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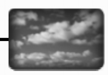

Rigid Porous Polyethylene Passive Diffusion Samplers

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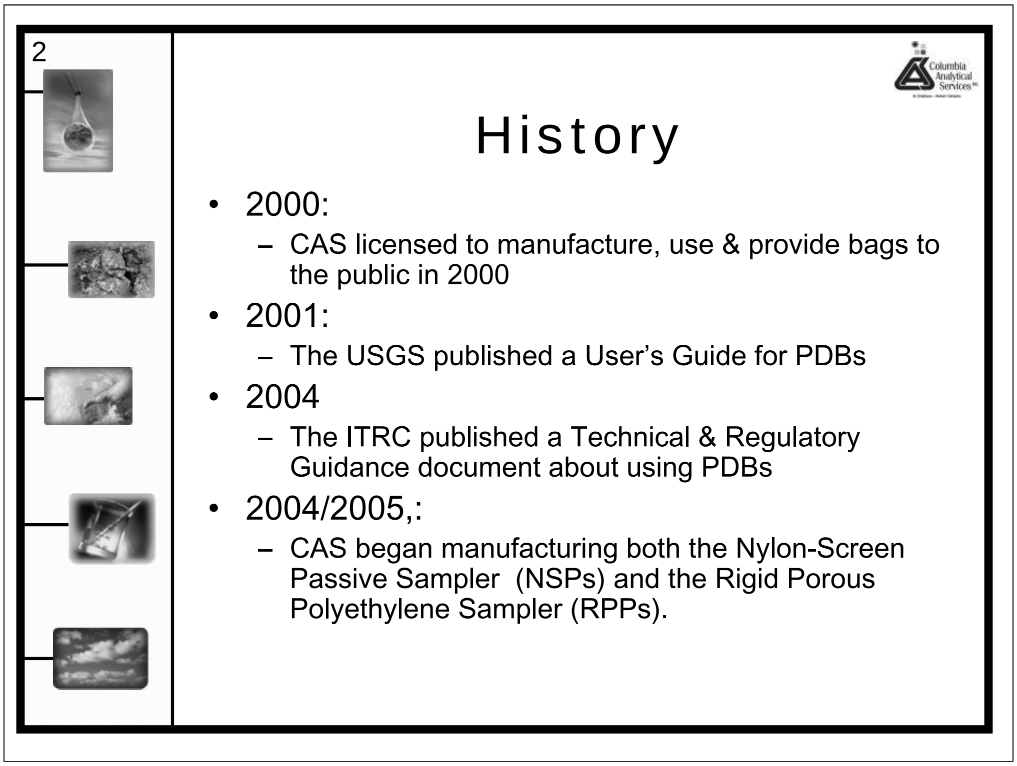
7th Passive Sampling Workshop and Symposium
Reston, VA – April 24-26, 2007



In late 1999, Columbia Analytical Services, Inc. (CAS) was asked by a client (GE, co-patent holder with Don Vroblesky of the USGS) to manufacture Passive Diffusion Bags (PDBs) One reason we were asked to make them was that the water used to fill the bags needed to be tested to ensure it was analyte-free.

CAS became licensed to manufacture, use & provide bags to the public in 2000

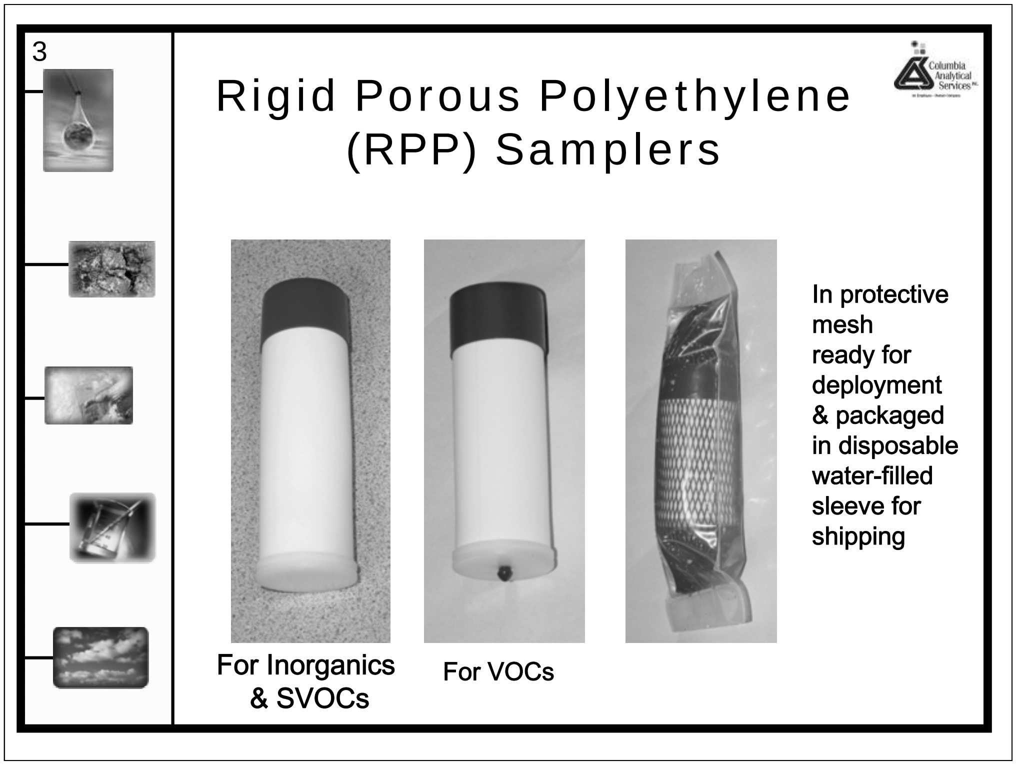
In 2001, the USGS published a User's Guide for PDBs

