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An Automated Field Sampler Incorporating Solid Phase Extraction Disks for the Quantification of Radionuclide Concentrations in Surface Streams

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ABSTRACT

Commercial ISCO, Inc. 3700 series portable samplers were modified to collect aqueous samples from surface streams and process the sample through 3M Empore™ solid phase extraction (SPE) disks at the time of collection. The modified samplers were placed at routine sampling points around the Savannah River Site, a former nuclear production facility, such that the data produced by this study could be directly compared with historical and standard analysis results. The SPE disks tested were the commercial Tc RAD disk, the Sr RAD disk, and a test material selective for isotopes of cesium. The samplers were programmed to collect 30 mL samples every 30 minutes. The SPE disks were changed weekly, returning the disks to the lab for quantification of the radionuclide activities. Data collected over a four month field test period compares very favorably with concurrent laboratory based analyses and historical data, at a reduction in cost and significant time savings.

INTRODUCTION

A routine environmental monitoring program has been in place at the Savannah River Site (SRS), a US Department of Energy nuclear materials production facility located near Aiken SC, since the beginning of production operations in the early 1950's. Although nuclear material production has been shut down the routine environmental monitoring program continues to function supporting present nuclear waste clean up operations. The Environmental Monitoring Section (EMS) has over 40 sampling points on the surface streams that run through the site. Automatic samplers are installed at these locations, collecting a composite sample over the course of 1-2 weeks. Weekly, or bi-weekly, technicians collect the water, returning it to the EMS labs. The water is then aliquoted for specific analyses. Often, due to the difficulty in performing an analysis, space limitations in the separations or counting labs, or to be more cost effective, samples are composited into bi-weekly or monthly samples prior to analysis.

Recently, the 3M Empore™ RAD disks were tested for use in sample analysis in the lab (Beals, et al., submitted). In an effort to simplify environmental sample collection and analysis the Savannah River Technology Center (SRTC) of the SRS, 3M Corp. of St. Paul MN and ISCO Inc. of Lincoln NE established a working relationship to develop and test an automatic portable field sampler which would incorporate the Empore™ RAD disks. ISCO Inc. designed a retrofitable modification for their standard 3700 series field samplers. The "SPE option" allows the 3700 series samplers to not only automatically collect water but also process the water through the 3M Empore™ disks at the time of collection. Six of these modified samplers were delivered to the SRS for field testing. Using the parameters established in the lab for flow rate, prefiltering, and volume of sample passed through the RAD disks (Beals, et al., submitted) the modified samplers were placed in the field for an extended test period.

The analytes chosen to study for the field test were strontium-90 (half-life 29.1 years), technetium-99 (half-life 213,000 years) and cesium-137 (half-life 30 years). These radionuclides are present on the SRS as a result of previous nuclear material production and separation activities. All three radioisotopes are produced by the fission of uranium and plutonium; all three are beta emitting radionuclides, with Cs-137 also emitting a gamma ray. All three elements can be accumulated in the body, and due to their longer half-lives, can result in a radiation dose if significant quantities are ingested. Cs-137 and Sr-90 are fairly easy to quantify, though time consuming, by standard methods. Technetium-99 is much more difficult to measure (Beals, 1996; Davis, et al., 1993; Chen, et al., 1990) thus only a limited number of samples are analyzed each year at the SRS.

Sampling Locations

The SRS encompasses over 300 square miles and has four major watersheds within its boundary. Locations of the modified field samplers are shown in Figure 1. The sampling locations were chosen based on historical radionuclide measurements, and also to be diverse in stream characteristics. Selected water quality parameters are shown for each creek in Table 1 (Arnett, 1994).

