

Groundwater Sampling for 1,4-Dioxane, PFAS, and Appendix I Constituents using the Dual-Membrane Passive Diffusion Bag Sampler

Andy Alexander – BLE
Brad Varhol – EON

“Testing for Emerging Contaminants”

Andrew Alexander – BLE

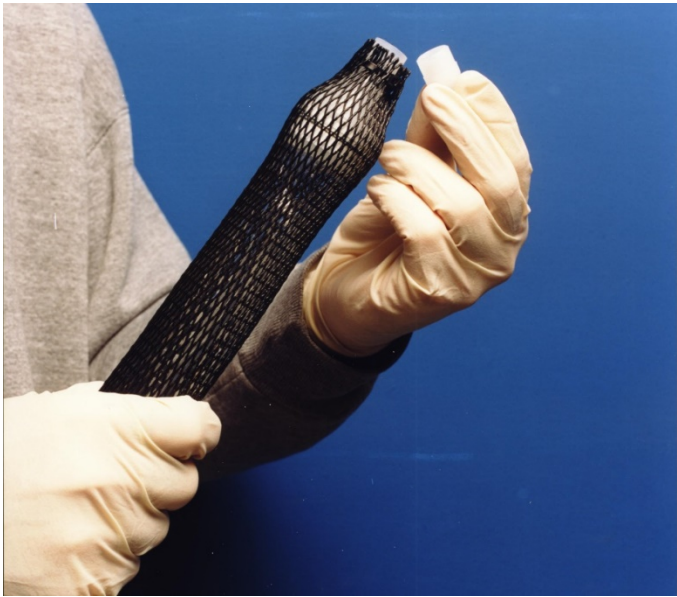
Brad Varhol – EON

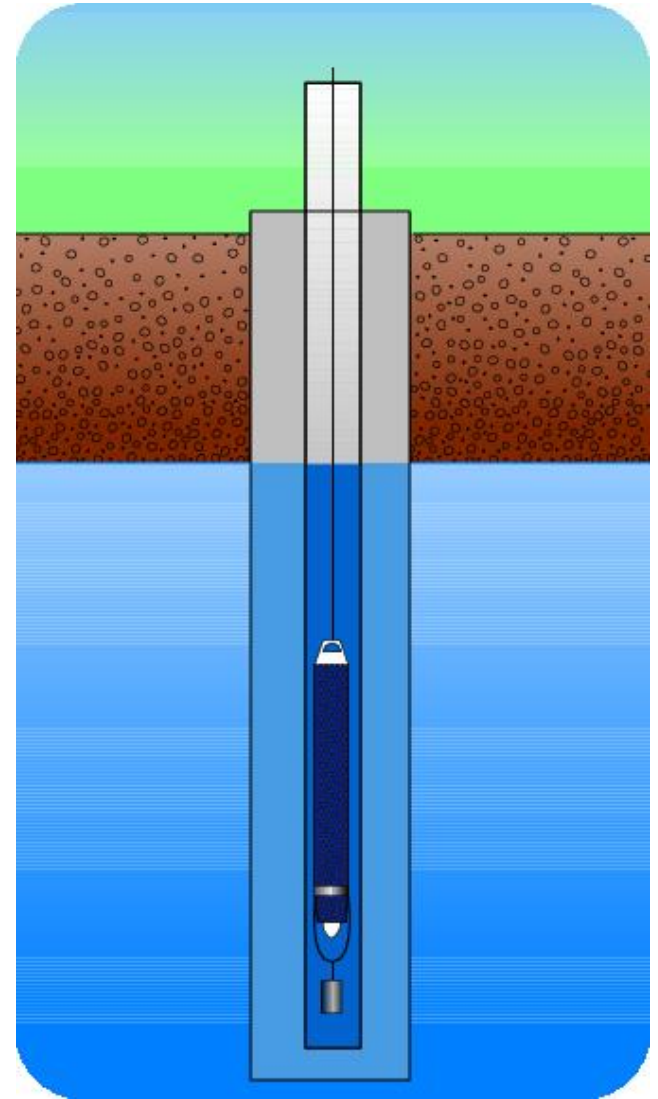
Why Diffusion Technology?

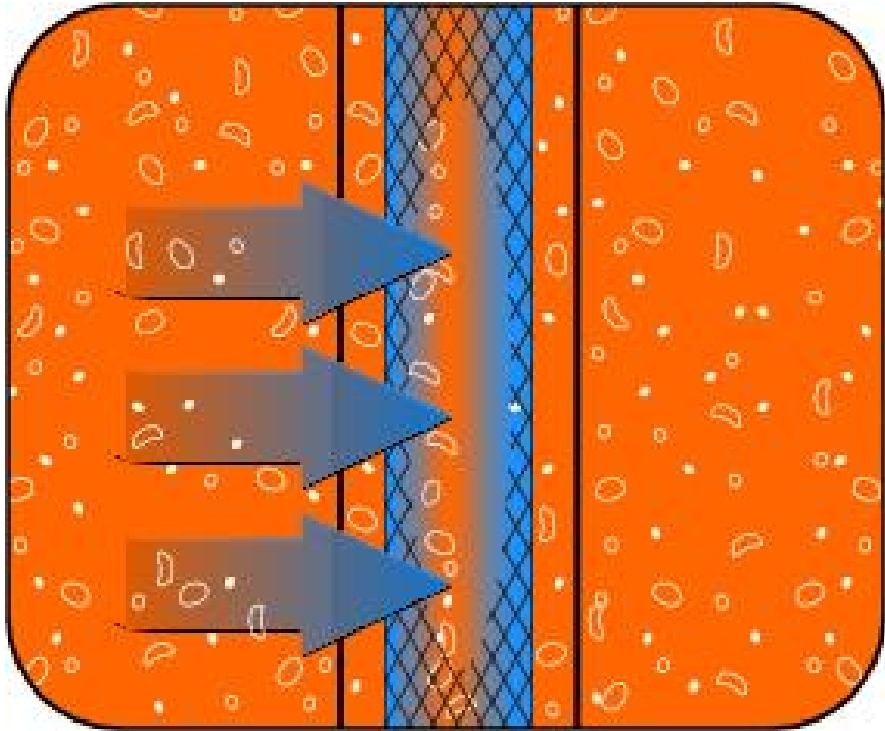
- No Purge Water Disposal
- Reduced Manpower
- Reduced PPE
- Reduced Cross Contamination
- Reduced Turbidity Issues
- Comparable (valid) Data
- Reduce Sampling Cost > 50%

What is Diffusion Sampling?