In 2004, The ITRC published a Technical & Regulatory Guidance document about using PDBs

The problem with PDBs limited to volatile organic compounds (VOCs). So by this time the hunt was on in earnest to identify a sampler that could do the same thing the PDBs did, but for all analytes

In late 2004 early 2005, CAS began manufacturing both the Nylon-Screen Passive Sampler (NSPs) and the Rigid Porous Polyethylene Sampler (RPPs) in conjunction with work being done by Don Vroblesky of the USGS.

> The NSPs proved to have too many technical obstacles to overcome to be commercially viable.
>
> CAS is focusing on the RPPs as a viable passive sampling device for sampling for water soluble analytes.



The RPP sampler was developed by Don Vroblesky of the USGS.

The RPP sampler is constructed of thin sheets of hard-foam-like porous polyethylene with pore size of 6-15 microns. The outside diameter is approximately 1.5 inch. They are 5 inches in length. If longer the higher head pressure in the sampler forces the water inside to “leak” out through the pores.

They are filled with de-ionized, analyte-free water, capped at one end and a Delrin plug inserted into the other end. The one in the picture on the left is equipped with a second smaller plug. This is for deployments where the analytes of interest are volatile organics. Use of the smaller plug will minimize potential loss of VOCs by any vacuum that may be created by the plug’s removal when sampling into the sample containers.

The RPP is placed in a mesh liner so that it may be attached to the deployment line with cable ties.

The picture on the right shows an RP ready for shipment. As you can see it comes in a water filled polyethylene bag. This is to ensure that the pores stay water filled. If they become blocked by air bubbles diffusion of water soluble analytes may not occur.

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How RPPs work

- By diffusion: water soluble analytes pass through the pores until equilibrium is reached with the aquifer immediately adjacent to the well screen.
- Equilibration time varies with analyte of interest,

In bench studies, equilibrium time ranged from hours to days to months, depending on the analyte. The more water soluble the analyte the quicker the equilibrium.

As a general rule of thumb it’s recommended that the majority of all passive samplers should be deployed not less than 14 days for most analytes other than VOCs and SVOCs. They can be left in the wells for a quarter, but we currently have no data for longer deployments. (Haven’t had a longer field study so far)

