Results from Recent Studies Evaluating the Snap Sampler







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What is the Snap Sampler?

- Equilibrated-grab sampler (ITRC 2006, 2007)
 - Grab sampler left in well for equilibration period prior to sample collection
 - Allows well to recover from disturbance caused by placing sampler in well
 - 2 week minimum (ITRC 2001, 2004, 2006, 2007)
 - Gives materials in sampler time to equilibrate with analytes in well water
- Collects sample from discrete interval in well screen
- Collects whole water samples
- Collects samples in "real time"



Components of the Snap Sampler

- Sampler body with trigger mechanism
- Snap Sampler bottles
 - Openings on 2 ends with spring-activated caps
 - Teflon caps
 - Teflon-coated spring
 - 40-mL VOA vials
 - 250-mL PP bottles
- Trigger line
 - Teflon-coated wireline cable inside PE tube
- Docking station
 - Holds sampler in place







Deploying the Snap Sampler

- Place bottle in sampler body
- Place end caps (of bottles) in open position
- Cock sampler & attach trigger line to sampler
 Can deploy up to 4 samplers on single trigger line
- Lower sampler by trigger line to sampling depth & attach to docking station
- Leave sampler in well for next sampling event
 - Quarterly, semi-annual, or annual sampling event
 - 2 week minimum equilibration time (ITRC)

Advantages

- Sample is sealed under *in-situ* conditions*
- No chance for interaction with water column as sample is brought to surface
- No sample transfer at well head required*
 - * Can be important for VOCs, gases, metals subject to oxidation/precipitation reactions





Experimental Approach Conduct laboratory and field studies to evaluate the performance of these samplers

Lab Studies- Compare concentrations of analytes in samples taken with sampler with control samples taken from a standpipe containing a test solution with known concentrations of analytes

Field Studies- Compare concentrations of analytes in samples taken with sampler with samples taken using EPA's low-flow purging & sampling protocol

Lab Studies Protocol

- Used a 8-in. ID, 8-ft. tall PVC standpipe
- Test Solution contained a suite of either VOCs, explosives, or inorganics
- Samplers deployed at same depth as sampling spigot
- Samplers left to equilibrate with test solution, typically 24 hours
- Control samples collected from spigot
- Alternate sampling order between samplers & control samples



Standpipe Study – Six Explosives (Parker and Mulherin 2007)

Test solution: HMX, RDX, 2,4,6-TNT, 1,3,5-TNB, 1,3-DNB, & 2,4-DNT Deployed 5 samplers (125-mL glass bottles) in standpipe Equilibration time = 24 hr Analyses: next day by RP-HPLC (Walsh & Ranney 1999,

	Mean Conc. (mg/L)			
	<u>Control</u>	<u>Snap S</u>		
HMX	0.682	0.704		
TNB	1.94	1.94		
RDX	5.93	5.92		
TNT	1.40	1.39		



No significant differences for any of 6 explosives at 95% confidence level using a paired t-test Holding-time Study – Explosives (Parker & Mulherin 2007)
Previous samples analyzed almost immediately
Objective : Determine if analyte recovery the same for samples held maximum holding time
Similar protocol except that samplers held for max. holding time prior to analyses (i.e., 7 days with no preservative)

	Percent recovery
	of Snap Sampler
TNB	99.8
RDX	99.3
DNB	99.4
TNT	99.4
NB	99.1
DNT	100



Essentially 100% recovery with 24-hr equilibration time

Standpipe Study – VOCS (Parker & Mulherin 2007) Deployed 6 samplers (40-mL VOA vials) Equilibration time = 24 hr Analyses: RP-HPLC (Parker & Ranney 1998)

	Mean Conc. (mg/L)			
	<u>Control</u>	Snap Sampler		
t-DCE	0.940	0.930		
BENZ	0.994	0.989		
TCE	0.970	0.965		
TOL	0.970	0.962		
o-DCB	1.02	1.01		
<i>m</i> -XYL	0.958	0.947		
PCE	0.906	0.895		



No significant differences for any of 7 VOCs at 95% confidence level using a paired t-test

VOCs Holding-Time Study (Parker & Mulherin 2007)