- Developed by the USGS and GE
- Polyethylene Membrane “Baggie” Sampler Filled with Clean Water
- Sampler is Submerged in Contaminated Water
- Contaminants Diffuse Across Membrane
- Sampler Retrieved and Water Analyzed







- Distilled/Pure Water
- Contaminated Water
- Contaminants

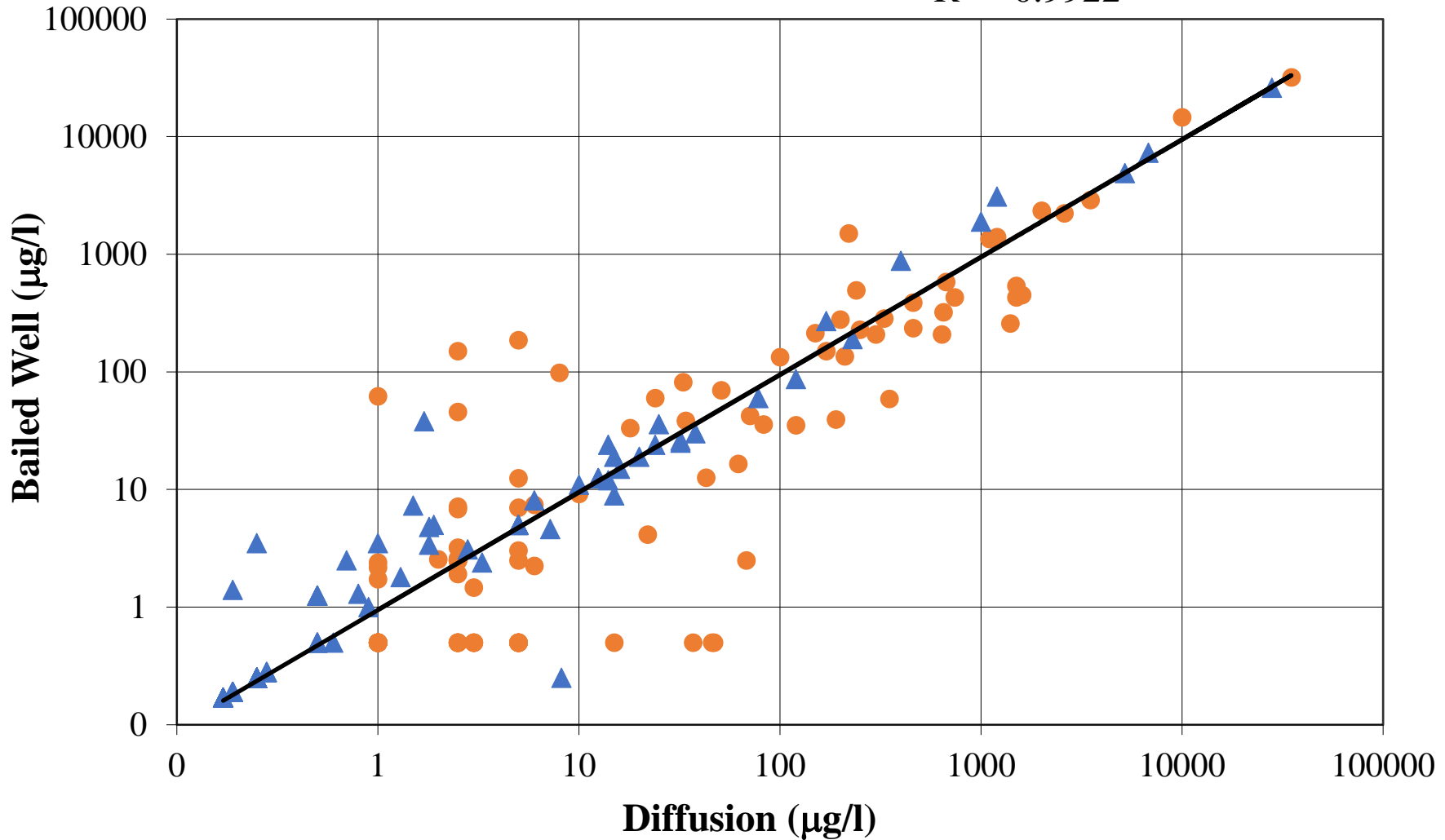


BLE 1997 to 1999 Results

Petroleum Hydrocarbons and Chlorinated Solvents

$R^2 = 0.973$

$R^2 = 0.9922$



Limitations of Single Membrane & Development of Dual Membrane

- Works Well for Most VOCs
- Not for Metals, SVOCs, 1,4-DX, PFAS
- Pores in Diffusion Membrane Too Small
- Dual Membrane Sampler Developed
- Small Pores & Large Pores