Figure 1. Map of the Savannah River Site showing locations of modified samplers

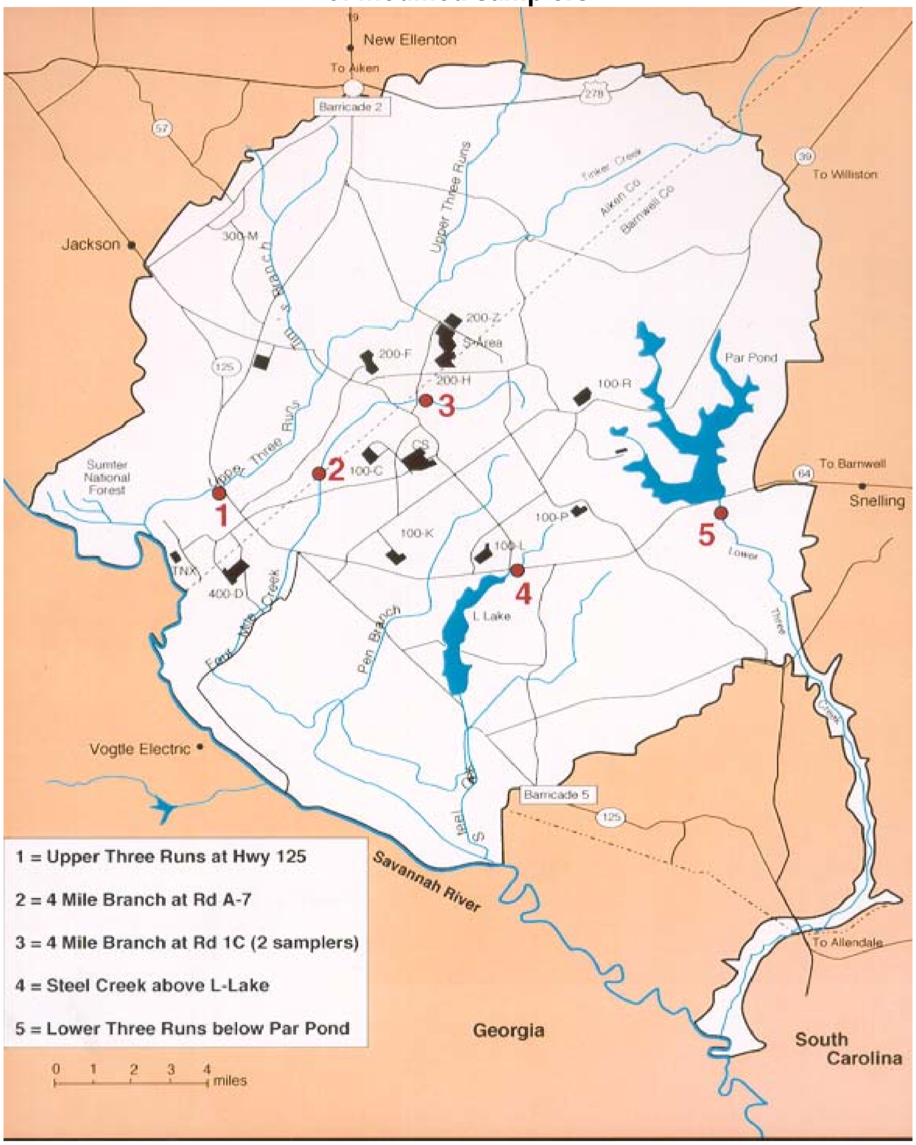


Table 1. Selected Water Quality Parameters of SRS Streams (from Cummins, et al., 1991)				
	U3R	L3R	SC	4MC
Water volume (L)	1.4e10	8.1e9	8.1e9	1.4e9
pH	6.4-7.7	6.3-7.8	6.5-7.3	6.3-7.5
diss. oxygen (mg/L)	7.3-11	6.4-10	5.5-10	5.7-12
alkalinity (mg/L)	1.0-6.0	24-51	1.0-16	6.0-21
tot organic C (mg/L)	1.0-12	NA	1.2-5.9	<1.0-3.8
suspended solids (mg/L)	2.0-15	1.0-11	1.0-6.0	2.0-7.0
tot diss solids (mg/L)	20-32	53-73	40-57	59-61
chloride (mg/L)	0.3-2.6	3.9-6.7	5.6-7.3	2.3-6.6
nitrogen (NO_2/NO_3;mg/L)	0.08-0.14	0.02-0.17	0.02-0.18	1.3-8.2

