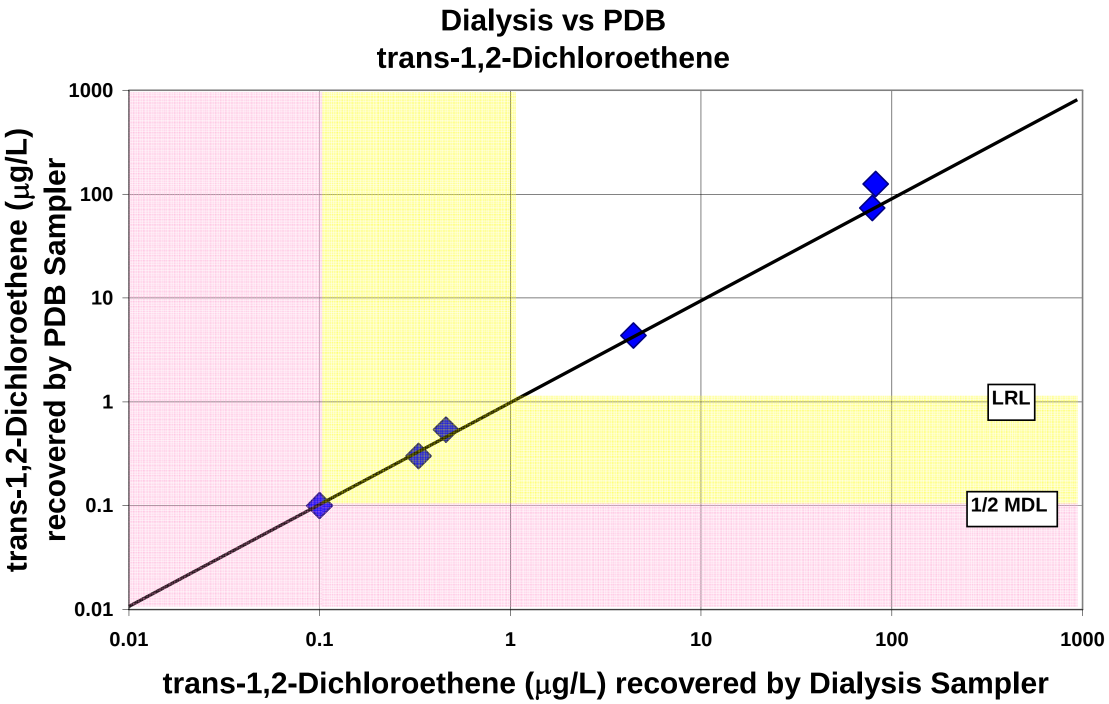


Figure A-45. Comparison of trans-1,2-dichloroethene concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

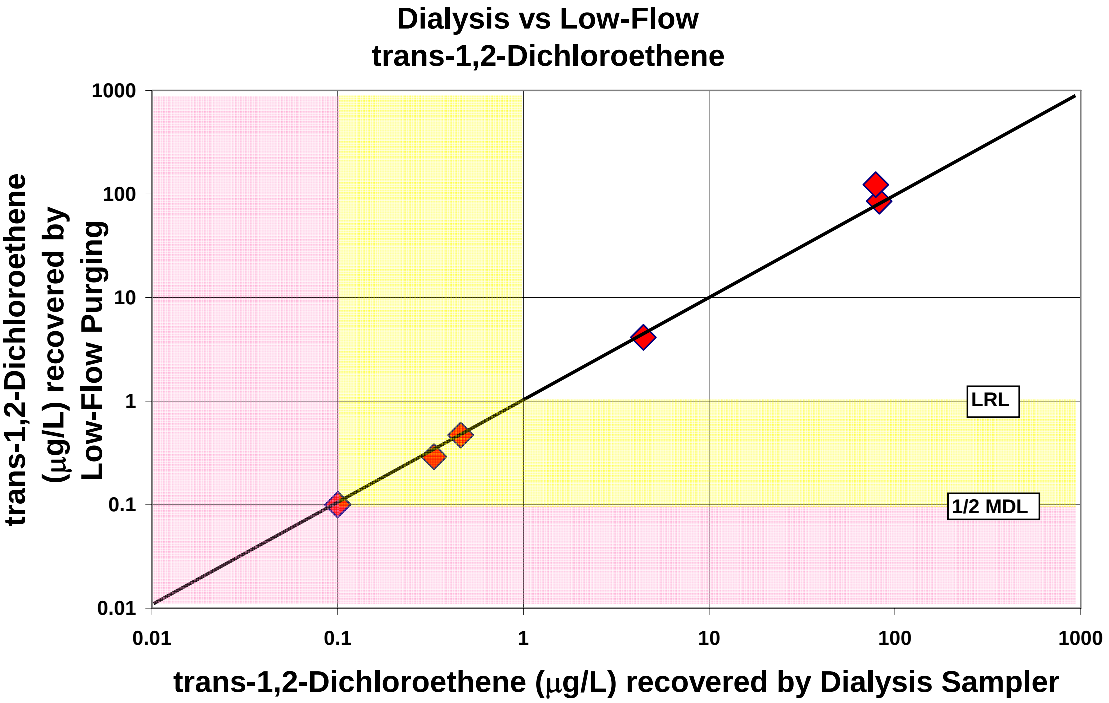


Figure A-46. Comparison of trans-1,2-dichloroethene concentrations recovered by the dialysis sampler and low-flow purging

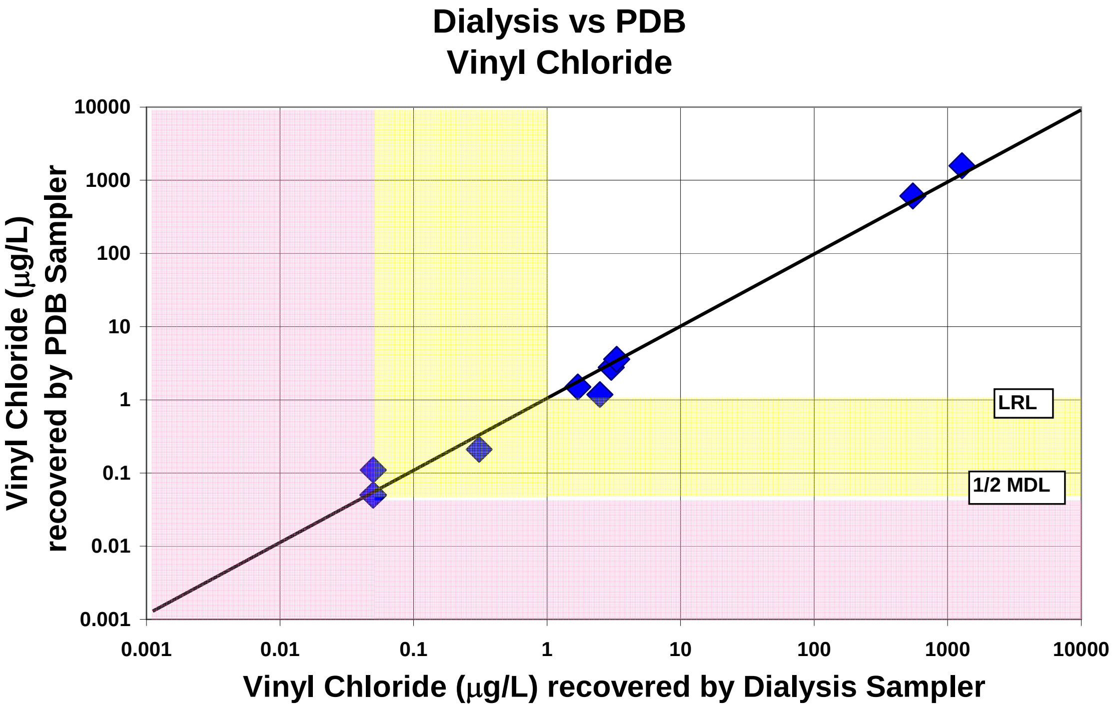


Figure A-47. Comparison of vinyl chloride concentrations recovered by the dialysis sampler and the polyethylene diffusion bag (PDB) sampler

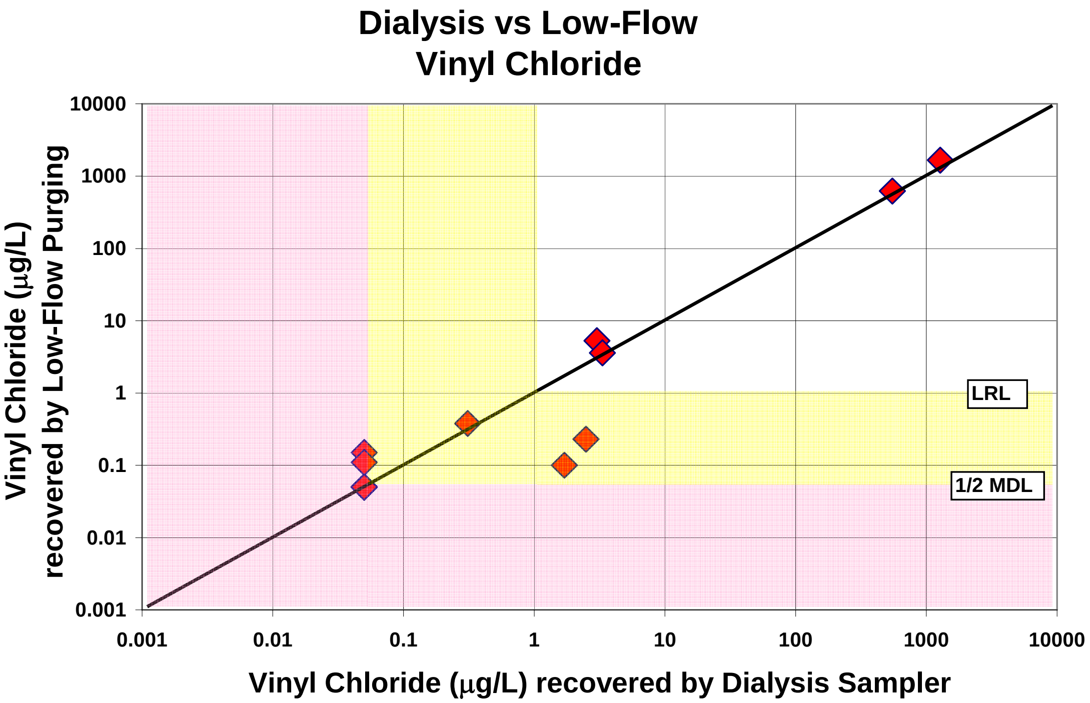


Figure A-48. Comparison of vinyl chloride concentrations recovered by the dialysis sampler and low-flow purging

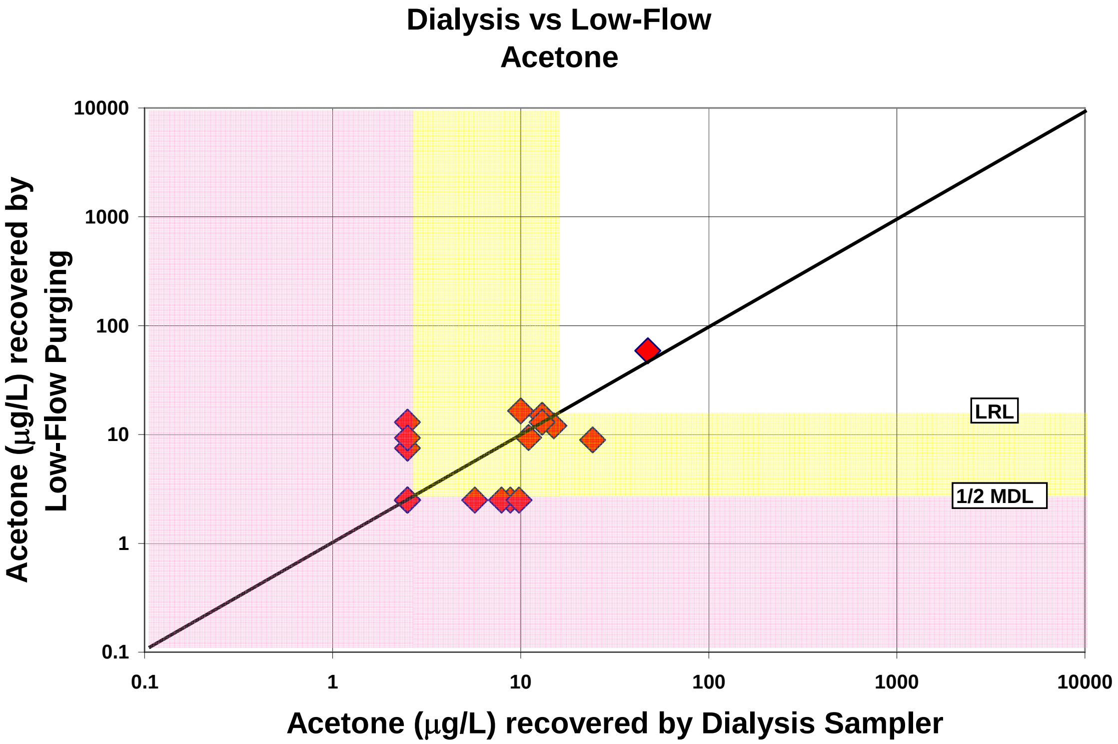


Figure A-49. Comparison of acetone concentrations recovered by the dialysis sampler and low-flow purging