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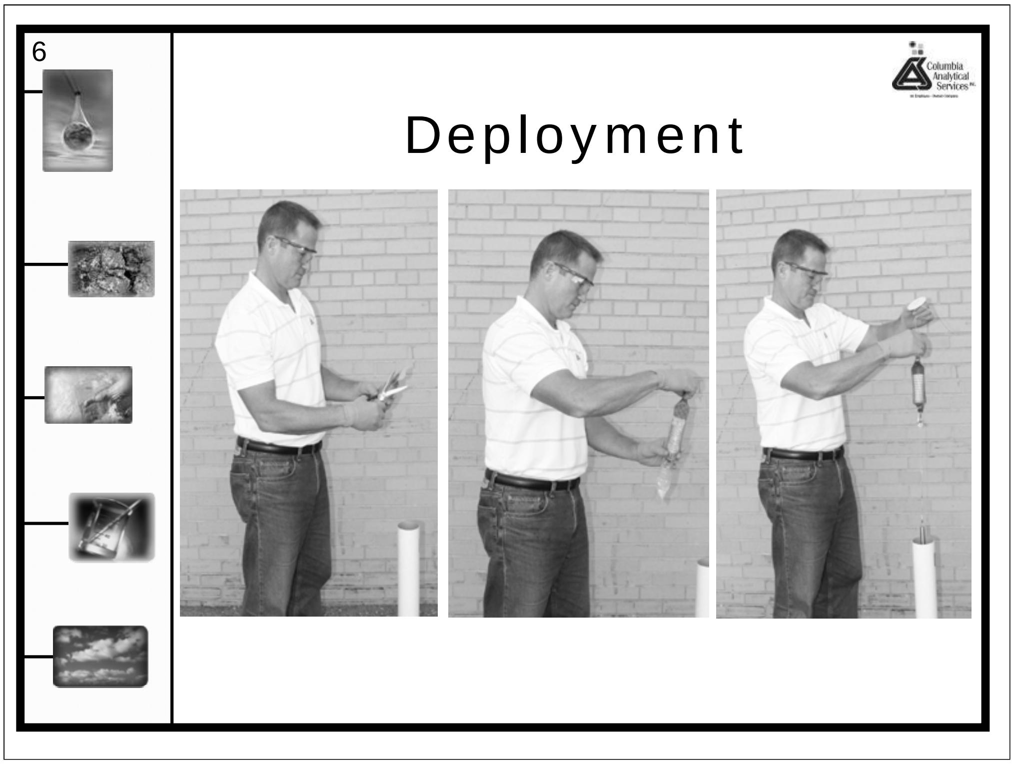
Select Equilibration Times

Analyte	Equilibration time (Days)
Dissolved Gases	14
Perchlorate, Chloride, Hexavalent Chromium, Nitrate, Sulfate, Soluble Iron	14
Methane, Ethane, Ethene (MEE)	14
Water Soluble VOAs (i.e. MTBE, MEK, Acetone, 1,4-Dioxane)	14
Water Soluble SVOCs (i.e. NDMA, Phenols)	14
Metals (Priority Pollutant List)	21 (all except silver and copper)
Explosives (i.e. HMX, TNB, RDX and TNT)	21

Please see the tables in the ITRC's Protocol Document, which will be cited at the end of this presentation, for the actual equilibration data. New analytes are being added as field studies continue. Additional field studies on water insoluble VOCs and SVOCs are needed. In bench studies, the VOCs and SVOCs with low water solubility (please see tables in Protocol document) disappeared from the carboy and were not found in the water in the samplers, leading to the conclusion they were adhering to the sampler itself. It's thought that with longer equilibration times, the sites on the sampler would become saturated and equilibration would occur, but field studies need to be done to see if this will happen.



The RPPs are shipped in a water-filled pouch to ensure that air does not enter the pores. To deploy, cut open the outer bag with the red cap pointed up and the plug end down. Slip out of the bag which you can then discard. Attach the RPP to the deployment line using cable ties. It's very important to keep the red cap up and plug down. Gently lower the sampler down the well taking care not to jerk the line or hit the slides of the well to avoid weaping from the walls of the sampler.

This deployment is in Rochester, NY.

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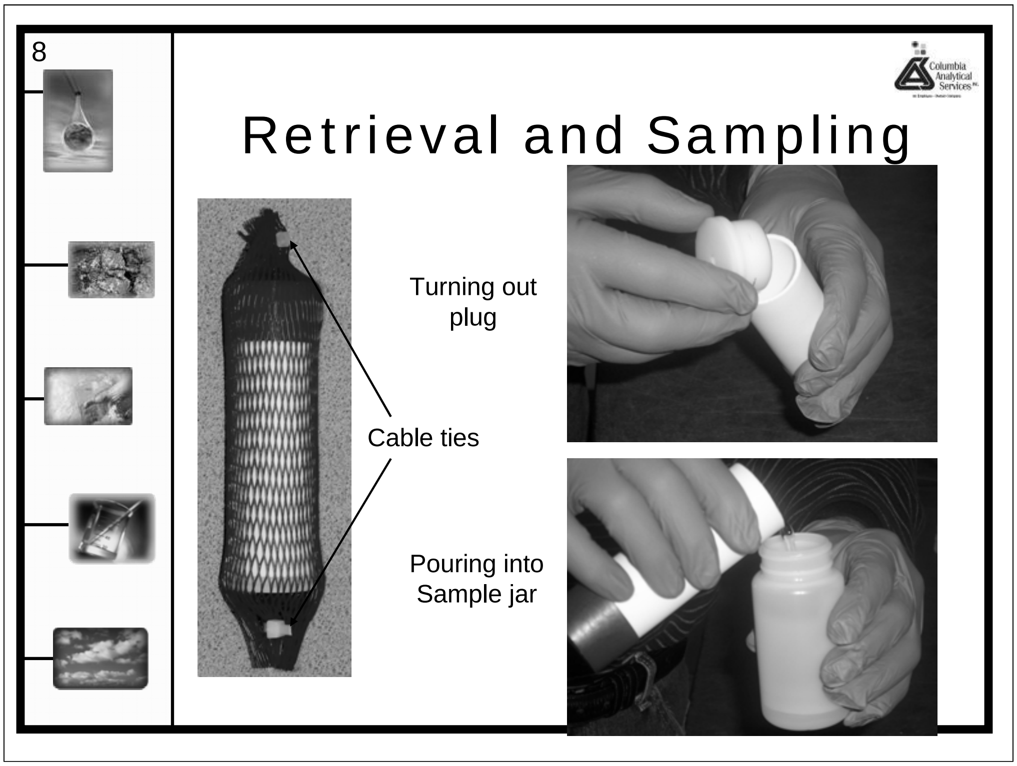
Deployment with PDB