Upper Three Run (U3R) Creek is the largest creek on the SRS and is the only SRS stream to originate offsite. The creek is slow moving and quite turbid. U3R receives discharges from the Effluent Treatment Facility (ETF) thus may occasionally receive small amounts of tritium not removed by the ETF process. Crouch Branch, which discharges into U3R, receives a small amount of discharge from the H chemical separation area seepage basins and the solid waste disposal facility, which are known to contain low levels of radioactivity. One sampler was placed on the lower reaches of U3R. The gross beta activity measured at this location in 1993 varied from 0.21-3.9 pCi/L (n=26); Sr-89,90 varied from nondetectable to 0.78 pCi/L in 1993 (n=12; Arnett, 1994); Cs-137 has been monitored but never found at detectable levels at this location. Bi-annual grab samples were analyzed for Tc-99 in 1993 and 1994 (Beals and Hayes, 1995); the concentration varied from 0.11-0.57 pCi/L (n=4).

Lower Three Run (L3R) Creek drains PAR Pond which is located on the SRS. PAR Pond served as a thermal cooling pond for discharges from the (now shut down) P and R reactors. Due to the discharges from the reactors, small amounts of radiocesium have been accumulated and stored in the sediments of the pond. The shorter lived Cs-134 (half life of 2 years) has decayed to undetectable levels however Cs-137 can still be measured in the sediment and waters in PAR Pond. The sampling point chosen on L3R is immediately below the PAR Pond dam. The stream channel is confined by riprap from the dam to our sampling point. The water is fairly rapidly flowing. Historically, measured Sr-89,90 varied from nondetectable to 1.3 pCi/L (n=12) and gross beta activity from 1.7-5.5 pCi/L (n=26; Arnett, 1994); Cs-137 was not detectable by routine EMS procedures at this location. In 1995, a single grab sample was analyzed for radiocesium by the SRTC at this same location. The calculated Cs-137 concentration was 1.21 pCi/L (Beals, et al. 1996). Two grab samples analyzed in 1994 for Tc-99 gave results of 0.32 and 0.08 pCi/L (Beals and Hayes, 1995).

Steel Creek (SC), at the sampling point above L Lake, has received discharges from P reactor operations in the past, and still receives discharges from the P area seepage basin. The streambed is composed mostly of fine silt and mud. In 1993, three of 12 samples had measurable Cs-137 which varied from 9-20 pCi/L; Sr-89,90 varied from nondetectable to 0.8 pCi/L (n=12; Arnett, 1994). A single Tc-99 measurement was made in 1994; the calculated concentration was 0.14 pCi/L (Beals and Hayes, 1995).

Two sampling locations were chosen on Fourmile Branch (4MC). 4MC originates near the middle of the SRS and is the smallest of the streams sampled during this study. A pair of samplers were installed at the 4MC-1C location, which receives discharges from H area and the Receiving Basin for Offsite Fuel (RBOF) as well as runoff from surrounding parking lots. The water flow at this location is the most variable of all the sampling sites in this study. Two samplers were placed at this location to determine if there was any systematic or a random error in the field sampling and analysis method. Gross beta analyses in 1990 indicated concentrations ranging from 7-103 pCi/L (n=52), with Sr-89,90 concentrations of nondetectable to 1.3 pCi/L (n=12) for 1990 (Cummins, et al., 1991). Cs-137 was not detectable by routine methods at this location.