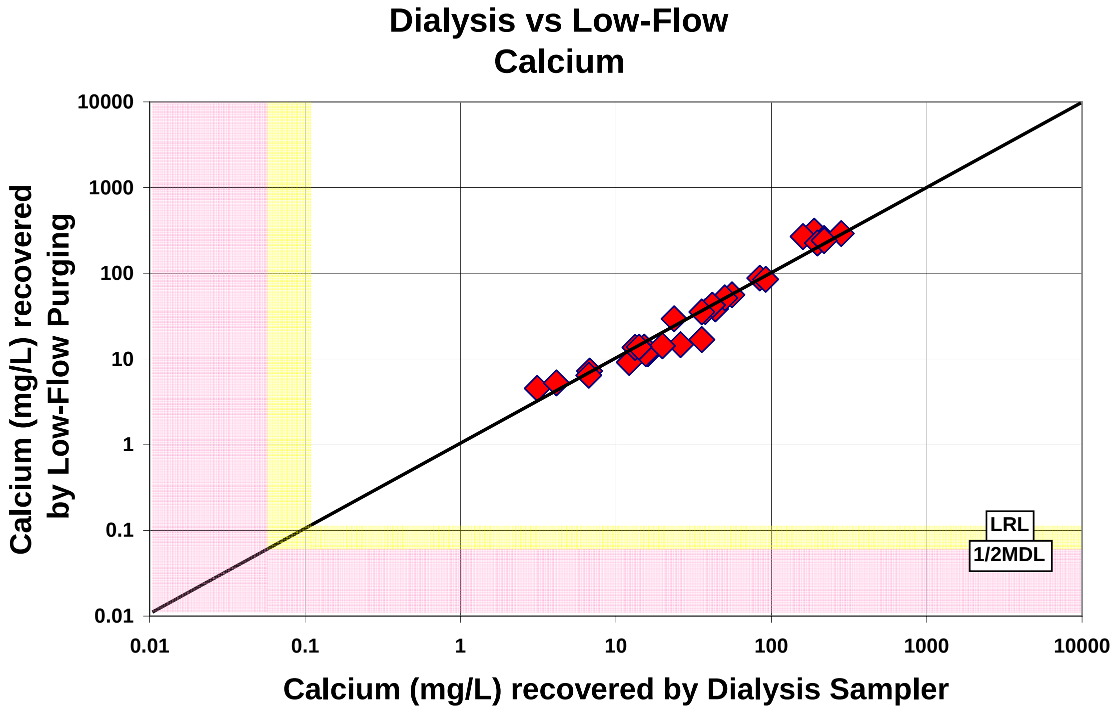


Figure A-50. Comparison of calcium concentrations recovered by the dialysis sampler and low-flow purging

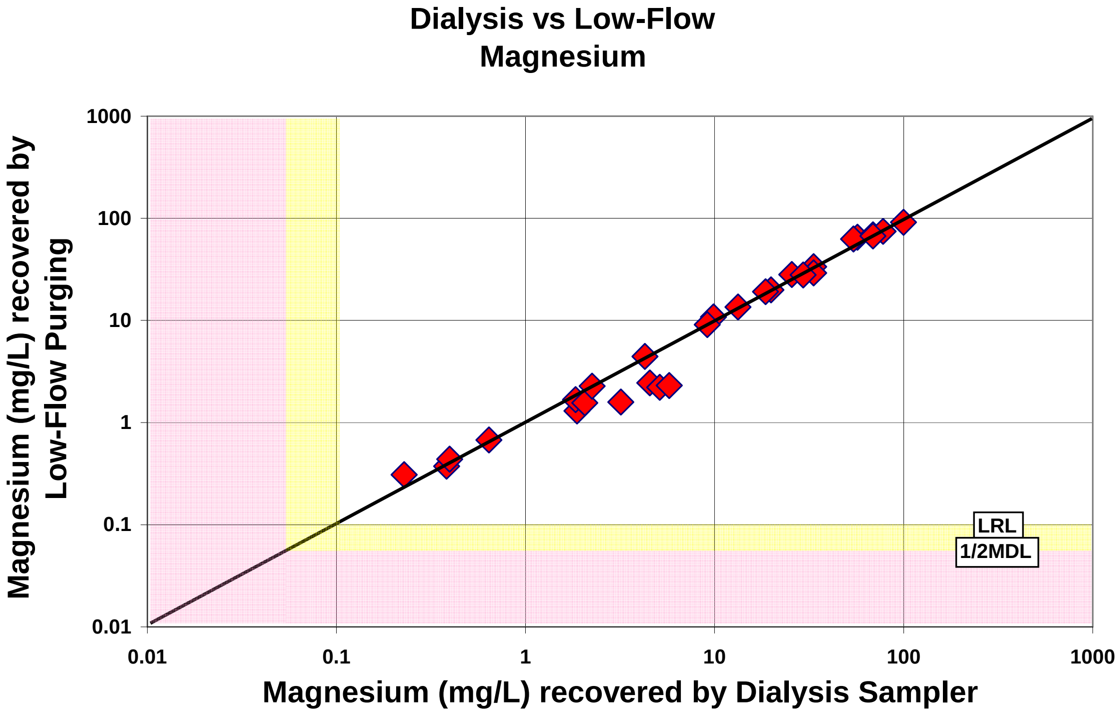


Figure A-51. Comparison of magnesium concentrations recovered by the dialysis sampler and low-flow purging

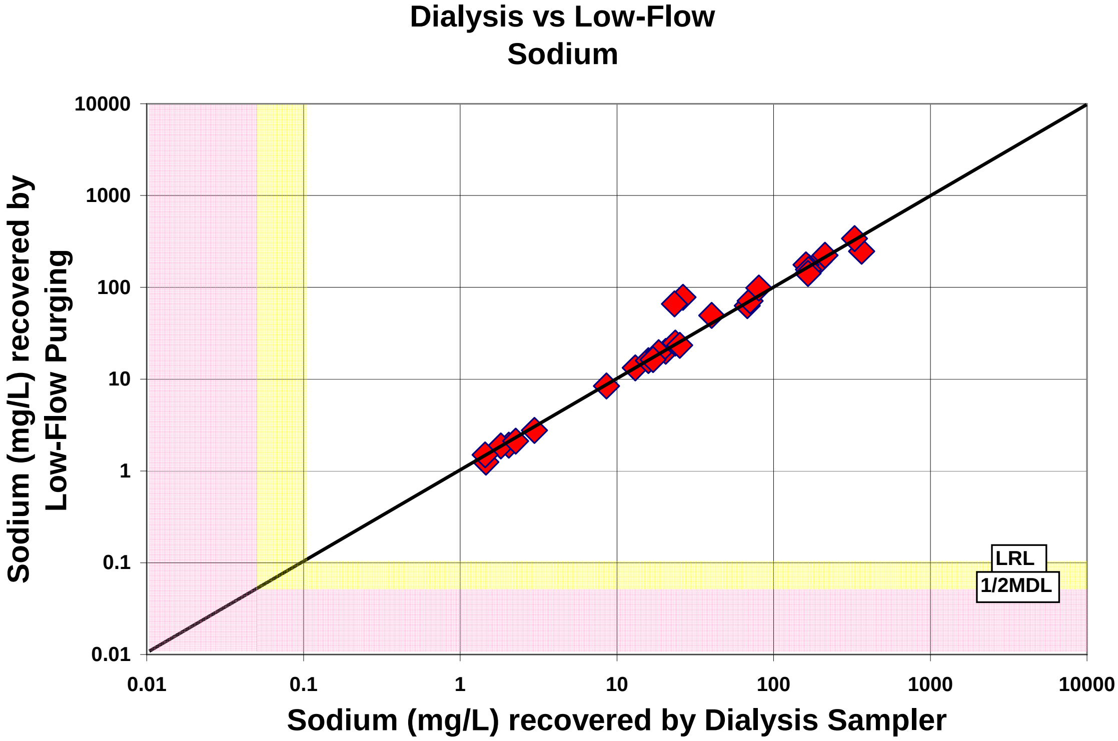


Figure A-52. Comparison of sodium concentrations recovered by the dialysis sampler and low-flow purging

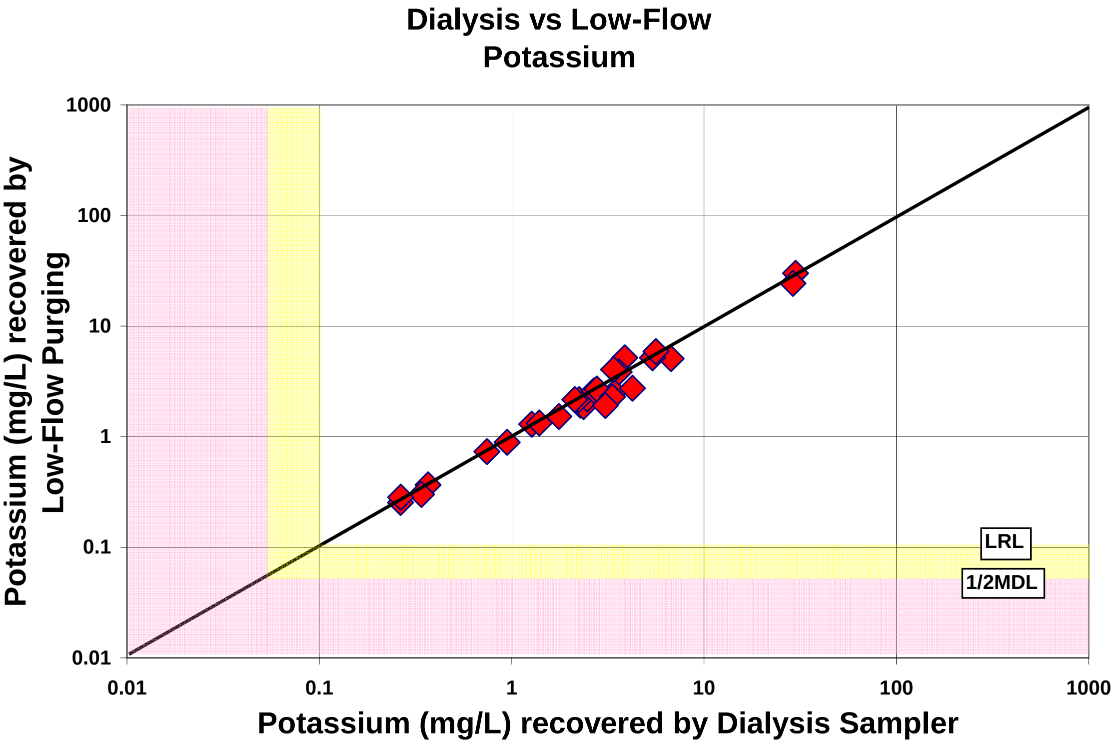


Figure A-53. Comparison of potassium concentrations recovered by the dialysis sampler and low-flow purging