Deployment of multiple PDBs and RPPs at a site where they were vertically profiling VOCs and perchlorate.

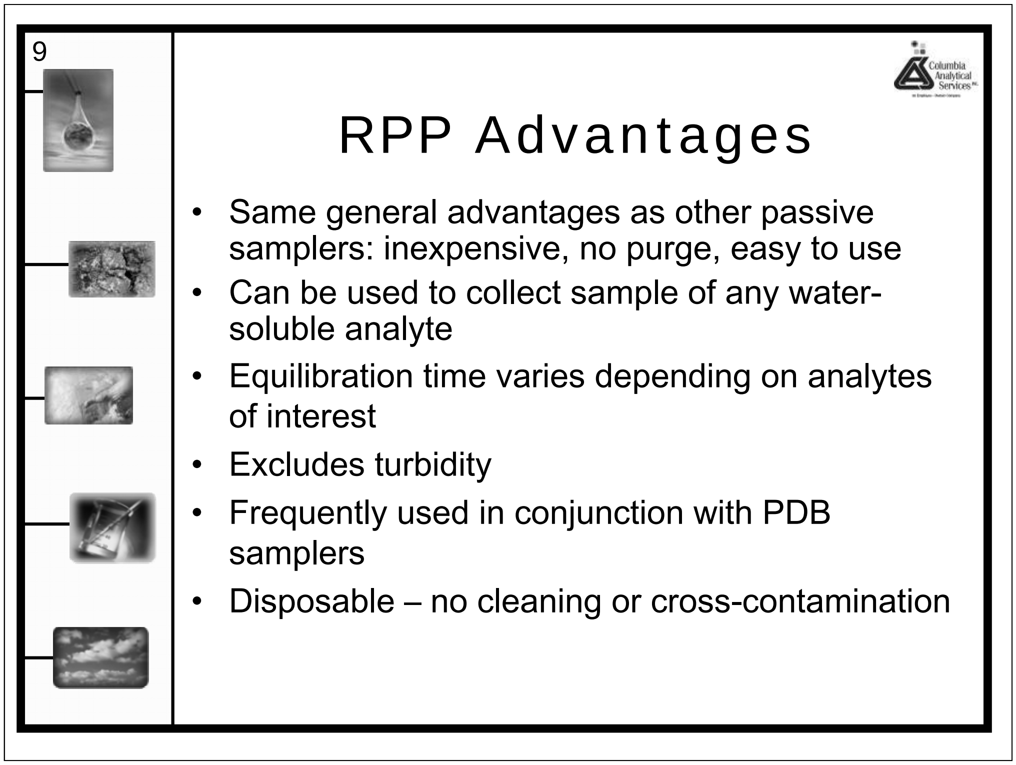
This site is in Arizona



Use the same care when retrieving the samplers as deploying them. When the RPP appears at the top of the well, cut the cable ties holding the sampler to the deployment line, keeping the sampler in the same orientation. Cut away the cable ties that hold the mesh together at the top and the bottom of the sampler. Push down on the red cap, through the mesh, until the white plug is free of the mesh still keeping it in the same orientation (cap up, plug down).

As soon as possible, pour the contents into your sample bottle. This is done by inverting the sample (plug end up), turning the plug out of the sample (do not squeeze the sampler!) and emptying the contents into your sample bottle. Cap your sample bottle and prepare for shipment to your lab and discard the sampler. Some samplers use saran wrap to surround the RPP to help minimize leaking.

If you are sampling for VOCs, the small red plug would be removed and the contents carefully poured into a VOA vial to prevent too much exposure to the surrounding air.