Dual Membrane Sampler Procedures



Barium Field-Scale Test

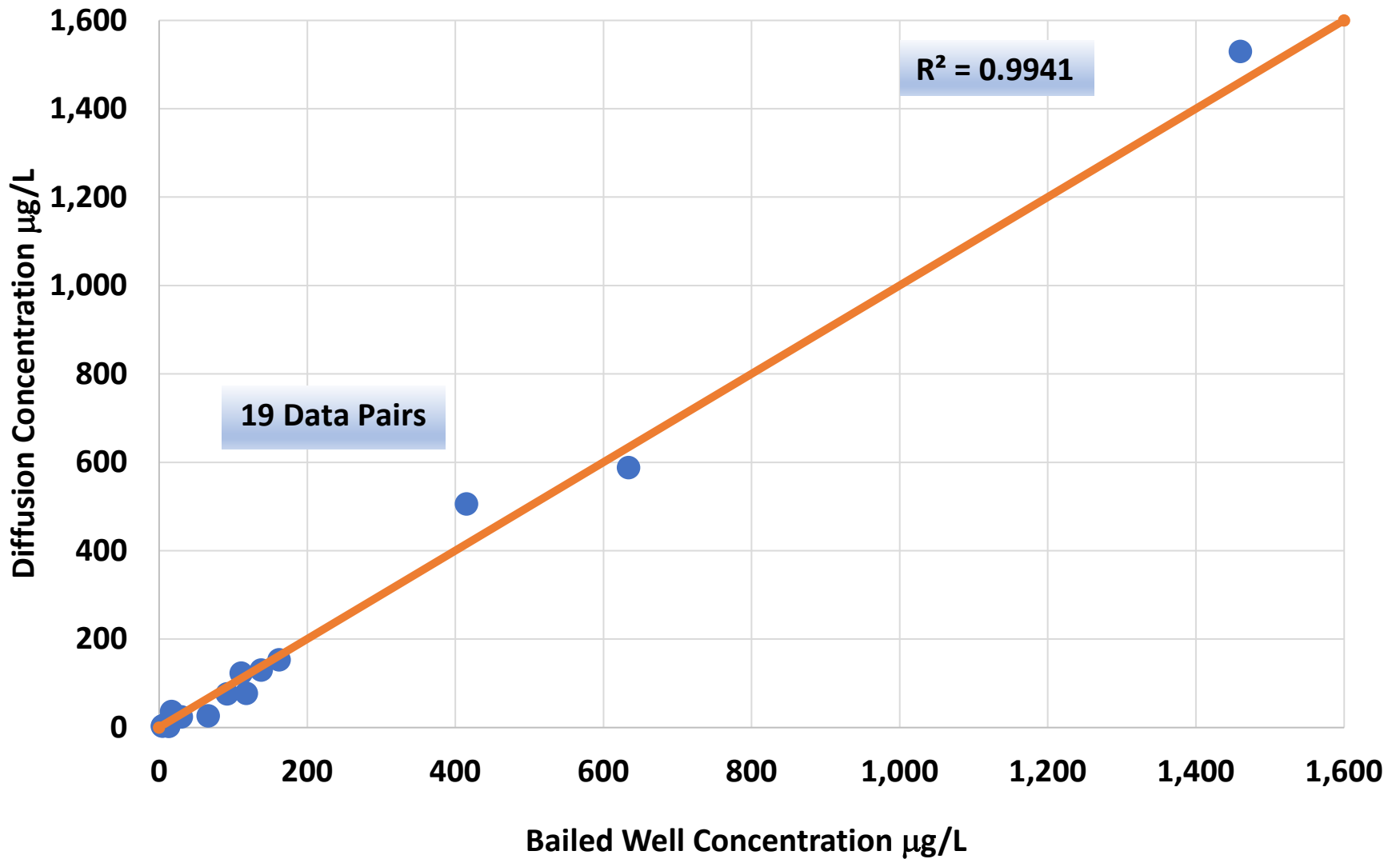
Why Barium?

- Pervasive
- Naturally Occurring
- Devoid of Trends
- Wide Range of Concentrations
- Significant Detection History

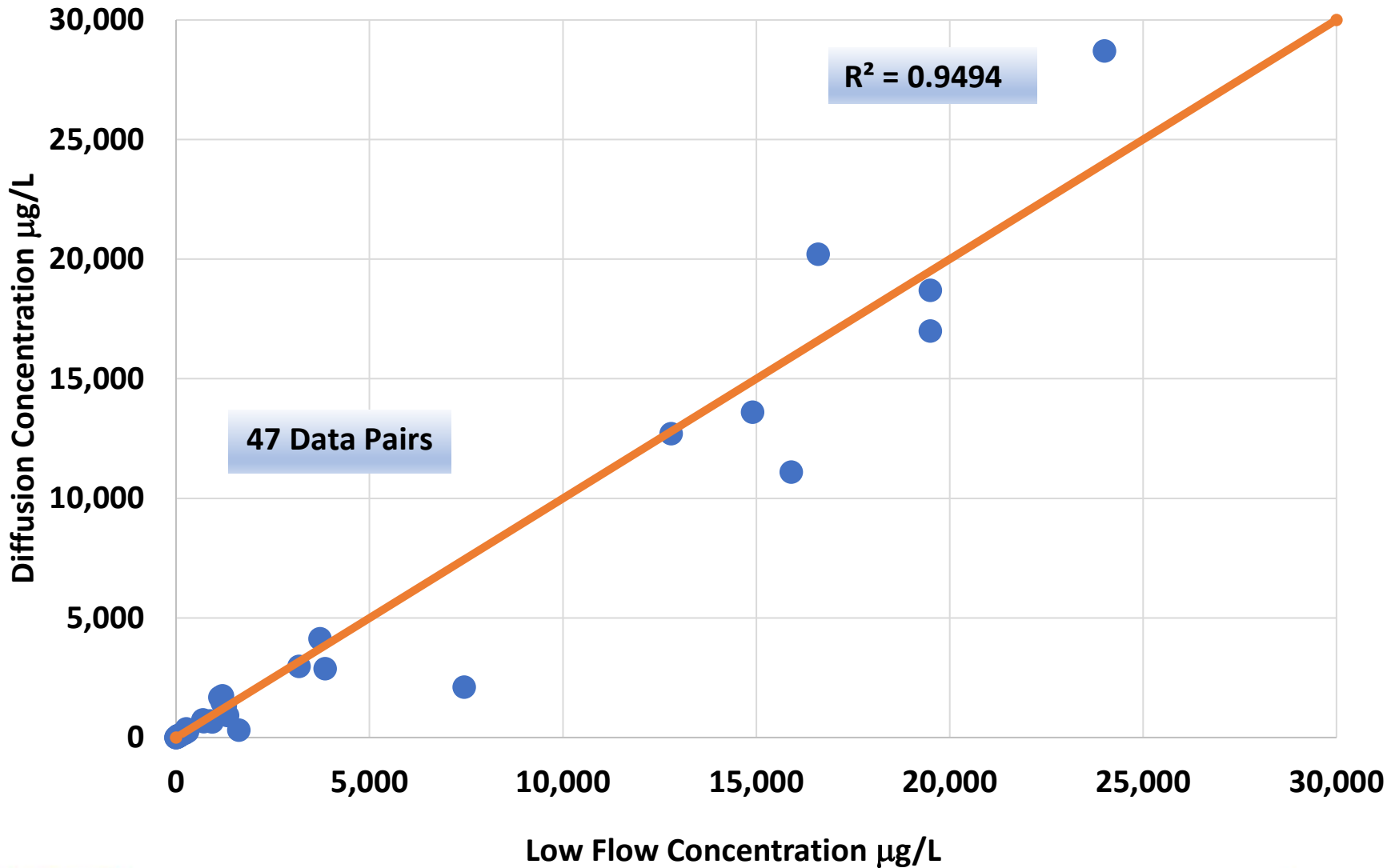
Contemporaneous Sampling

- Landfills, DoD, Industrial, Mines
- USGS, US EPA, DoD, Consultants (BLE)
- Bailing vs. Dual Membrane Diffusion
- Low Flow vs. Dual Membrane Diffusion
- Cross-Plots to Compare Methods