Deployed 5 samplers

Samples acid preserved & held for max. holding time

Mean percent recovery	(14 days)
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quilibration time =	<u>1 day</u>	<u>3 days</u>
<i>t</i> -DCE	95.4*	101.5
BENZ	99.5	102.9*
TCE	94.1*	100.5
TOL	94.1*	96.5*
o-DCB	91.1*	98.0*
<i>m</i> -XYL	64*	77*
PCE	84*	96.2*

*Values were significantly different from control values

Conclusions: After 3 days equilibration, differences < 5% except for *m*-xylene

~3 days equilibration is needed for VOCs

- Similar protocol to previous studies – Used 125-mL PP Snap Sampler bottles
- Deployed 5 trigger lines with 3 samplers per line
- Test solution contained suite of metals
 - As, Cd, Cr, Pb, Ni, & Zn
 - Concentrations ranged from ~200 to 400 mg/L
- Recovered one set of samples after 24, 48, & 72 hr
- Analyses by ICP
 – Atomic Emission Spectroscopy
 - ERDC-EL using EPA method 6010B



Percent recovery of metals¹ for different equilibration times

Analyte	<u>24 hr</u>	<u>48 hr</u>	<u>72 hr</u>	
As	100.0	99.6	100.1	
Cd	100.7	98.0	100.5	Good recovery
Cr	98.5	98.4	99.5	
Pb	95.1	94.3	94.4	
Ni	94.5	91.7	91.9	Not as good
Zn	78.3	80.9	79.6	

¹ (Snap Sampler conc./ Control conc.) * 100

Percent recovery of metals¹ for different equilibration times

Analyte	<u>24 hr</u>	<u>48 hr</u>	<u>72 hr</u>	<u>50 day</u>
As	100.0	99.6	100.1	100.9
Cd	100.7	98.0	100.5	100.7
Cr	98.5	98.4	99.5	100.2
Pb	95.1	94.3	94.4	89.5
Ni	94.5	91.7	91.9	93.4
Zn	78.3	80.9	79.6	69.2

¹ (Snap Sampler conc./ Control conc.) * 100

Mean conc.	(mg/L)
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	Ars	enic	Le	ead	Nie	ckel	Zi	nc
<u>Time</u>	<u>C</u>	Snap	<u>C</u>	Snap	C	<u>Snap</u>	C	<u>Snap</u>
24 hr	195	195	197	188	373	353	438	343
48 hr	195	194	198	187	387	355	428	346
72 hr	194	194	199	188	398	365	441	351
50 day	188	190	231	207	478	447	1031	714

% increase in controls from day 1 17% 28% 135%

C = Control sample





Conclusions

- Lower concentrations of Pb, Ni, & Zn in Snap Sampler samples due to leaching of metals from spigot into control samples
- Snap Sampler able to recover representative concentrations of As, Cd, & Cr
- Need confirmation for wider range of inorganics

Standpipe Study – Cations & Anions

- Similar protocol to previous study – Used replacement HDPE spigot
- Deployed 3 trigger lines with 2 samplers per line
- Test solution contained suite of cations and anions
 - Ca, K, Mg, Mn, & Na
 - Bromide, chloride, nitrate, perchlorate, & sulfate
 - Concentrations ranged from 10 to 80 mg/L
- Recovered one set of samples after 24, 48, & 72 hr
- Analyses by IC
 - ERDC-EL-MS using EPA methods 300.0 & 314.0 (perchlorate)

Standpipe Study – Cations

Snap Sampler % recovery

<u>Analyte</u>	<u>24 hr</u>	<u>48 hr</u>
Ca	98.7	100
Κ	100	102
Mg	97.4	100
Mn	98.3	99.4
Na	99.2	101

Standpipe Study – Anions **Snap Sampler % recovery 48 hr Analyte** 24 hr **Bromide** 100.6 99.1 Chloride 96.2 107 100.0 100.8 Nitrate Perchlorate 100.8 106 Sulfate 102 102

Conclusion: Able to recover 99% or more of all anions and cations after equilibrating sampler for 48 hours