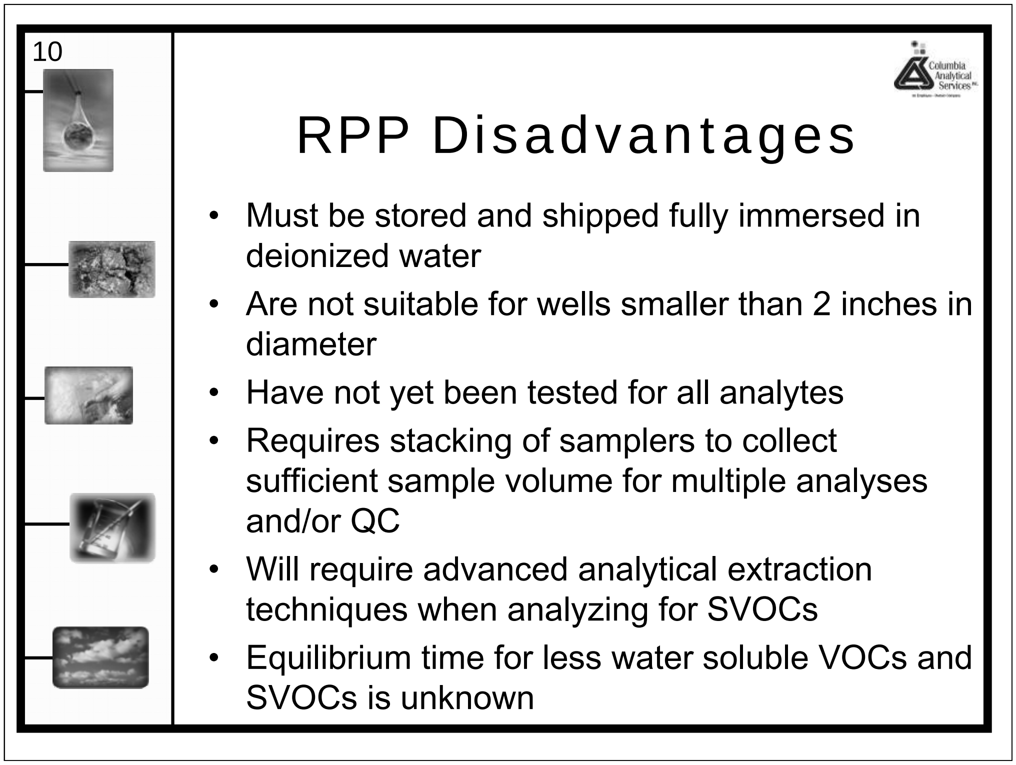
Passive sampling advantages:

•eliminate purge water collection

•are easily deployed and retrieved

•reduce field sampling costs significantly

The RPPs are frequently used with a PDB. The RPPs for inorganics and the PDB for VOAs. We have PDBs and RPP currently deployed for VOCs and 1,4-dioxane, respectively and for VOCs and perchlorate.



They must be shipped submerged in water-filled sleeves to prevent air entering the pores.

Wells must be 2 inches or more in diameter to accommodate the diameter of the RPPs.

They only hold 90-100 mLs of sample, so if additional sample volume is needed they must be stacked.

It is very important that you discuss the low sample volume with your laboratory to ensure they can meet your DQOs. (i.e., do they have SPE, LVI, LC/MS/MS capabilities?)

We don’t yet know how long it would take for VOCs and SVOCs to equilibrate. Please see the Protocol document for additional information about water solubility and equilbrium. (Table 5-5)

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Bench Studies & Deployments

Analyte	Laboratory Study	Field Study
Water Soluble VOCs	✓	
Phenols	✓	
Explosives	✓	✓
MTBE	✓	✓
Water Soluble SVOCs	✓	
NDMA	✓	✓
1,4-Dioxane	✓	✓
Metals	✓	✓
Hexavalent Chromium	✓	✓
Perchlorate	✓	✓
Chloride	✓	
Nitrate	✓	✓
Sulfate	✓	✓
Methane, Ethane, Ethene (MEE)	✓	✓
Dissolved Gasses	✓	✓

Some of these studies are detailed in the protocol document, some are confidential by client's request.

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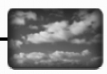

Select RPP Studies

Study	# of Wells/ Samplers	Type	Test Parameters	Results
Arizona Ground Water 2005 to present (Confidential Client)	10 wells	Field	Perchlorate	Excellent comparison with low-flow; qrtly monitoring started without additional comparison.
	10 wells	Field	Perchlorate	Results not yet reviewed with historical
	Deep well profile with 15 samplers	Field	NO_3 and As	Pending
California Ground Water – 2006 (Confidential Client)	15 wells	Field	1,4-Dioxane	Pending