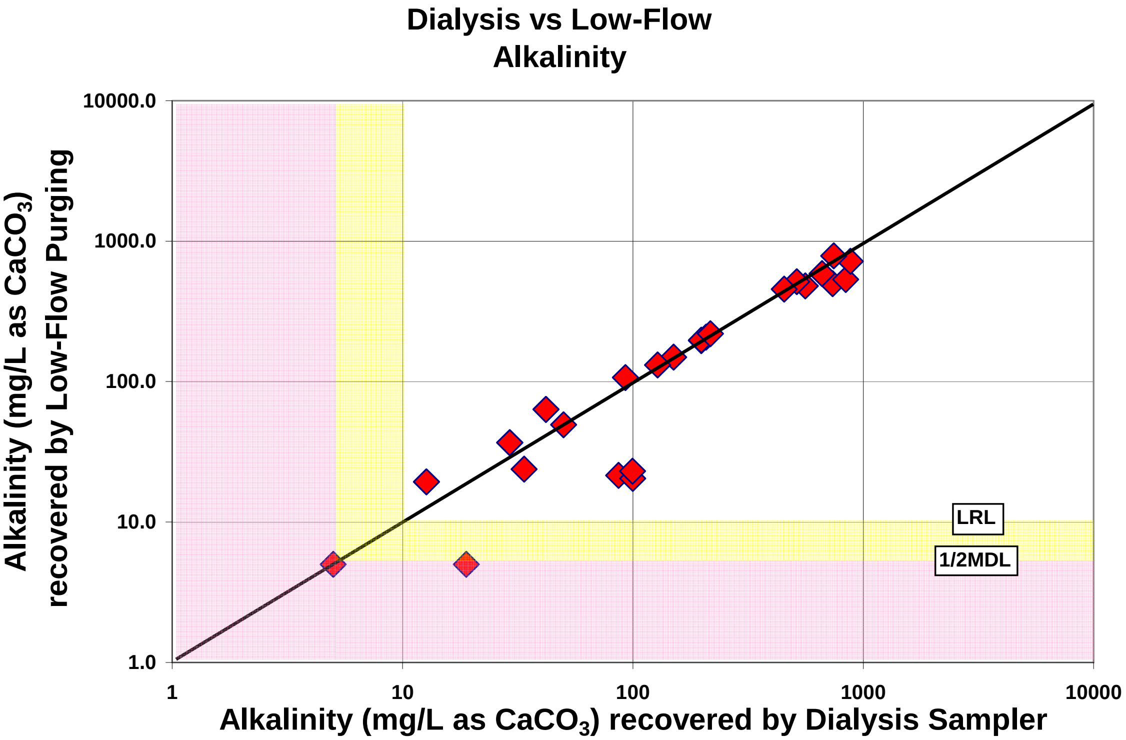


Figure A-54. Comparison of alkalinity (bicarbonate) concentrations recovered by the dialysis sampler and low-flow purging

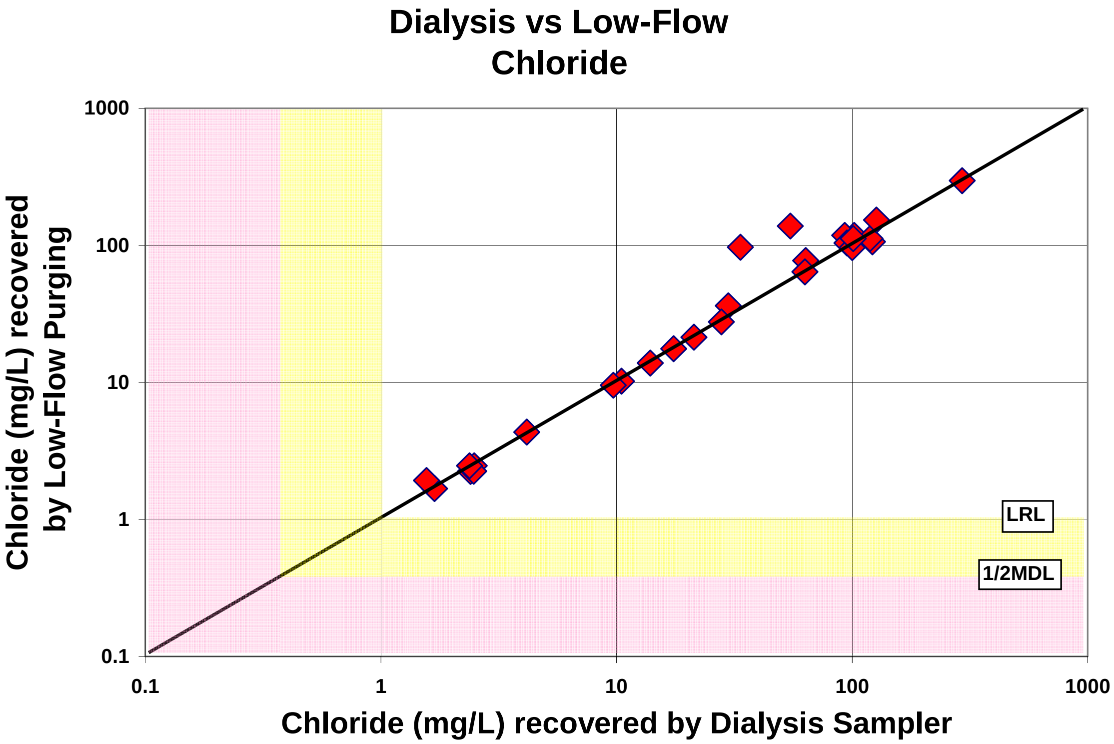


Figure A-55. Comparison of chloride concentrations recovered by the dialysis sampler and low-flow purging

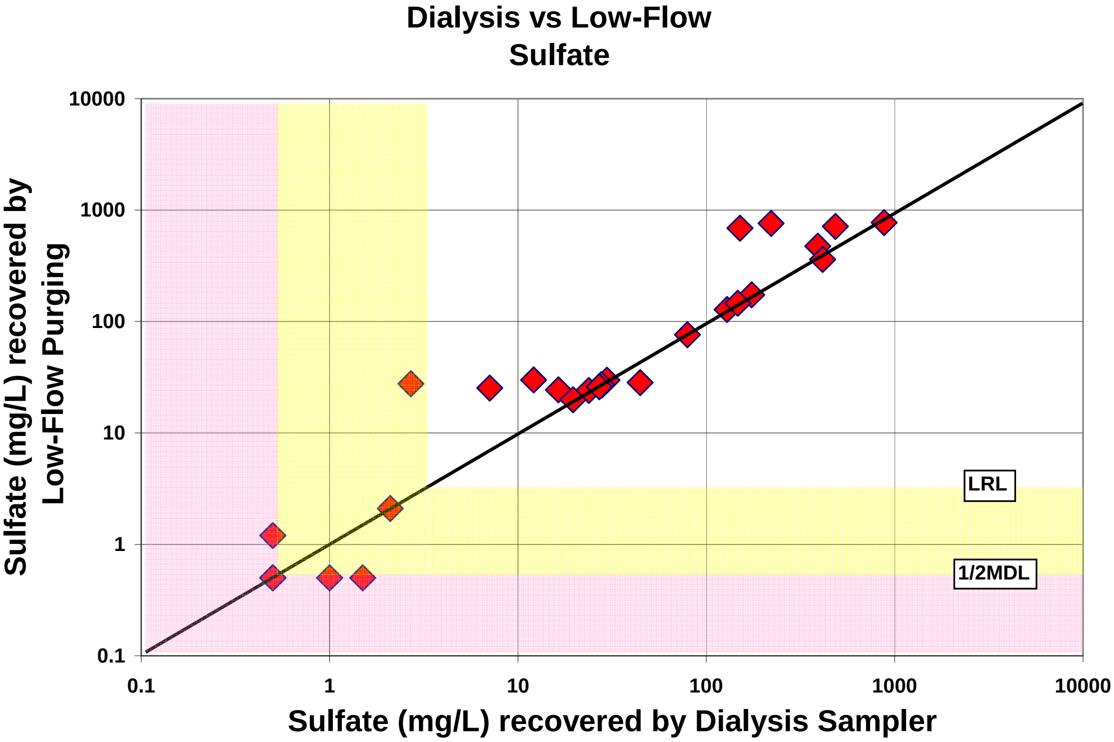


Figure A-56. Comparison of sulfate concentrations recovered by the dialysis sampler and low-flow purging

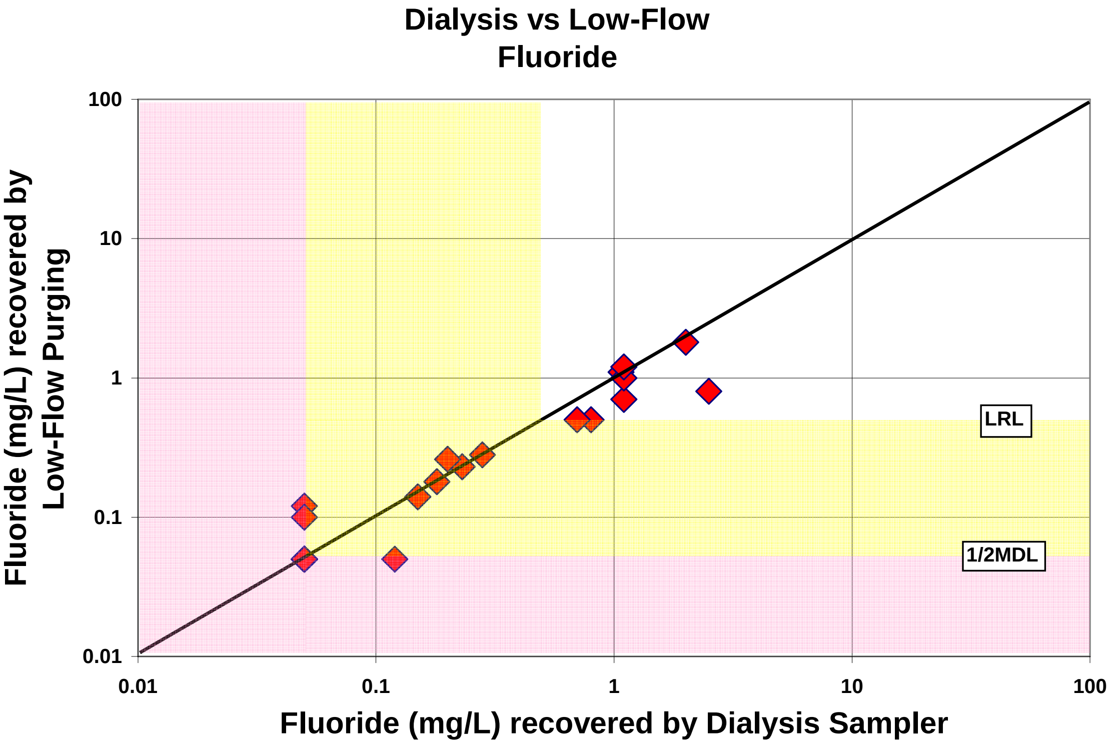


Figure A-57. Comparison of fluoride concentrations recovered by the dialysis sampler and low-flow purging