CRREL Field Study – TCE (Parker & Mulherin 2007) Used CRREL 4-in, well contaminated w/ TCE Low-flow samples collected with $\frac{3}{4}$ -in. bladder pump **Deployed Snap Sampler at same depth as pump inlet** (1 VOA vial on trigger line) Equilibration time = 24 hr **Triggered Snap Sampler closing sampler Collected low-flow samples Removed Snap Sampler from well and recovered** sample vial Placed new vial in Snap Sampler & returned it to well Repeated the process until 5 sets of samples were collected Samples taken to lab & analyzed same day using **RP-HPLC** (Parker and Ranney 2000)

CRREL Field Study – TCE (Parker & Mulherin 2007)



	TCE conc.	mg/L
	Low-flow	Snap S
10- May	0.070	0.070
11- May	0.064	0.067
12- May	0.066	0.067
13- May	0.062	0.063
17- May	0.061	0.063
Mean	0.064	0.066



No significant difference at 95% conf. level

Field Study – VOCs Silresim Super Fund Site Lowell (Parker & Mulherin 2007)

- Analytes: 13 VOCs included chloroethanes, chloroethenes, & BTEX compounds
- Used similar protocol to previous study except that
 - Sampled four wells; each well sampled once
 - Three 2-in. wells & one 6-in. well
 - Deployed a ³/₄-in. bladder pump in each well
 - Deployed one trigger line with 2 Snap Samplers in tandem in each well
 - Used 40-mL VOA vials
 - Samplers straddled pump inlet
 - Allowed the samplers to equilibrate 3 or 4 days
 - Samples shipped samples on ice to lab for analyses by GC/MS (EPA Method 8260B)





Field Stuc	ly- VOCs	Silresim	Site	
(Parker	& Mulherin	n 2007)	Conc. (µ	g/L)
Examples:	<u>Analyte</u>	<u>Well #</u>	<u>Snap</u>	Low-flow
	Benzene	701B	80	80
		702B	2500	3000
		703A	150	170
	1,1-DCE	EW-10	75	70
		701B	495	445
		702B	9500	11500
		703A	2	2
No statistica	Ily signific	ant difforon	cos for any	of VOCe

No statistically significant differences for any of VOCs Using either paired t-test (95% confidence level) or Wilcoxon signed rank test Field Study – Explosives Former Louisiana Army Ammunition Plant (Parker & Mulherin 2007)

Protocol similar to previous study except that

- Sampled five 4-in. diameter wells
- Each trigger line had three 125-mL glass bottles
- Analyses by RP-HPLC (EPA Method 8330)

Deployment time was 3 or 4 days





Field Study – Explosives (Parker & Mulherin 2007)

Mean Concentration (mg/L) **HMX** TNT RDX Well # LF* <u>SS</u> LF* <u>SS</u> <u>SS</u> LF* 104 2.39 2.18 16.6 16.9 7.50 7.56 105 0.448 0.424 4.30 4.28 0.736 0.676 0.031 108 0.025 0.330 0.407 0.896 0.771110 0.497 5.43 0.749 0.604 0.526 5.37 140 0.087 0.079 1.36 1.26 0.345 0.312

No significant difference for any of the 6 analytes at 95% confidence level using a paired t-test

* LF = Low-flow samples

ESTCP-Sponsored Demonstration at former Pease AFB

Analytes: Inorganics (As, Ca, Fe, Mg, Mn, K, & Na) Location: Newington & Portsmouth, NH Geology:

Unconsolidated Units: Fill, Upper Sand, Marine Clay & Silt, Lower Sand, & Glacial Till Bedrock: Kittery or Elliot formation Eight monitoring wells used in the study Six 10-ft screens, one 5-ft screen, two 15-ft screens Bottom of wells ranged from 13' to 60' bgs Top of screens were 2' to 35' below the water table



- Area 13 Bulk fuel storage area 1 overburden well 1 bedrock well
- Area 32 Building 113 UST 3 overburden wells 3 bedrock wells

Pease Field Demonstration–Inorganics

Ten sampling events Two wells sampled twice **Deployed at same depth** ³/₄-in. bladder pump **1** RGC sampler 2 Snap samplers w/ baffle & weight **Deployment time 14 - 17 days** Samples collected **Snap Sampler, filtered & unfiltered RGC** sampler Low-flow Purging & Sampling filtered & unfiltered QA/QC samples Field duplicates (10%) Matrix spikes & MSDs (5%)