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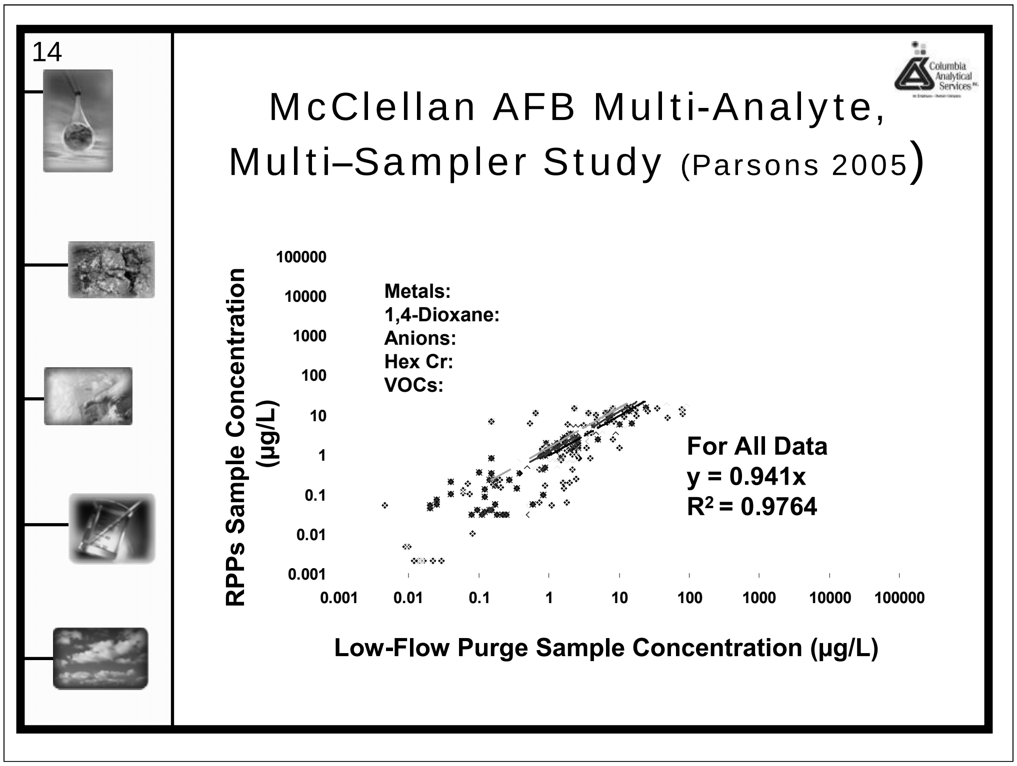
Select RPP Studies

Study	# of Wells/ Samplers	Type	Test Parameters	Results
Colorado Ground Water – 2005 to present	3-wells	Field	1,4-Dioxane	2 of 3 excellent correlation, 3rd restudied
	35 wells, qrtly	Field	1.4-Dioxane	Qtly historical correlated well, no additional comparison needed, monitoring continues with RPP
ACE CRREL - 2006 by Louise Parker	12 Samplers	Field	Explosives	Pending

There's a new pilot study in a large aquifer beginning in Texas in April using PDBs, RPP and the Gore Module (only gathers samples for organic analyte analysis).

Have another client that is going in front of their regulator to request a comparison study of the use PDBs and RRPs to the conventional low-flow they are using now for their monitoring wells.

Now lets take a look at a couple of studies



This study compared 4 passive sampling devices (PDB, Nylon-screen, regenerated-cellulose membrane sampler and the polysulfone-membrane sampler) and 2 equilbrated grab samplers (Hydrasleeve and Snap Sampler) against low-flow and conventional 3-volume well purging sampling. This graph depicts RPPs against low-flow sample results.

The authors concluded that RPPs “appear to be a technically viable method for monitoring hexavalent chromium, metals and anions. Although concentrations of VOCs and 1,4-dioxane obtained using this method are statistically similar to low-flow concentrations of these analytes, they tended to be biased low relative to concentrations obtained using the three-volume purge method.” [1]

Subsequent laboratory studies have shown that RPPs should not be used for VOCs unless further equilibration studies are completed. Subsequent field studies have shown that they may be used for 1.4-dioxane.

1. Parsons. 2005. *Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California*. Prepared for the U.S. Army Corps of Engineers Omaha District, the Air Force Center for Environmental Excellence and the Air Force Real Property Agency. 7-2.