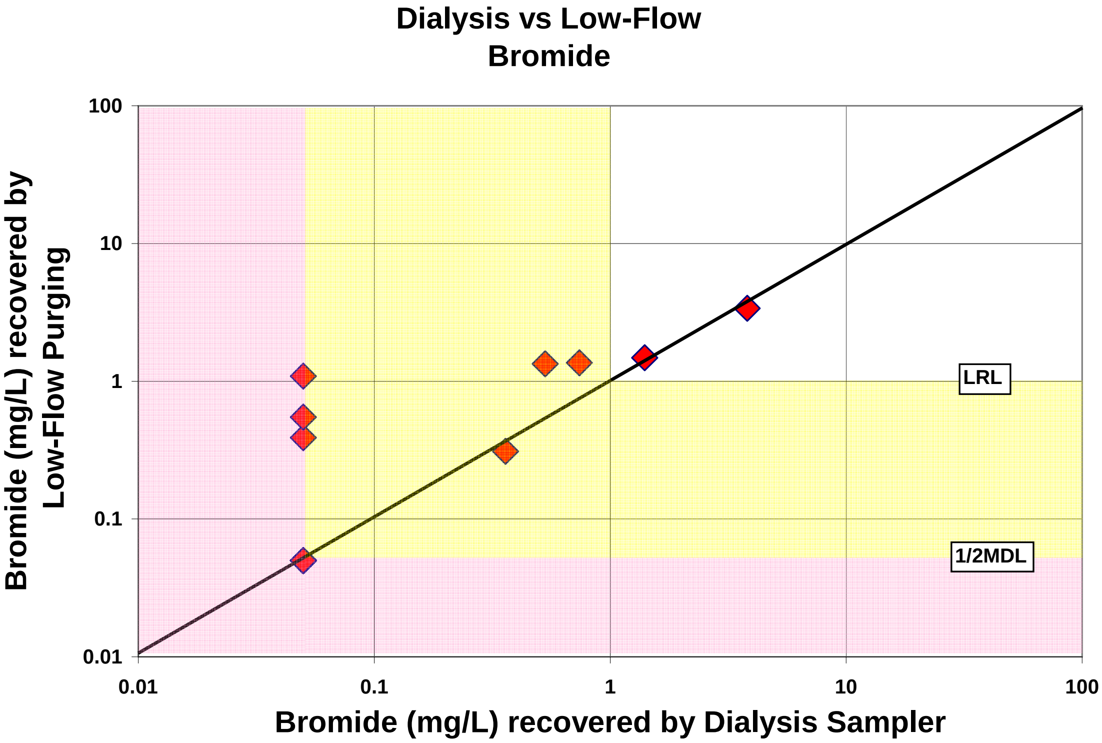


Figure A-58. Comparison of bromide concentrations recovered by the dialysis sampler and low-flow purging

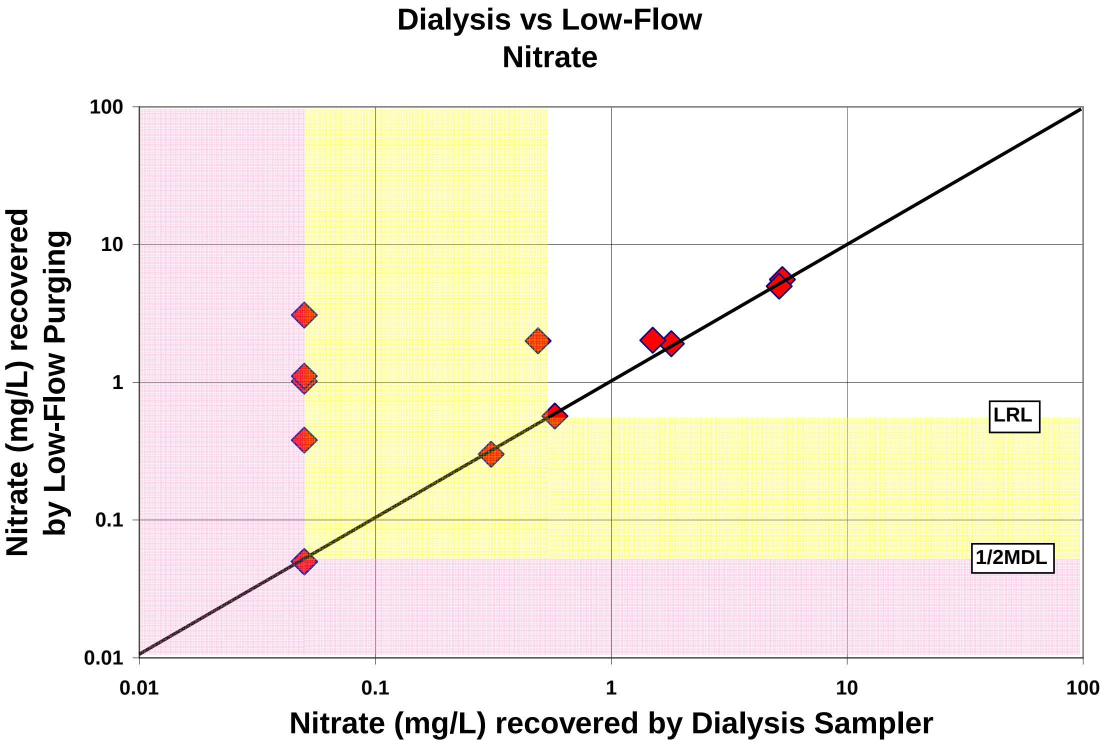


Figure A-59. Comparison of nitrate concentrations recovered by the dialysis sampler and low-flow purging

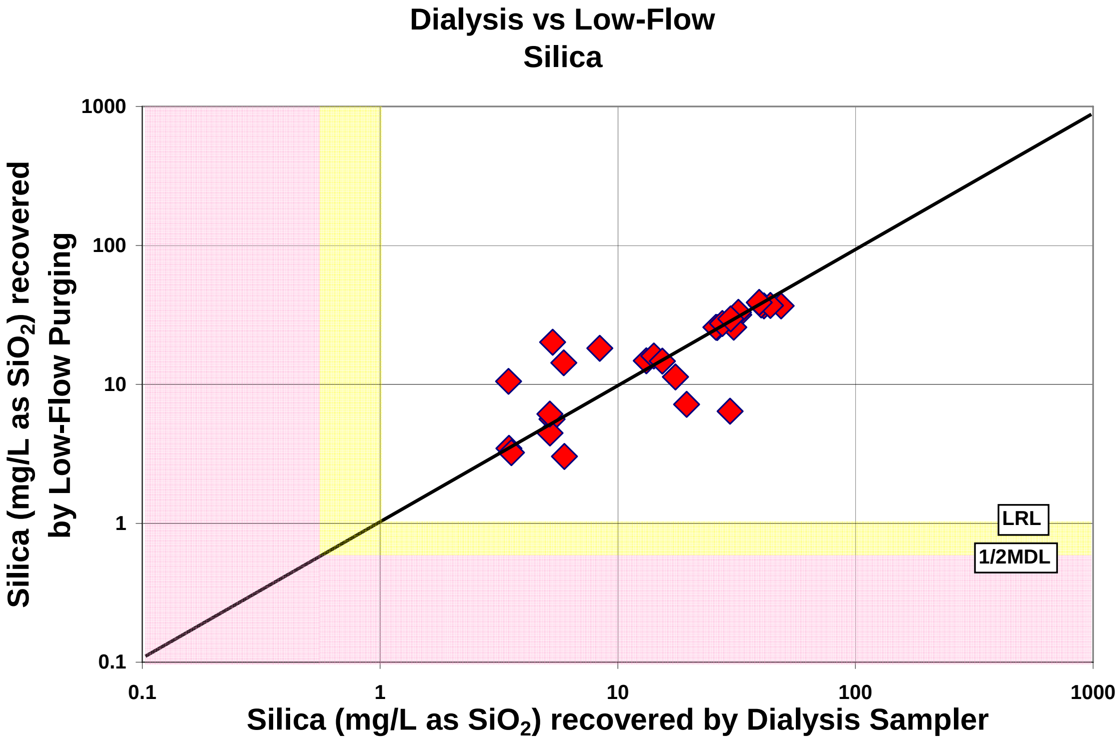


Figure A-60. Comparison of silica concentrations recovered by the dialysis sampler and low-flow purging

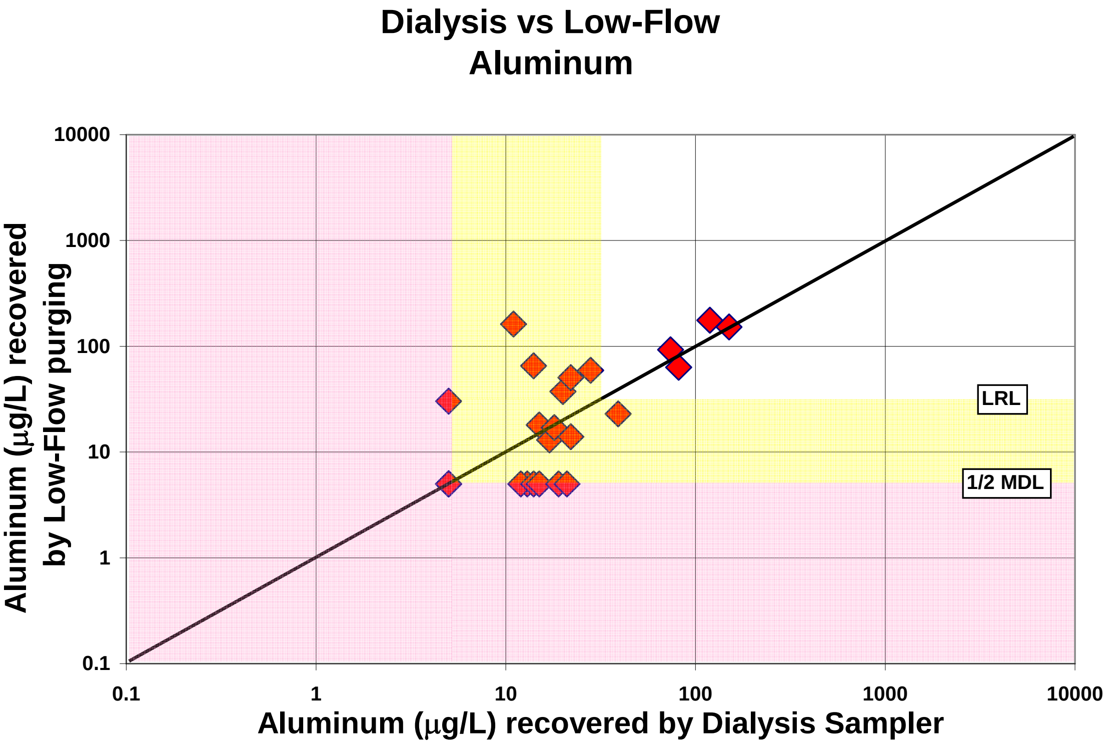


Figure A-61. Comparison of aluminum concentrations recovered by the dialysis sampler and low-flow purging

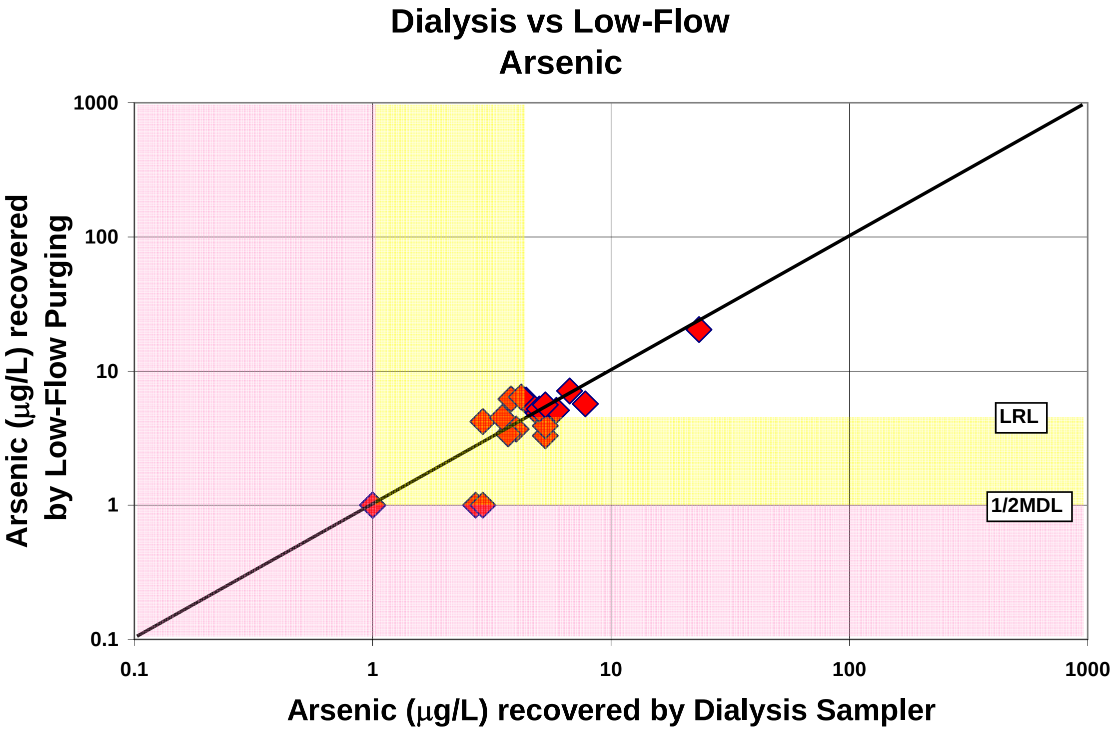


Figure A-62. Comparison of arsenic concentrations recovered by the dialysis sampler and low-flow purging