Barium – Bailed Well



Barium – Low Flow

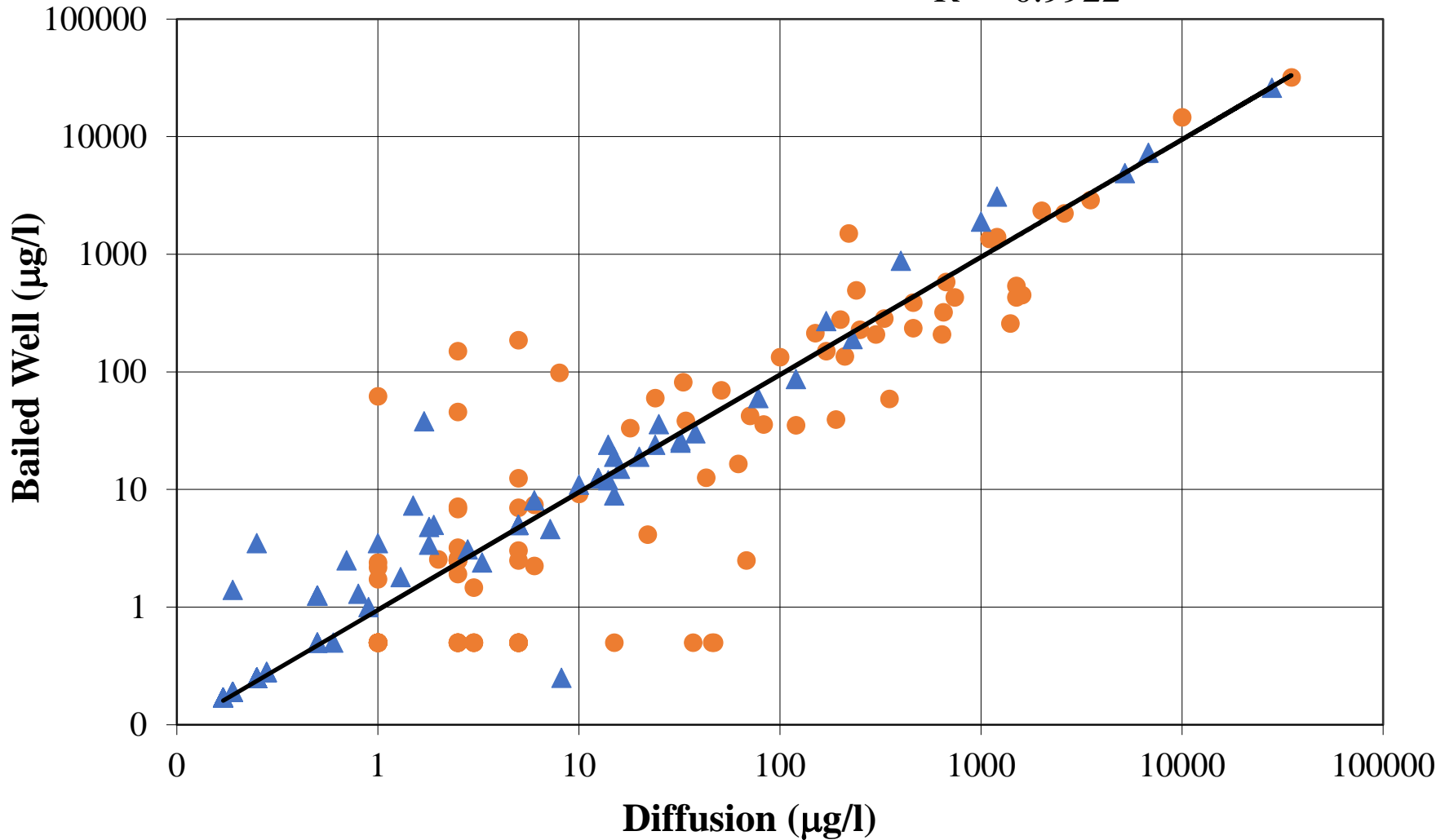


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