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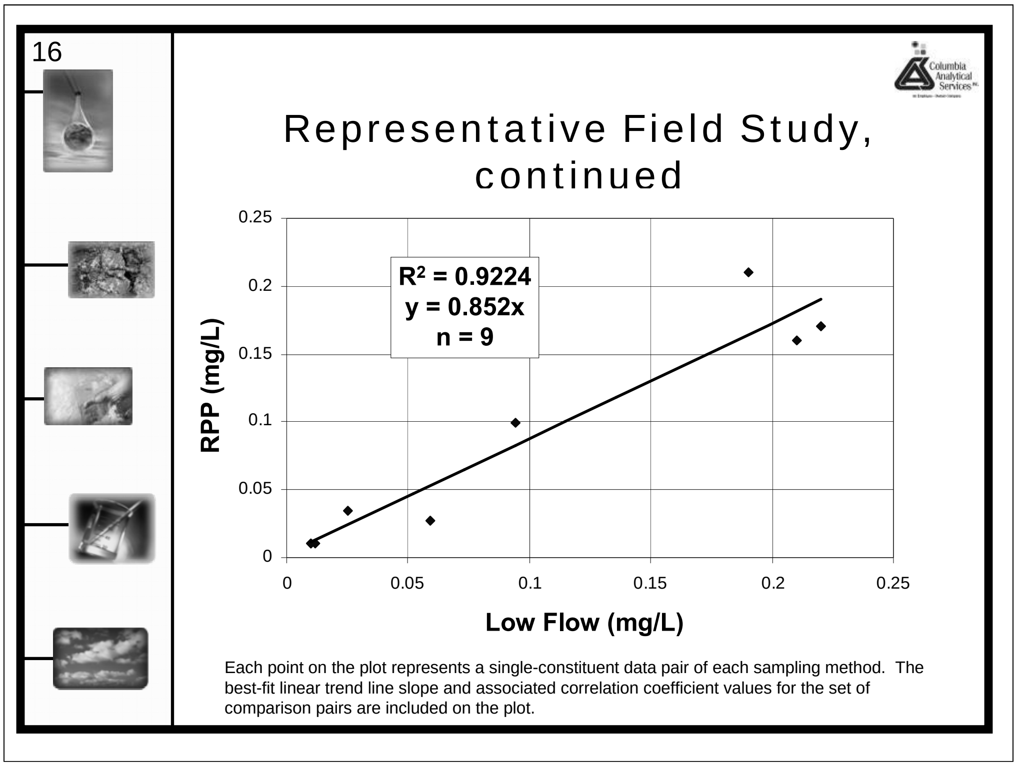
Representative Field Study