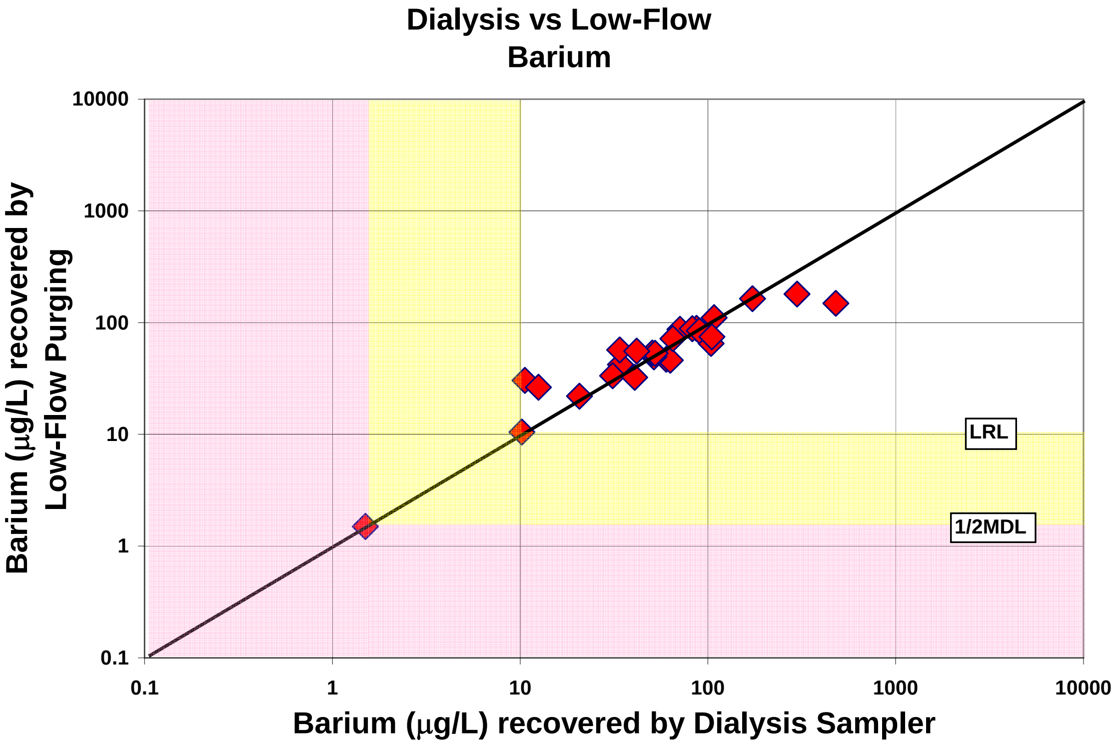


Figure A-63. Comparison of barium concentrations recovered by the dialysis sampler and low-flow purging

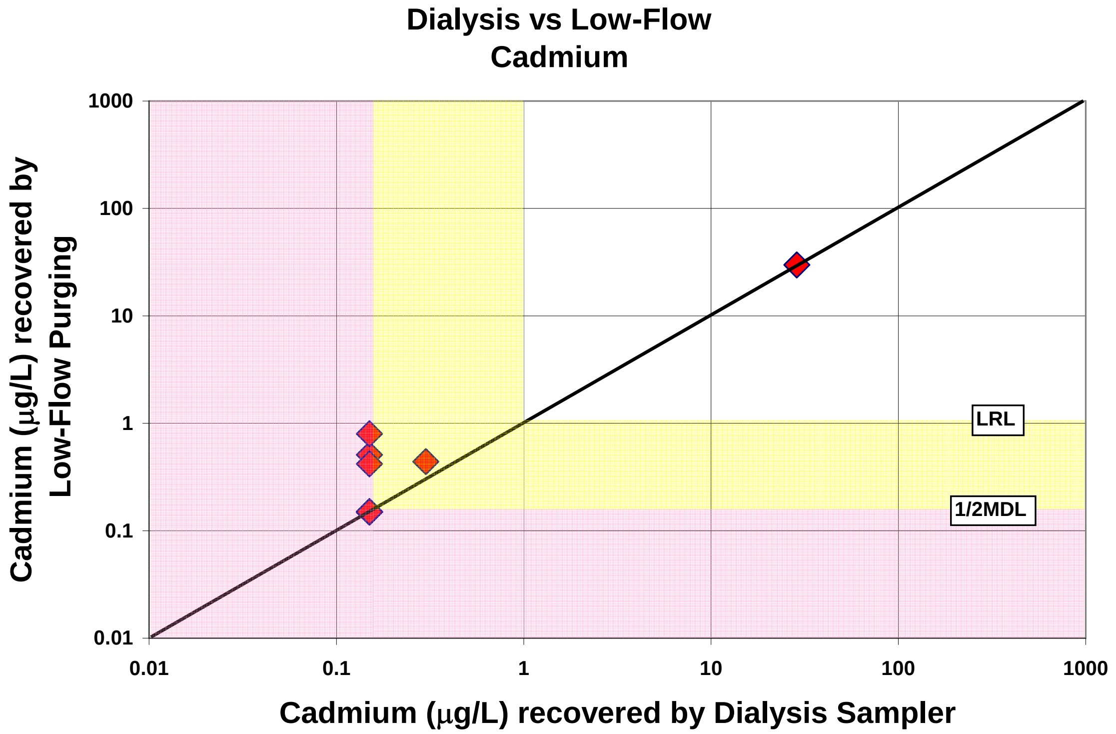


Figure A-64. Comparison of cadmium concentrations recovered by the dialysis sampler and low-flow purging

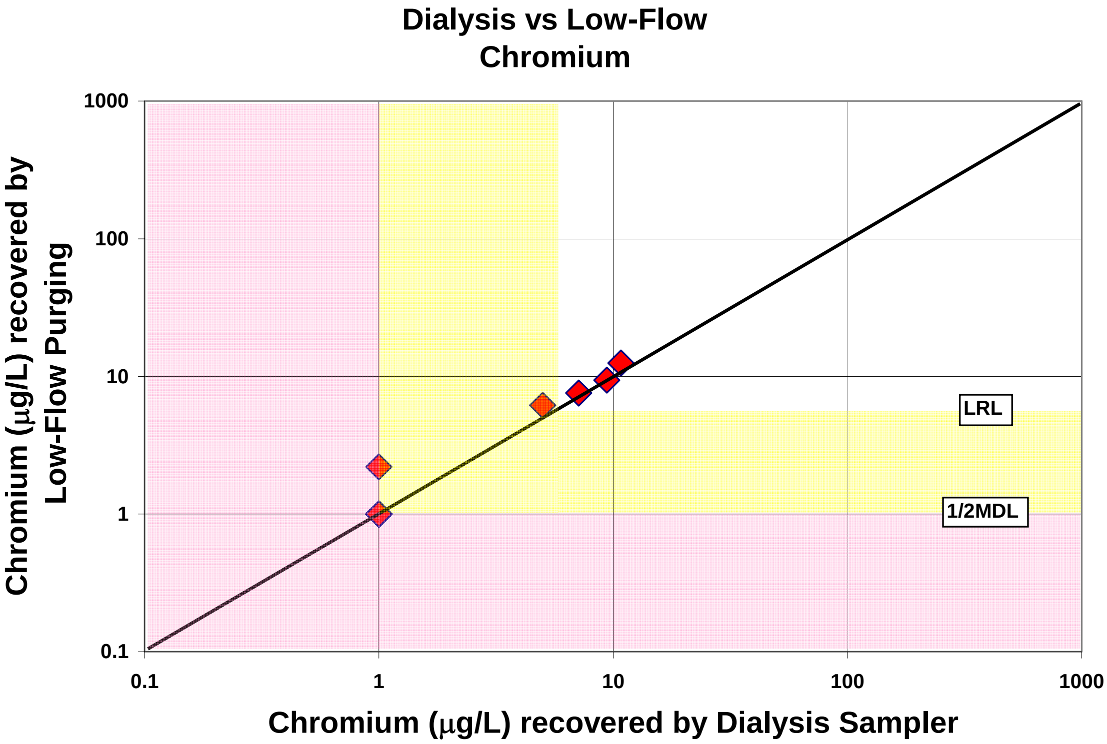


Figure A-65. Comparison of chromium concentrations recovered by the dialysis sampler and low-flow purging

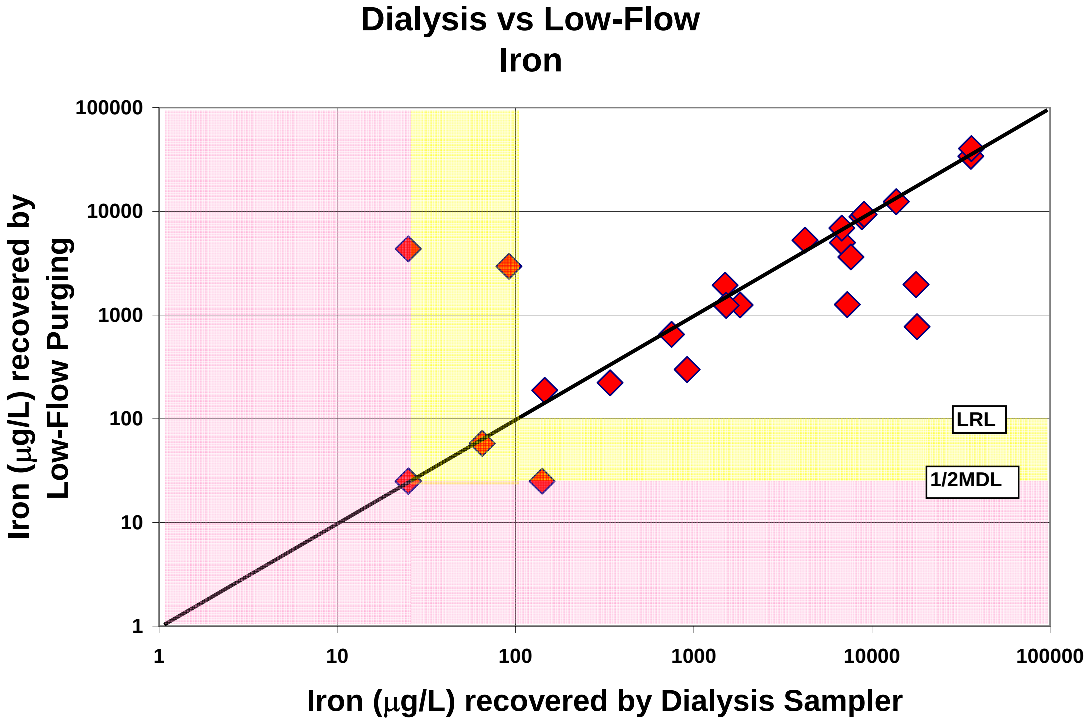


Figure A-66. Comparison of iron concentrations recovered by the dialysis sampler and low-flow purging