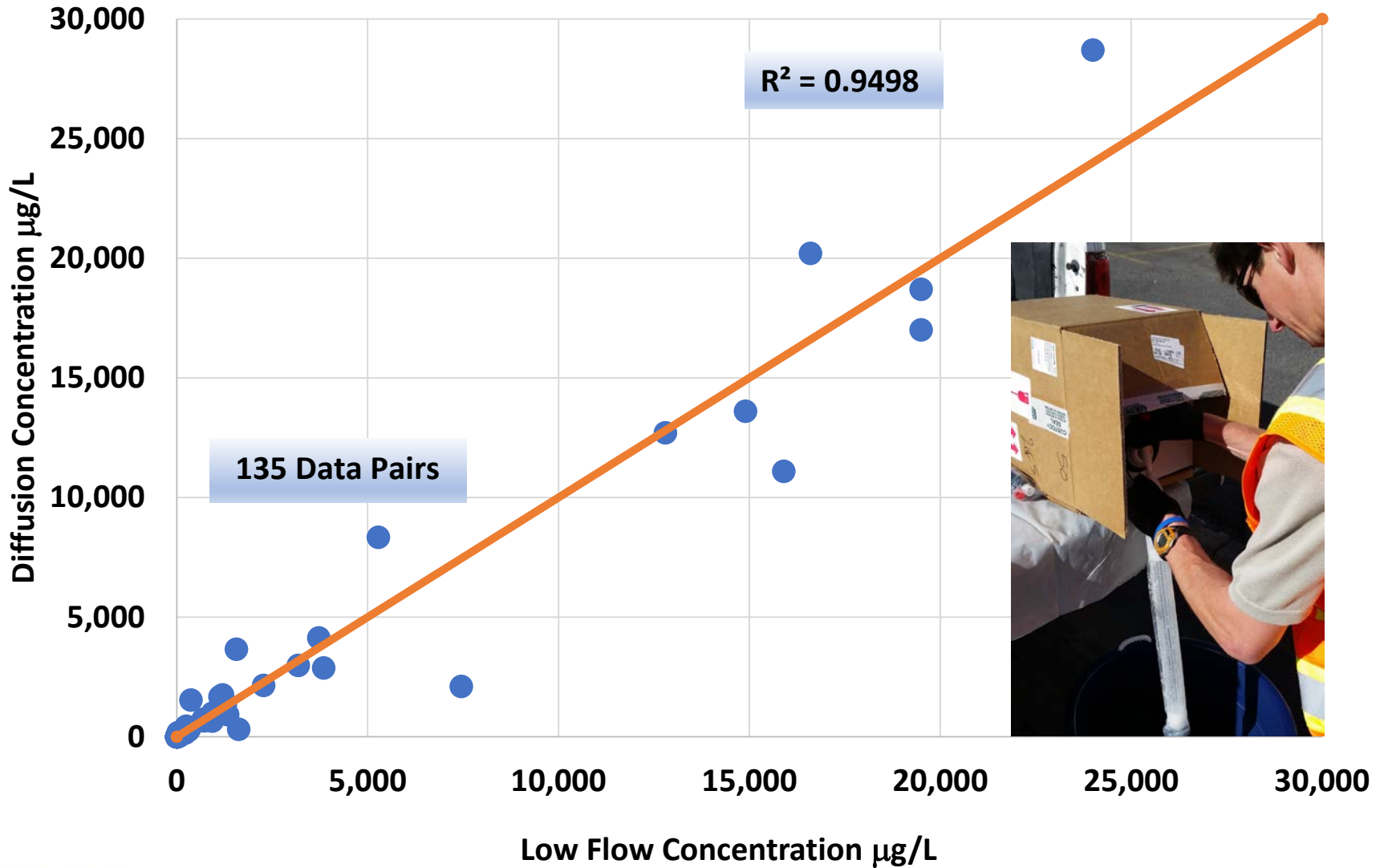
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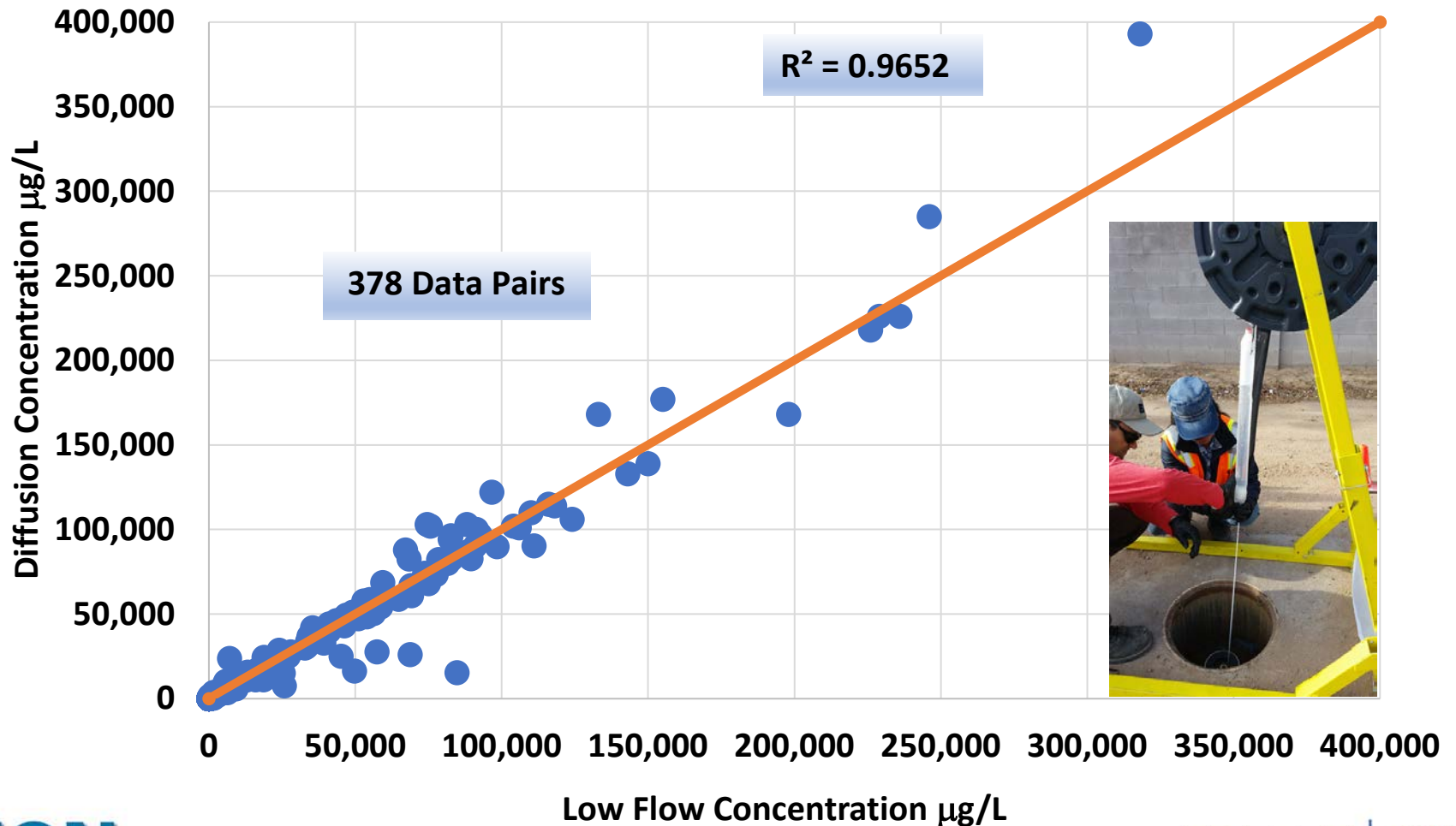
Brad Varhol – EON Products