Pease Field Demonstration Plan continued

Sampling order First two wells (32-6064, 32-5020) Snap (left in well), RGC, & low-flow All remaining wells Snap (left in well), low-flow, RGC **Chemical Analyses** EPA Method 6020B, ICP/MS **Data Analyses** For each analyte, concentrations in Snap Sampler were compared with concentrations in the low-flow samples & **RGC** samples Filtered samples were compared with RGC samples Unfiltered samples were compared w/ RGC samples **Statistical Analyses Repeated Measures ANOVA (RM-ANOVA) or** Freidman RM-ANOVA (non-parametric)



Pease Demonstration Results Example: Conc. Calcium (mg/L)– unfiltered samples

Low-flow RGC Well # Snap 13-5045 72 71 66 42 43 41 13-6095 32-5020 230 250 190 32-5020 150 150 30 32-5031 75 86 97 53 **58 58** 32-5076 100 32-6008 **98** 98 32-6064 170 170 180 110 32-6064 110 110 5.1 32-6135 4.3 4.4 Mean **101**° **102**^c **99**c



No statistically significant difference between values with same letter

Results for Unfiltered Low-Flow and Snap Samples vs. RGC Samples

		10 events		
		Unfiltered		Unfiltered
Analyte	<u>% RSD*</u>	<u>Low-flow</u>	<u>RGC</u>	<u>Snap</u>
As	0-3.8%	0.086 ^c	0.090 ^c	0.10 ^c
Ca	0-4.9%	101 ^c	102 ^c	99 c
Fe	0-12%	3.8 ^c	4.2 ^c	7.4 ^d
Mg	0%	27 °	27 ^c	27 ^c
Mn	2.7- 5.7%	1.8 ^c	1.9 ^c	1.9 ^c
K	3.1-6.4%	6.7 ^c	6.7 ^c	7.0 ^c
Na	2.0- 10%	77 °	68 ^c	66 ^c

* For field duplicates No statistically significant difference between values with same letter

Results for filtered Low-Flow and Snap Samples vs. RGC Samples

<u>Analyte</u>		Mean conc. (mg/L) for 10 events			
	<u>% RSD*</u>	<i>filtered</i> Low-flow	<u>RGC</u>	<i>filtered</i> <u>Snap</u>	
As	0 - 2.6%	0.055 ^a	0.090 ^b	0.045 ^a	
Ca	1.7 - 5.1%	100 ^a	102 ^a	103 ^a	
Fe	0%	1.1 ^a	4.2 ^b	1.2 ^a	
Mg	4.4 - 9.3%	27 ^a	27 ^a	27 ^a	
Mn	1.8 - 3.3%	1.9 ^a	1.9 ^a	1.9 ^a	
K	4.0 - 4.4%	6.8 ^a	6.7 ^a	6.7 ^a	
Na	0 - 11%	74 ^a	68 ^b	69 ^{a,b}	

* For lab duplicates No statistically significant difference between values with same letter

Summary of Findings from Demonstration at former Pease AFB

- Snap Sampler shown to be able to recover equivalent concentrations of inorganic analytes to those recovered using lowflow sampling
 - True for both filtered and unfiltered samples,
 - -with possible exception of unfiltered Fe

 True for both bedrock and overburden wells

Final Conclusions

- Lab Studies Snap sampler samples compared with control samples
 - Able to recover equivalent concentrations of explosives, with equilibration time of 1 day
 - Able to recover equivalent concentrations of VOCs, with equilibration time of ~3 days
 - Able to recover equivalent concentrations of metals, with equilibration times of 1 to 2 days
- Field Studies Snap Sampler samples compared with samples taken using EPA's low-flow purging & sampling method
 - Able to recover equivalent concentrations of VOCs
 - Able to recover equivalent concentrations of explosives
 - Able to recover equivalent concentrations of inorganics

Thanks to our sponsors!

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603-646-4393 To download Parker & Mulherin (2007): Go to our website http://www.crrel.usace.army.mil/

Technical and Regulatory Guidance

Protocol for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater



& go to technical publications For additional information on this & other passive samplers: <u>http://www.itrcweb.org/</u>