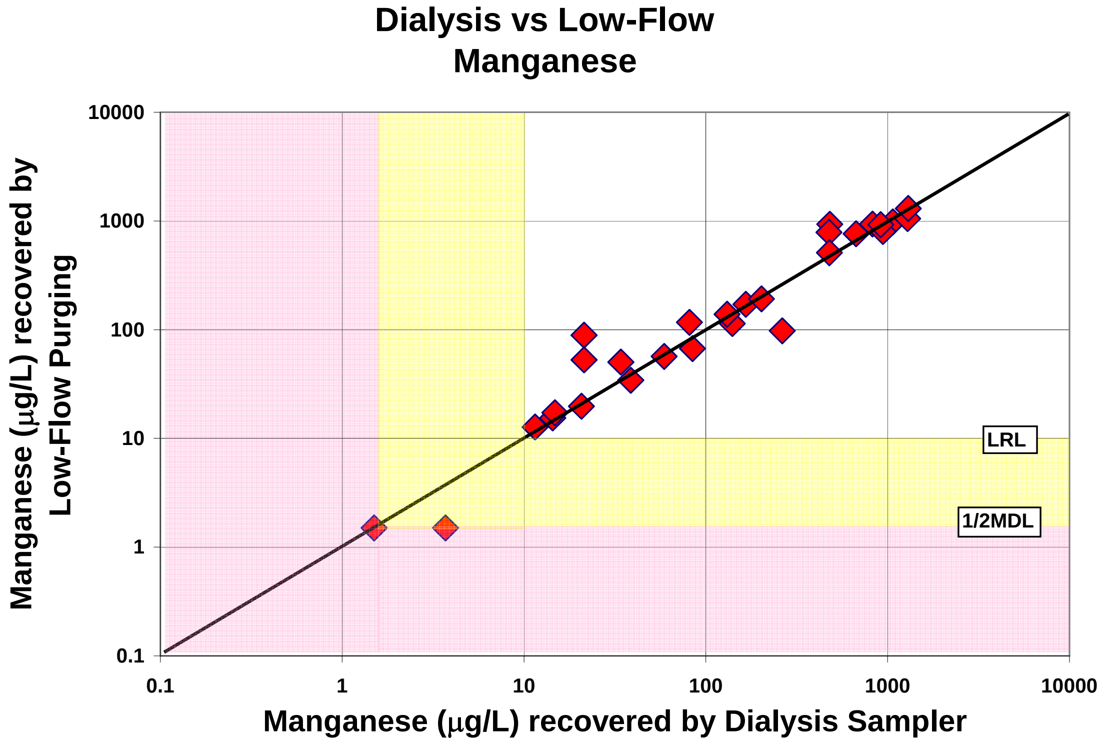


Figure A-67. Comparison of manganese concentrations recovered by the dialysis sampler and low-flow purging

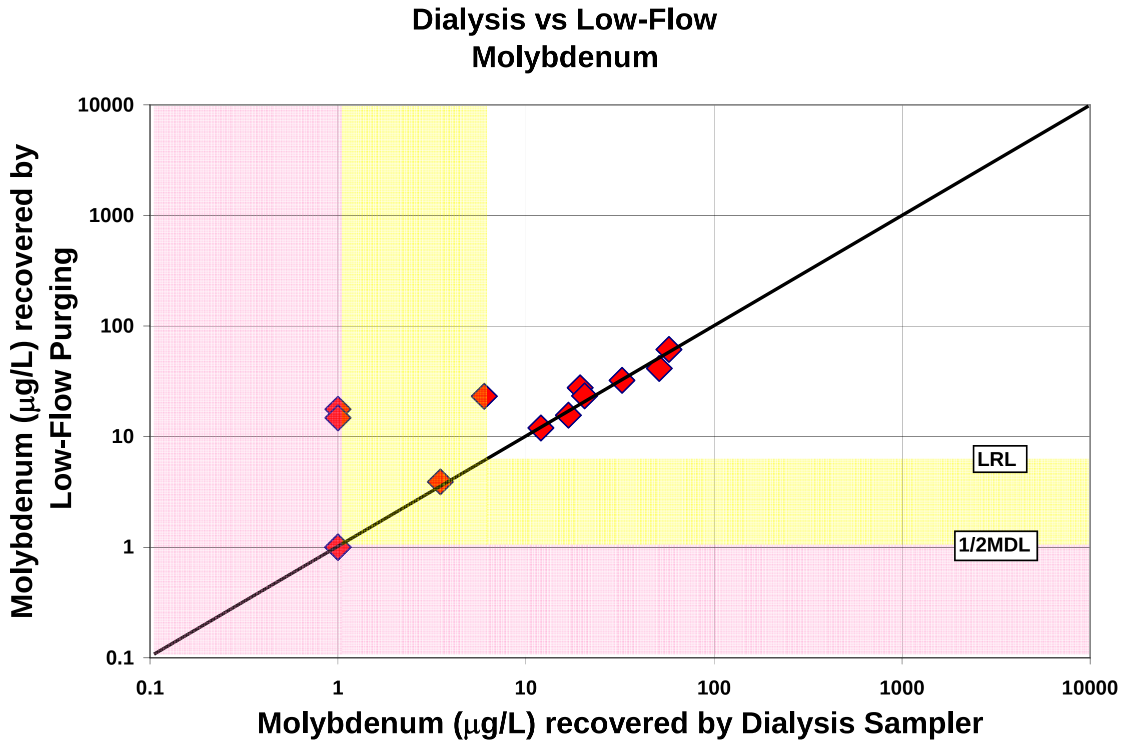


Figure A-68. Comparison of molybdenum concentrations recovered by the dialysis sampler and low-flow purging

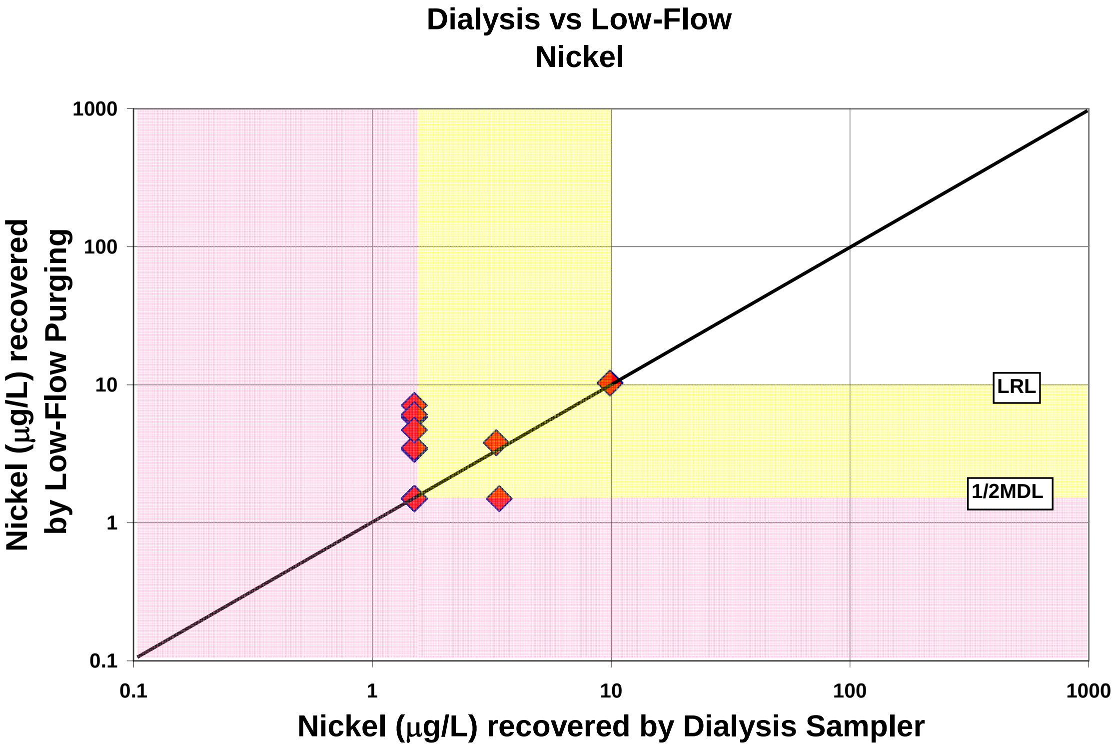


Figure A-69. Comparison of nickel concentrations recovered by the dialysis sampler and low-flow purging

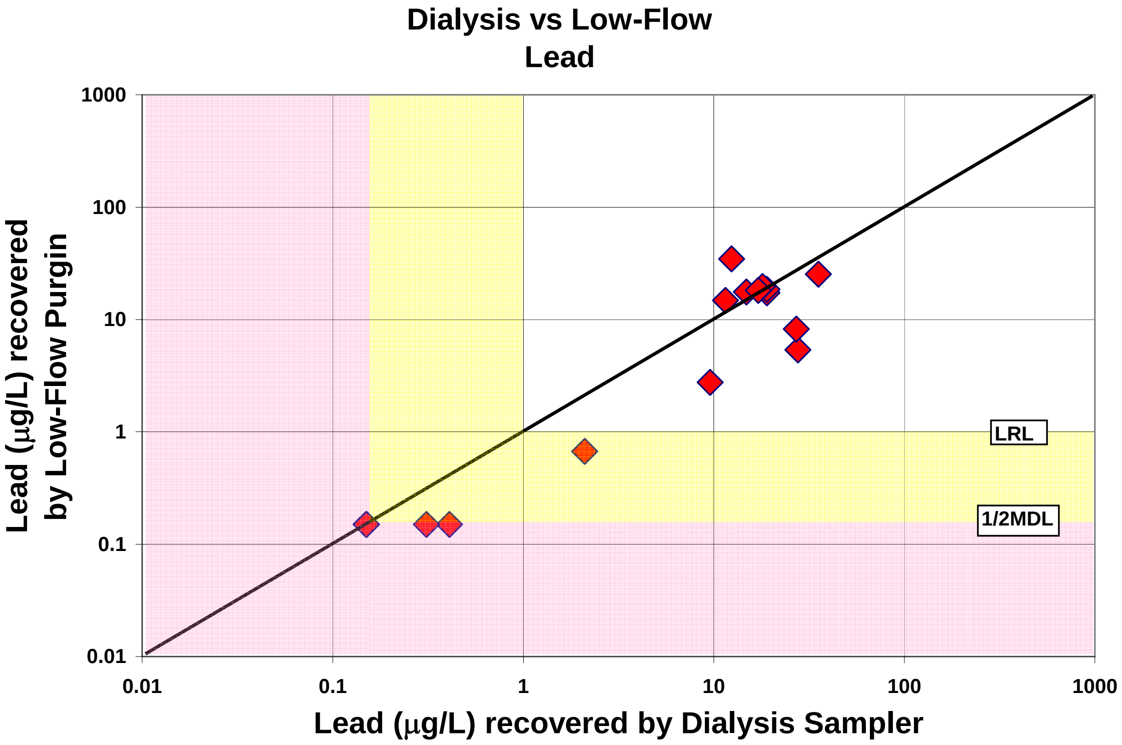


Figure A-70. Comparison of lead concentrations recovered by the dialysis sampler and low-flow purging