- Field Results - Appendix I Metals, TAL Metals, Inorganics, & PFAS
- Bench Testing Program
- Bench Test Results PFAS & 1,4-Dioxane
- Diffusion Publications/Protocol
- Diffusion Use and Conclusions

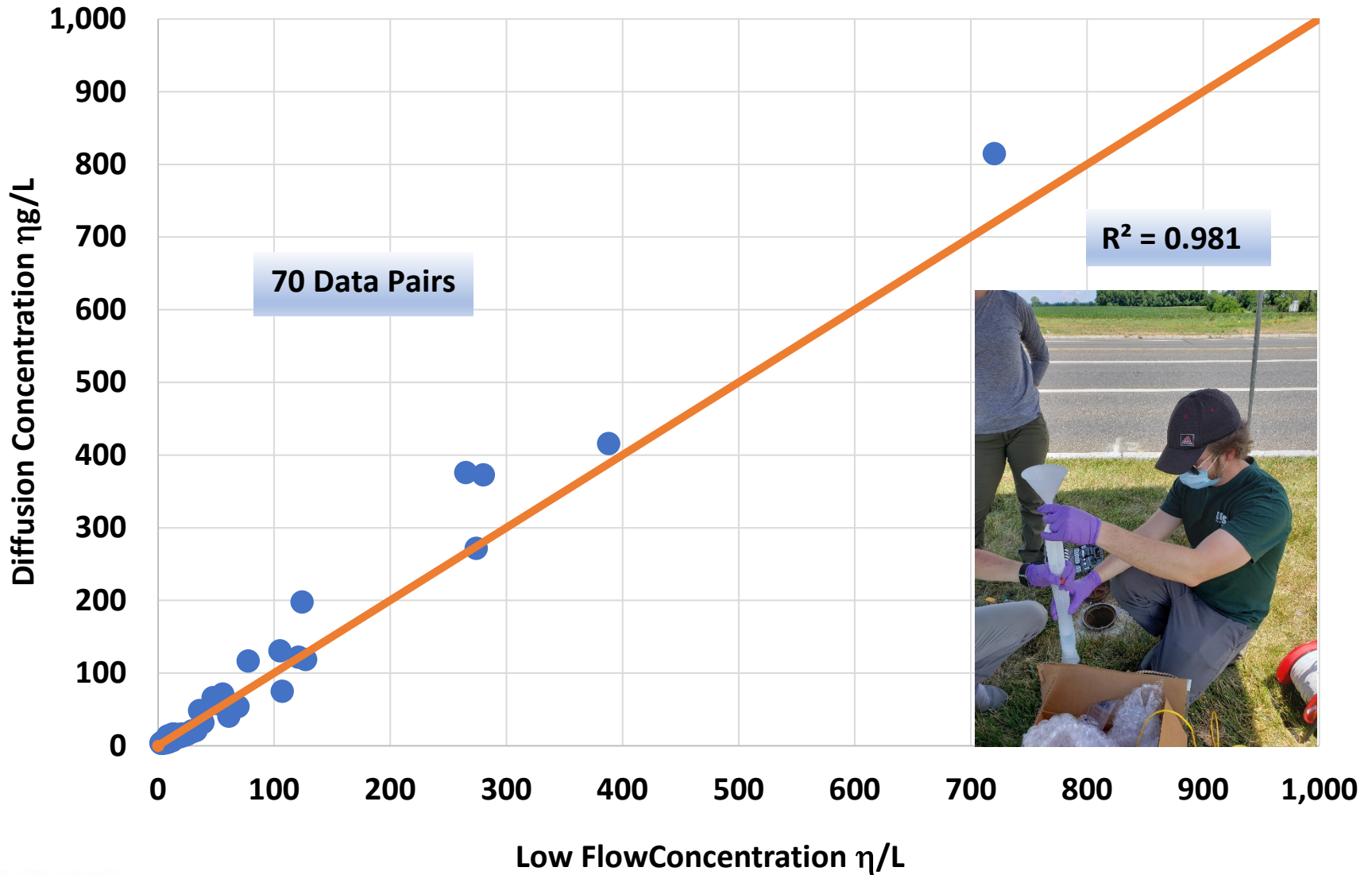
Appendix I Metals



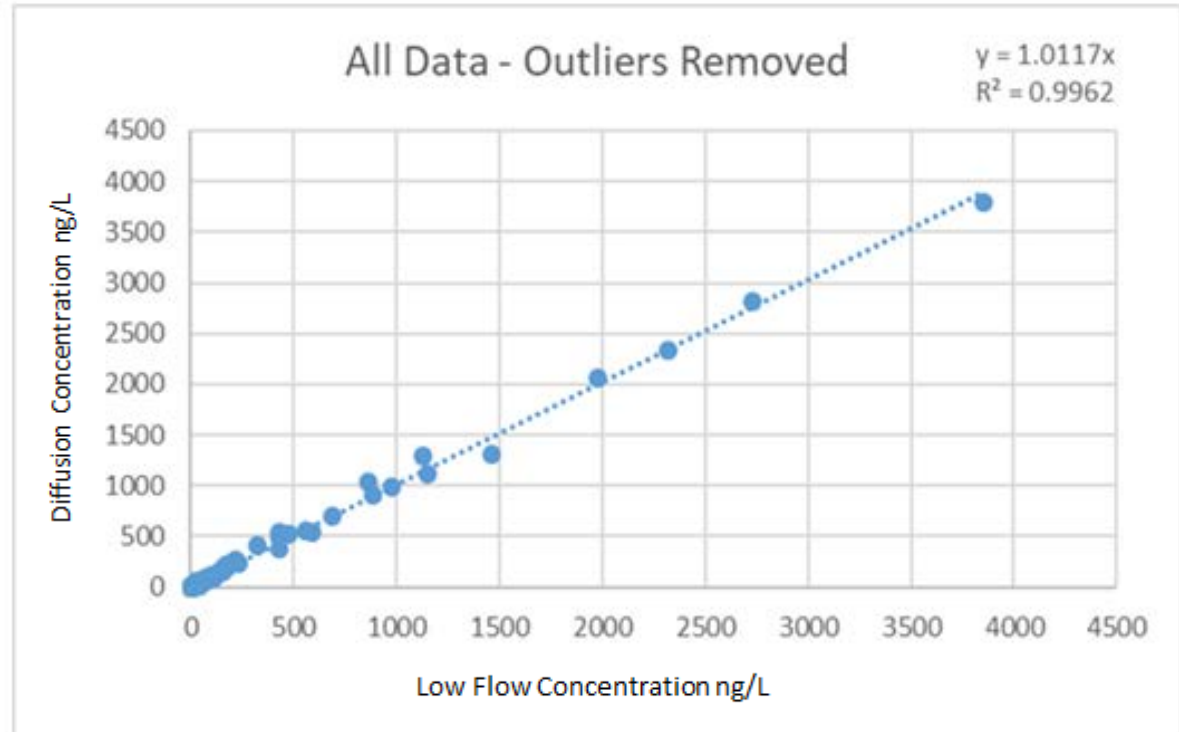
US EPA Superfund TAL Metals & Sulfate, Sulfide, & Nitrate