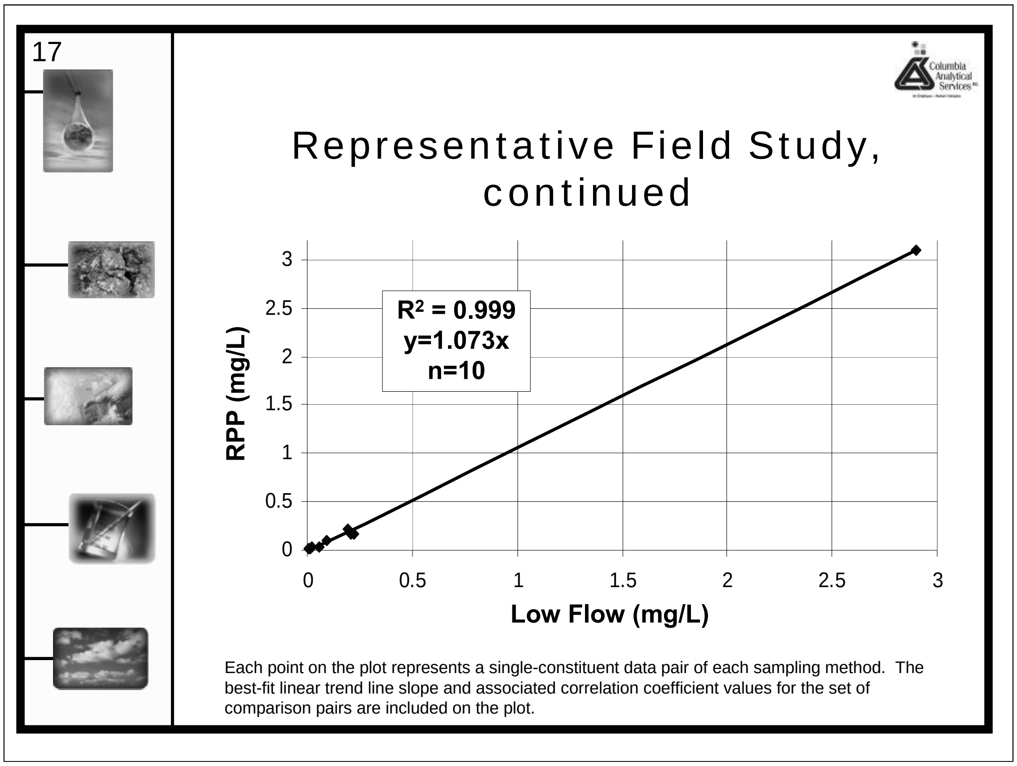
North Carolina Site

Well	Depth (ft)	1,4-Dioxane, conventional sampling (mg/L)	1,4-Dioxane, RPP sampling (mg/L	% Difference
C	49	0.01	0.01	0
J	29	0.010	0.01	0
J[1]	59	0.012	0.010	-16.7
P	58	0.21	0.16	-23.8
T	35	0.094	0.099	5.3
V	23	2.9	3.1	6.9
V[1]	65	0.22	0.17	-22.7
KK	55	0.19	0.21	10.6
LL	110	0.025	0.034	36.0
NN	105	0.059	0.027	-54.2

And here is one of the studies that showed that RPPs could be used for 1,4-dioxane. The interest in RPPs for this particular project was because a number of the wells at this site are very deep (some more than 200 feet). The depth of the well screens was below the low-flow pumps operating capability. The RPPs were tested against low-flow pumps in 10 wells at the site from 23 to 110 feet deep to see how they compared to decide whether they were a viable option for the deep wells. The concentrations of 1,4-Dioxane were low in these wells (0.010 to 0.22 mg/L) with the exception of one well, V-23, where the concentration was approximately 3 mg/L. Including the data from that well gives an R^2 of 0.999 and y=1.073x, but the representation puts the lower concentrations quite close together which makes the data points hard to see. So we've provided a graph depicting the results from the lower concentration wells (i.e without the results from V-23) and one showing the results from all wells.



Result minus well V-23



This is the graph of all wells.

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Cost Comparison

- Though not as inexpensive as the PDBs, approximately double the cost, these samplers still provide significant cost savings over conventional sampling methods.

	Cost Savings* over:	
	Conventional (3 volume purge)	Low-Flow
PDB Samplers	65%	63%
RPP Samplers	58%	55%

* Based on calculations of the average cost savings from PDB projects over the last 4 years if RPPs replaced PDBs with no differences in analytical costs or number of samplers used.

One question we're asked frequently is "What are the Cost savings?" It's a very hard question to answer unless we know a lot more about the situation.

This does not take into account differences in analytical costs or the number of samplers used. For instance, PDBs only can be used for VOCs. RPPs can be used for other analytes, the analyses for which may cost less or more. If multiple tests are needed, RPPs may need to be stacked for additional volume, which would increase RPP costs.

However, in all cases so far RPPs have saved our clients anywhere from 45-75% of their field costs.

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Summary

RPP Applications

- Inorganic anions
- MNA parameters (MEE, dissolved gases, etc.)
- Metals, with possible exceptions of Cu and Ag
- Hexavalent chromium
- Perchlorate
- Explosives
- Selected water soluble VOCs (i.e. MTBE, 1.4-Dioxane, etc.) and SVOCs (i.e. Phenols, NDMA, etc.)

Others…stay tuned

RPPS may be used to sample for most inorganics, but further studies are needed to determine suitability for some organics, especially less water soluble VOCs and SVOCs.

Studies are on-going

Summary

- Can be used in deep wells
- Can be used in conjunction with PDBs
- Inexpensive, disposable sampler
  - No decontamination required

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ITRC's Passive Sampling Team

- Formed in 2000
- Initial goal: develop guidelines for use of the polyethylene diffusion bag sampler (PDBs) for collection of groundwater samples for VOC analysis
- Overall goal: provide guidance, provide resources (http://diffusionsampler.itrcweb.org) and promote regulatory adoption of passive sampling techniques
  - This led to publication of : *ITRC Protocols for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater* (DSP-5, 2007)

Steve – you can dump this slide if you want. I usually leave it in so I have the information if someone wants it.

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Free On-line Training from ITRC

- ITRC Internet-based training course "Protocol for Use of Five Passive Samplers"
  - June 7 (Thursday), 11:00 a.m. - 1:15 p.m. EASTERN
  - September 11 (Tuesday), 2:00 p.m. - 4:15 p.m. EASTERN
  - November 29 (Thursday), 11:00 a.m. - 1:15 p.m. EASTERN
- Course registration opens four to six weeks prior to the course offering
  - www.itrcweb.org under "Internet-based training"
  - or directly at www.clu-in.org/studio/
- Associated guidance documents: Available from www.itrcweb.org under "Guidance Documents"

NOTE: Course dates and times are subject to change.
Please check www.itrcweb.org for the latest schedule

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Questions?

Thank you for your attention

Full copy of the Protocol of Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater (DSP 5, 2007) may be found on the ITRC's website: www.itrcweb.com