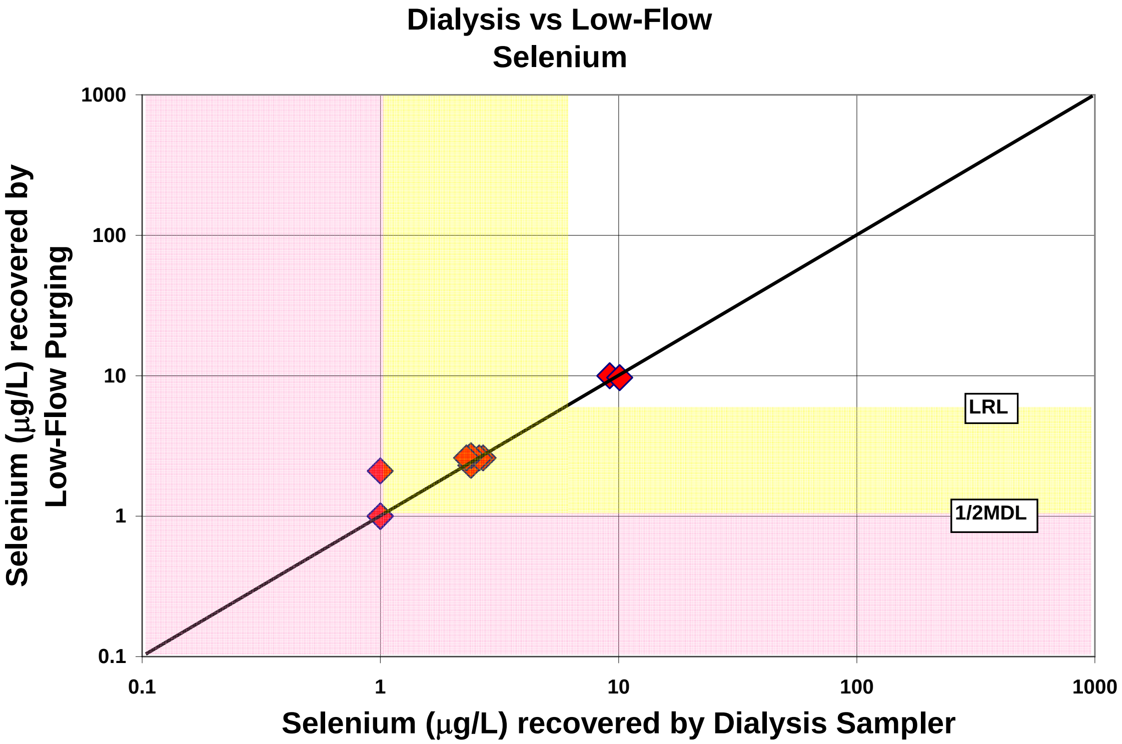


Figure A-71. Comparison of selenium concentrations recovered by the dialysis sampler and low-flow purging

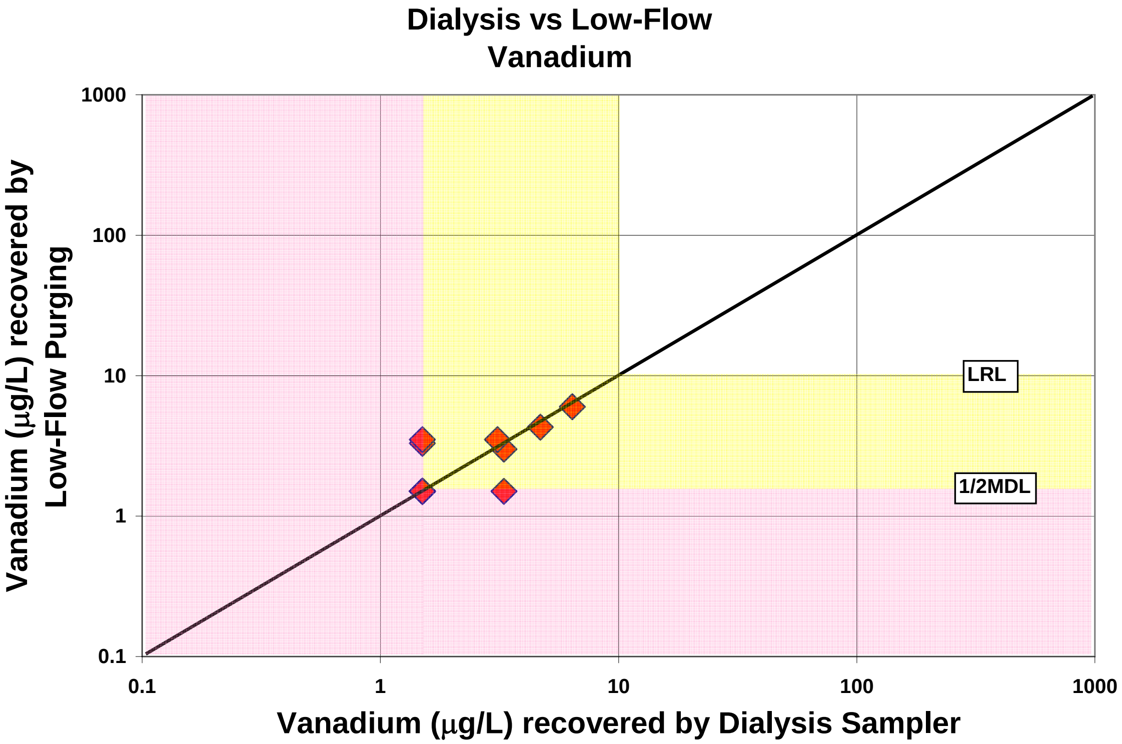


Figure A-72. Comparison of vanadium concentrations recovered by the dialysis sampler and low-flow purging

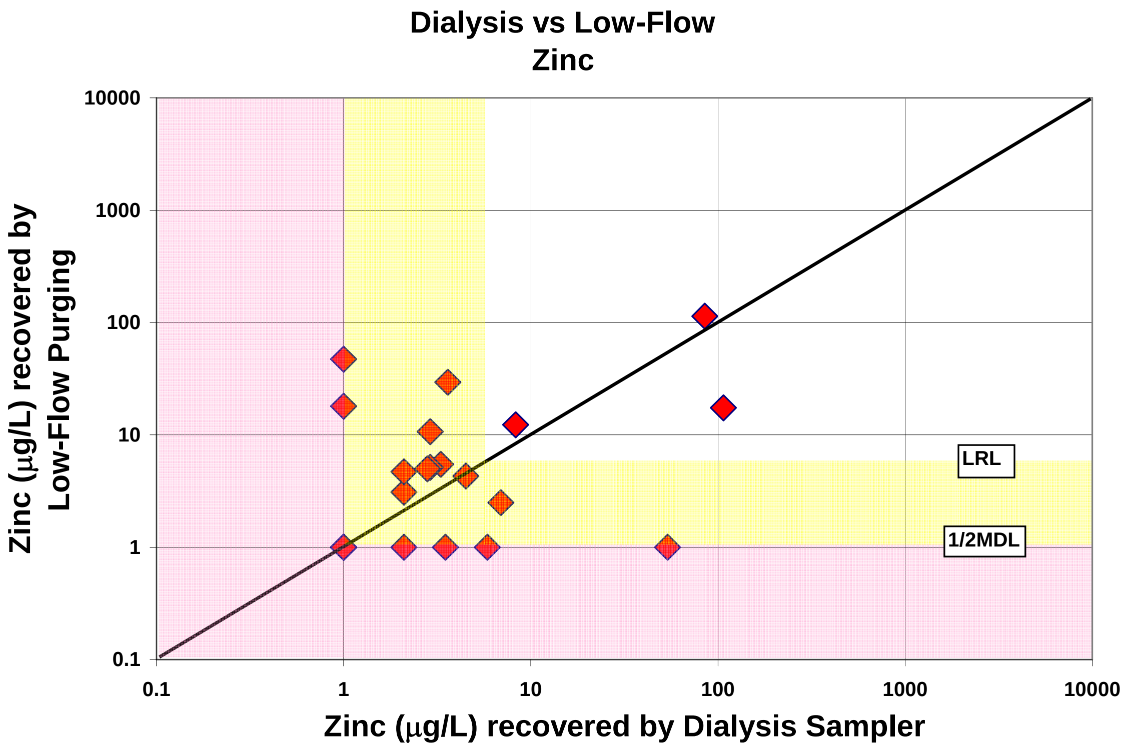


Figure A-73. Comparison of zinc concentrations recovered by the dialysis sampler and low-flow purging

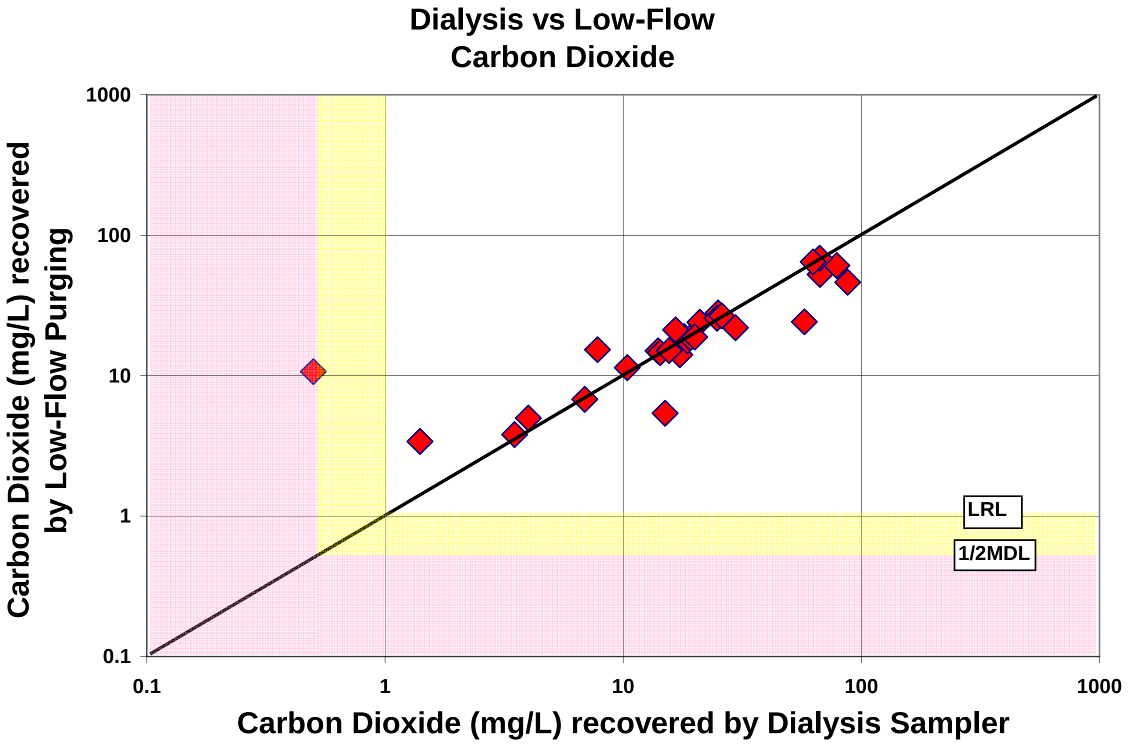


Figure A-74. Comparison of carbon dioxide concentrations recovered by the dialysis sampler and low-flow purging

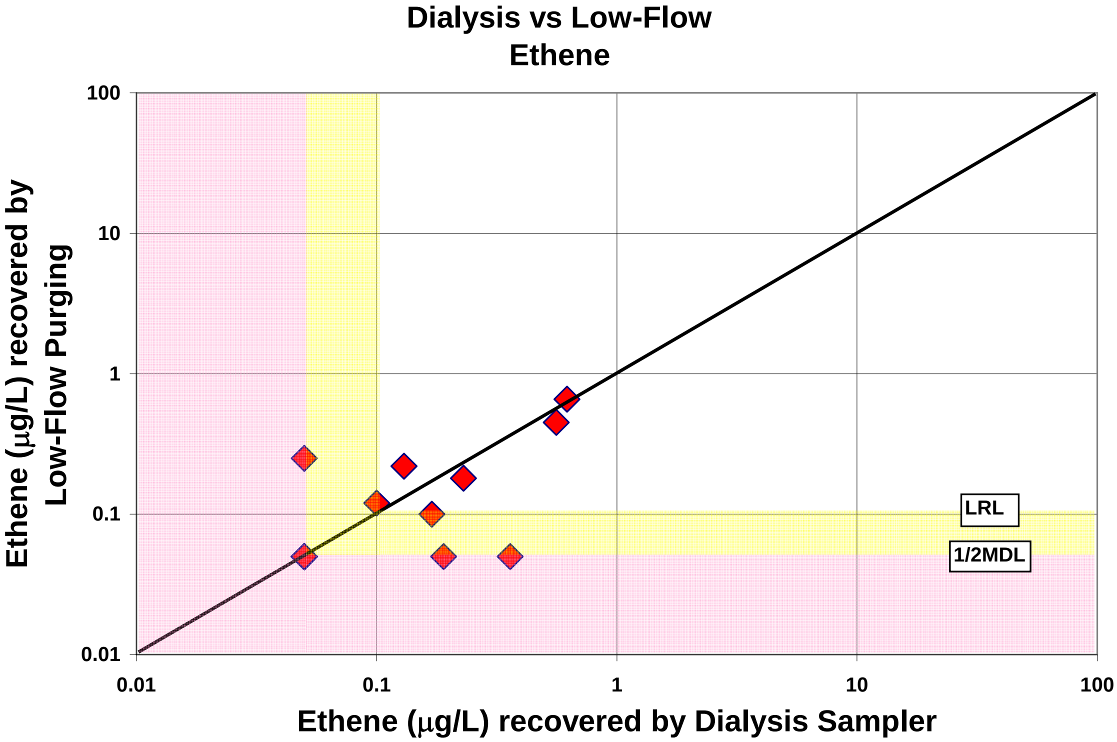


Figure A-75. Comparison of ethene concentrations recovered by the dialysis sampler and low-flow purging