USGS PFAS Study



US DoD PFAS Study



Bench Test Chamber



- 8in Diameter x 8ft Tall PVC Pipe
- Filled with ~71 Liters of Water
- Spiked with Contaminants of Interest
- 3 to 9 Dual Diffusion Samplers are Installed & Left In-Place for the Test Period

Control Samples



- Collect Samples of the Chamber Water as Control Samples to Represent the Well Water Around the Sampler
- Send the Control Samples to the Lab for Analysis

Diffusion Samples



- Remove the Diffusion Samplers After Controls are Collected
- Obtain Samples from each Diffusion Sampler
- Send the Diffusion Samples to the Lab for Analysis

Compare Control to Diffusion



1. Sample the Chamber Water



2. Sample the Diffusion Water



3. Compare the Lab Results

Ba 23.00 ug/L
Cr 10.50 ug/L



Ba 22.50 ug/L
Cr 10.35 ug/L

1,4 Dioxane

Residence Time: 21 days (ug/L)

Bench Test Results	2 Control Samples		6 Diffusion Samplers	
	Analyte	Average	Range	Average
1,4 Dioxane	0.58	0.55-0.63	0.57	
1,4 Dioxane	4.20	3.60-4.20	3.90	

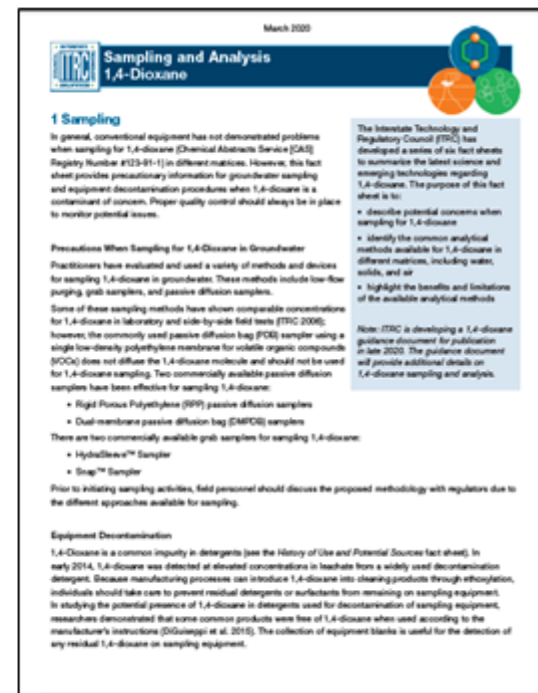
PFAS: High Concentration

Residence Time 21 Days (ng/L)			
	2 Control Samples	3 Diffusion Samples	
Bench Test Results	Mean	Range	Mean
6:2 FTS	29	28 - 30	29
PFOS	19	19 - 21	20
PFBS	36	33 - 34	34
PFHpA	27	26 - 30	28
PFHxS	28	24 - 27	26
PFHxA	30	30 - 31	31
PFOA	36	33 - 36	35
PFPeA	30	29 - 30	29

PFAS: Low
Concentration

Residence Time: 21 Days (ng/L)			
Bench Test Results	2 Control Samples	9 Diffusion Samples	
Analyte	Mean	Range	Mean
6:2 FTS	6.9	6.1 - 7.3	6.7
PFBS	8.8	8.2 - 10.0	9.0
PFHpA	7.2	6.6 - 7.4	7.0
PFHxS	7.4	7.0 - 7.5	7.3
PFHxA	8.4	8.4 - 9.2	8.8
PFOS	6.2	5.8 - 14.0	7.0
PFOA	10.0	9.7 - 11.0	10.1
PFPeA	7.4	6.7 - 8.1	7.3

Technical Review & Publications



August 2021 Publication



SPECIAL REPORT: NEXT-GEN TECHNOLOGIES

Collecting Groundwater Samples for PFAS ANALYSIS

Bench and field scale studies indicate that dual membrane passive diffusion bags may be a viable, readily available technology for the collection of groundwater samples of per- and polyfluoroalkyl substances.

By Ben Spies, P.E., KJ-SOIL, Inc.; Nathan KJ-SOIL and Steve Spies, DWR

Due to the historical use of aqueous film forming foam with per- and polyfluoroalkyl substances (PFAS), the Department of Defense (DOD) is currently managing a growing number of sites with known or suspected contamination. Groundwater monitoring for PFAS at these locations is conducted using low flow well sampling procedures, which employ portable pumps, dedicated tubing, and time sensitive quality measurements, and may require management of contamination-derived waste.

A research team comprising I.A. Engineering, Science, and Technology Inc., POC, DOD Products Inc., and the OnSite District of the U.S. Army Corps of Engineers evaluated the effectiveness of Dual Membrane Passive Diffusion Bag (DMDFB) technology to collect representative groundwater samples for PFAS analysis. Although passive sampling groundwater technologies have been

mainly used for more than 20 years at DOD sites for volatile organic compounds, metals, and inorganic anions, their reliability for monitoring PFAS in groundwater is the subject of ongoing bench scale and field study research.