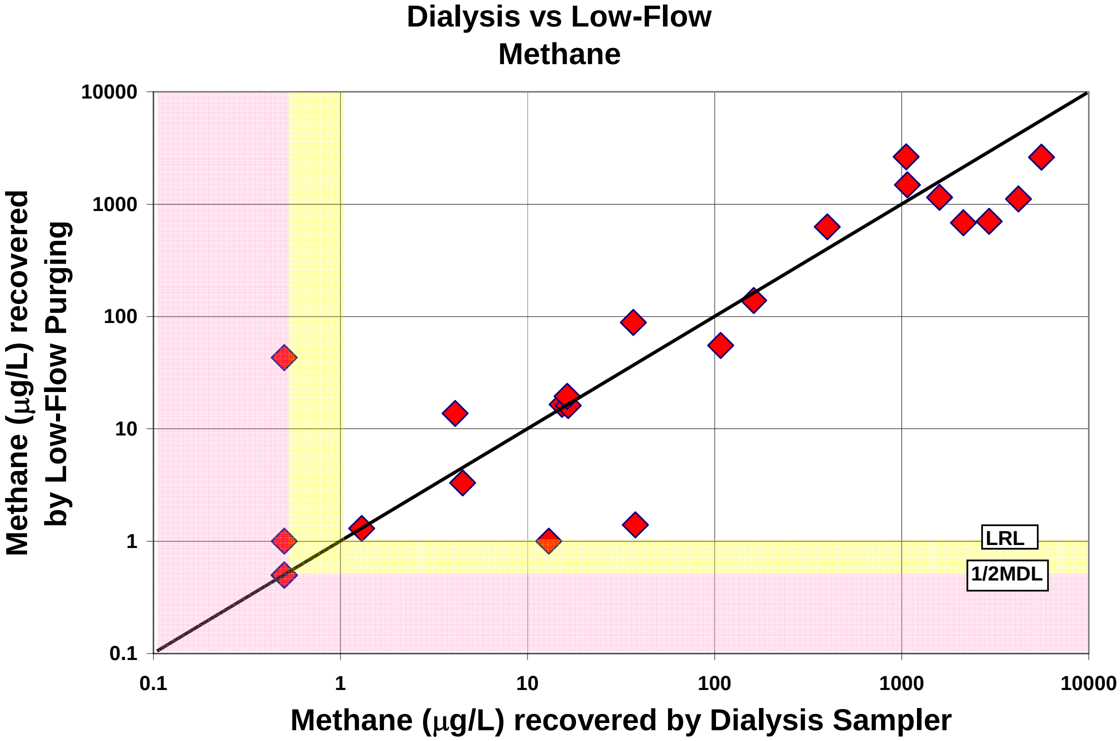


Figure A-76. Comparison of methane concentrations recovered by the dialysis sampler and low-flow purging

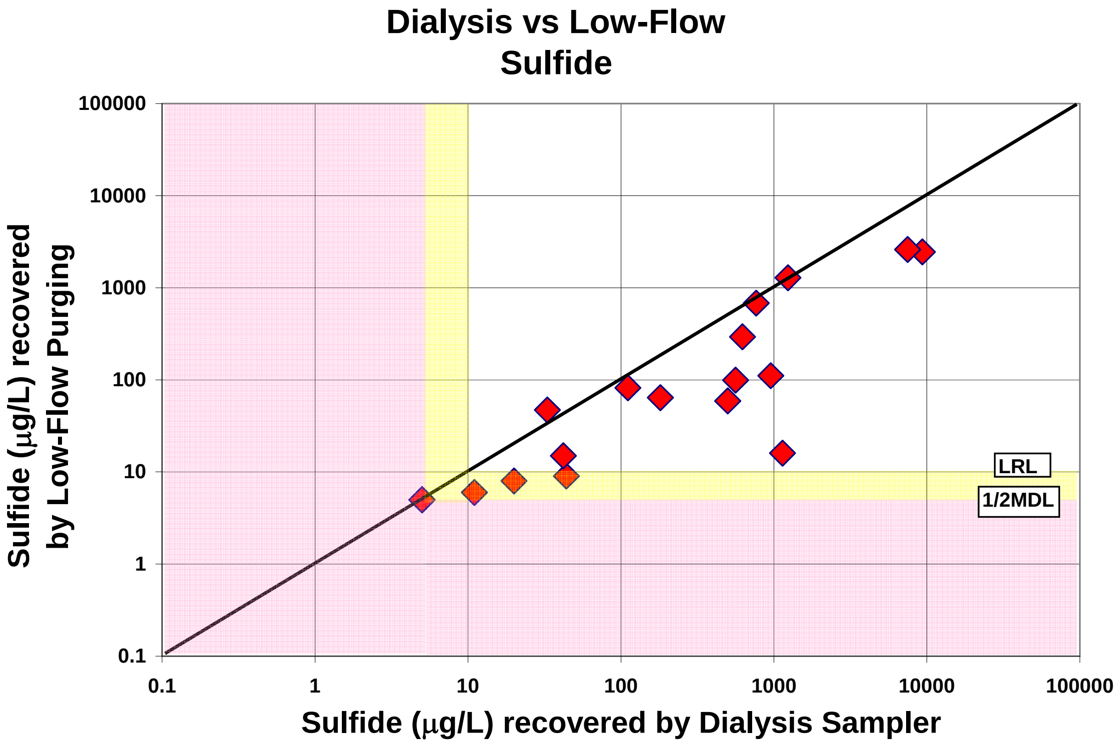


Figure A-77. Comparison of sulfide concentrations recovered by the dialysis sampler and low-flow purging

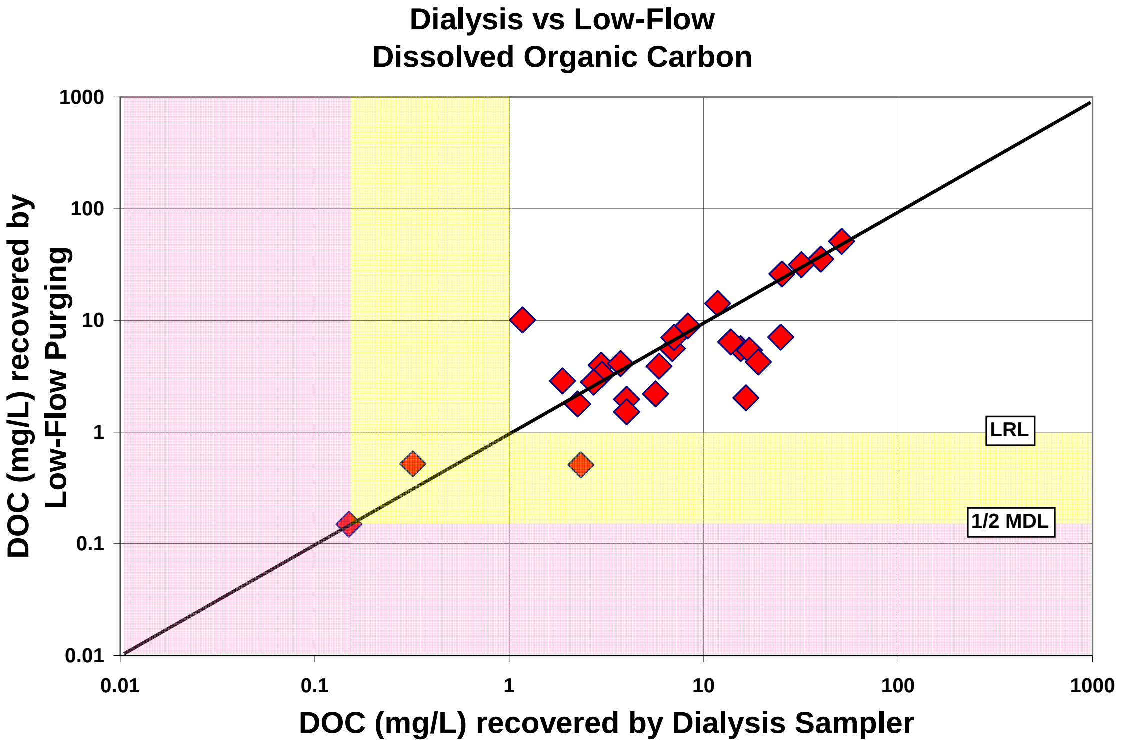


Figure A-78. Comparison of dissolved organic carbon (DOC) concentrations recovered by the dialysis sampler and low-flow purging

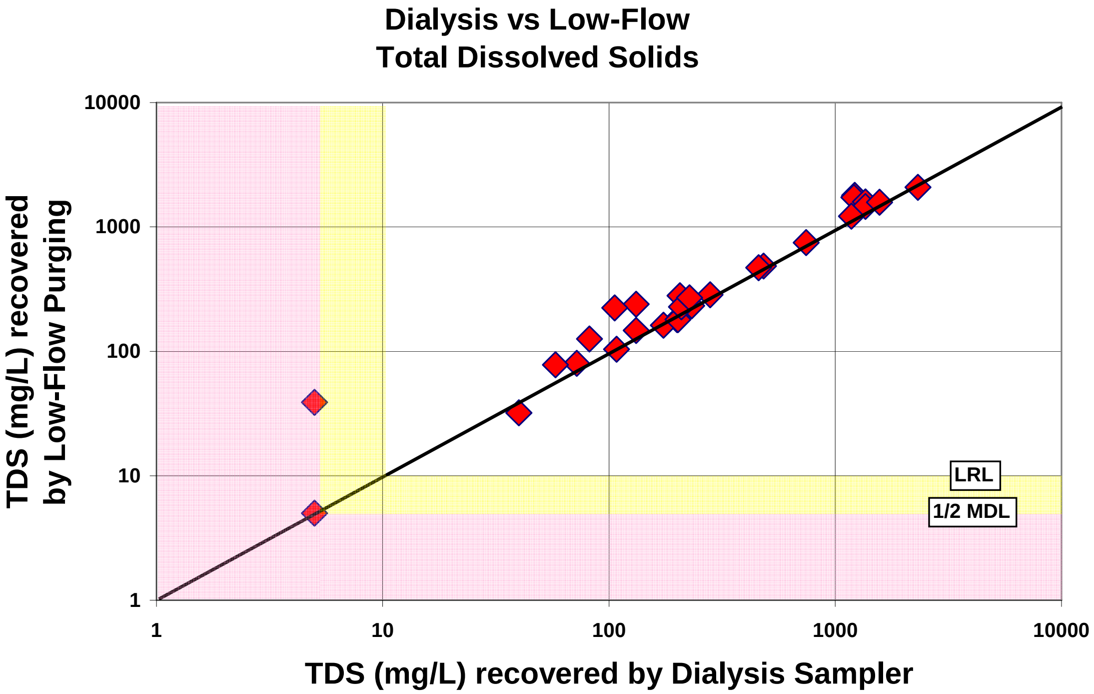


Figure A-79. Comparison of total dissolved solids (TDS) concentrations recovered by the dialysis sampler and low-flow purging