CURRENT ALTERNATIVES

There are several passive samplers under evaluation for the collection of groundwater samples for PFAS analysis. These include grab samplers for instantaneous recovery, syringe-type samplers where contamination time accumulated over a known duration is used to calculate concentration, and equilibrium-type samplers that reach and maintain equilibrium with the sampled medium.

Traditional FDMs consist of semi-permeable membrane bags filled with deionized water. The bags are placed in the saturated water intervals of groundwater monitoring wells where molecules diffuse across the membrane pass into the sampler until the concentration equates between the groundwater and the inside of the sampler. The single polyethylene diffusive membrane utilized in traditional FDMs is permeable to non-polar volatile organic compounds but not to other common analytes.

It has been well documented that the collection of groundwater samples using passive samplers results in both significant cost and time savings relative to other common sampling techniques. Due to lower equipment and labor costs, passive samplers also lower the chance of cross-contamination, allow for depth-specific profiling, and generate less contamination-derived waste. This is of particular concern at PFAS sites where treatment and disposal techniques are still evolving.

FUTURE RESEARCH EFFORTS

While active well sampling methods have been used to collect samples in large quantities, these methods are not always the most efficient or cost-effective. The use of passive sampling methods for PFAS analysis is a promising alternative. The use of passive sampling methods for PFAS analysis is a promising alternative. The use of passive sampling methods for PFAS analysis is a promising alternative.

An additional research effort could be the evaluation of and the impact of monitoring equipment used at the DMDFB. During this study, a conservative period of 21 days was used to ensure the collection of samples at the bench scale. This duration for comparison purposes is used for other studies and could be modified with this sampling to provide more immediate results.

TECHNOLOGY DESCRIPTION

DMDFBs apply the same concept as FDMs, but utilize two membranes with different diffusion capabilities to expand the DMDFB materials are considered to be sources of PFAS. The upper membrane, made of polyethylene, has larger pores and is hydrophobic, this facilitates diffusion of polar and larger molecules into the sampler, such as metals, carbon, nitrate, and 1,4 dioxane. PFAS, which consists of carbon chains bonded to fluorine atoms with hydrophobic polar functional groups, are both polar and

DATA AND RESULTS

Some apparent stratification was observed in one of the two wells with tandem DMDFBs. As a result, only the lower DMDFBs were used for comparison to low flow samples for consistency. PFAS were reported in 126 pairs of the 202 pairs of results that were analyzed. All pairs with detections were used for comparison on a 1:1 regression plot, with low flow results on the x-axis and DMDFB results on the y-axis. However, only pairs with results greater than five times the reporting detection limits were used for relative percent difference analysis to eliminate artificially high results produced from comparing low values.

The greater data was used to analyze results from a set of low flow field duplicate samples collected during the field event for comparison, and for field study results less than 300 ng/L, which are more representative of values within the range of existing monitoring levels.

REAL WORLD APPLICATION

DMDFB PFAS results correlated well with the bench scale and field study samples. They were comparable to the low flow field duplicate samples, and did not produce any results that affected comparison

It has been well documented that the collection of groundwater samples using passive samplers results in both significant cost and time savings relative to other common sampling techniques, due to lower equipment and labor costs. Passive samplers also lower the chance of cross-contamination, allow for depth-specific profiling, and generate less investigation-derived waste. This is of particular concern at PFAS sites where treatment and disposal techniques are still evolving.

FIELD STUDY METHODS

Side-by-side samples were collected from 10 wells with known PFAS impacts at a DOD facility using DMDFB and low flow pump techniques. DMDFBs were filled with PFAS-free priming water, installed in one wellbore, and allowed to equilibrate for 21 days. This duration was applied based on the duration of the two duration well during bench scale (21 days and 41 days), where comparable results were observed. There is no maximum known timeframe for retrieval. A sample of the water used to fill the DMDFBs was collected to confirm it was PFAS-free. A single DMDFB was placed in the center of the water of each well, and two DMDFBs were deployed as tandem in two of the wells.

After 21 days, the DMDFBs were retrieved from each well and sampled. High-density polyethylene tubing and a submersible pump were then deployed to pump and collect another sample using low flow procedures. Low flow, DMDFB, and field quality control samples were pushed to ice and shipped to a DOD on-military analytical laboratory for analysis in accordance with Quality Systems Manual Volume 1, Table B-21 for 24 PFAS.

SPECIAL REPORT: NEXT-GEN TECHNOLOGIES

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Coming Soon....



Diffusion Sampling is Widely Used

- Over 1 Million PDBs In Use Since 1998
- Over 12,000 Dual Diffusion Since 2014
- Diffusion Sampling is Used In All 50 U.S. States & Territories and in 20+ Countries
- Used for Wide Ranging Contaminants
 - Used on Solid Waste Facilities
 - Superfund Sites
 - DoD Sites
 - Private Sites



Conclusions

- Strong Correlation Between Dual Diffusion and other Sampling Technologies
- Monthly, Quarterly, Semi-Annually, Annually
- Accurate Results for a Wide Range of Compounds & Concentrations Including; VOCs, Metals, 1,4-Dioxane, and PFAS
- Used by the USGS, US EPA, US Army Corps of Engineers, & Many Consultants

From “Why Use Diffusion...”

- No Purge Water Disposal
- Reduced Manpower
- Reduced PPE
- Reduced Cross Contamination
- Reduced Turbidity Issues
- **Reduce Sampling Costs > 50%**

Cost Comparison

FINAL

Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California

Prepared For



U.S. Army Corps of Engineers
Omaha District



and

Air Force Center for Environmental Excellence

and

Air Force Real Property Agency



U.S. AIR FORCE



Contract F44650-99-D-0005
Delivery Order DK01

October 2005

Sampling Method	Per Well, Per Event Cost
3-Volume Purge	\$310
Low-Flow Purge	\$280
Snap Sampler	\$155
RPPS	\$104
PsMS*	\$91
RCS*	\$80
PDBs	\$68
HydraSleeve	\$63

* Not Commercially Available

Questions for Andy or Brad?