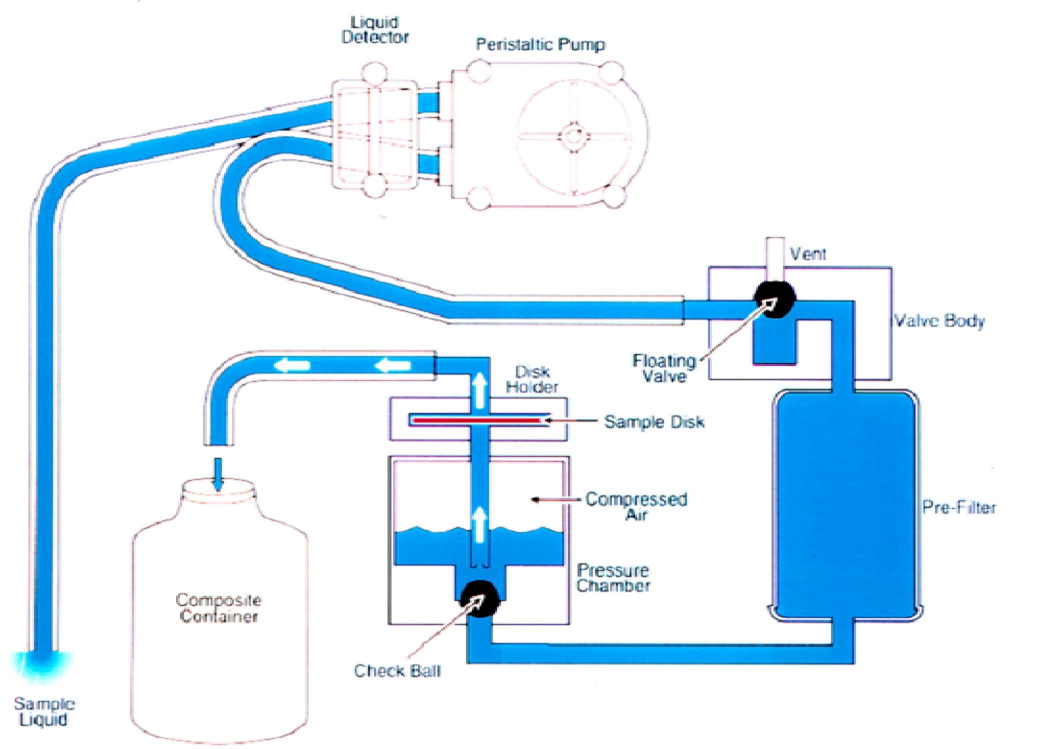
The other sampling location on 4MC was at the Road A-7 crossing. The 4MC-A7 sampling point is a few river miles below the 4MC-1C sampling point. Between 4MC-1C and 4MC-A7, 4MC receives discharges from both the F and H chemical separation area seepage basins. In the past, discharges from C reactor also entered 4MC above Road A-7. Measured radionuclide concentrations during 1993 (Arnett, 1994) at this location are as follows: Cs-137 varied from non-detectable to 19 pCi/L (n=12), Sr-89,90 varied from 10-15 pCi/L (n=12). Tc-99 was measured on biannual grab samples from 1992-1994; concentrations varied from 0.57-3.1 pCi/L (n=5; Beals and Hayes, 1995).

EXPERIMENTAL

Laboratory Tests

Prior to passing significant volumes of stream water through the 3M Empore™ disks, the water must be filtered. Laboratory studies showed that a 0.45 µm filter was acceptable (Beals, et al., 1997). Flow rates of 10-20 mL per minute were possible through the Empore™ material, and

Figure 2. Illustration of the Modified ISCO 3700 Automatic Field Sampler



resulted in nearly quantitative extraction of the selected radionuclide. Given these parameters, ISCO Inc. designed modifications that could be retrofit on the ISCO 3700 series automatic field samplers. As shown in Figure 2, water is collected from the stream using the standard ISCO 3700 series peristaltic pump and controller.

The water is then passed through a 0.45µm particle filter and into a sealed reservoir with a one way valve. The water finally passes through a filter housing containing the Empore™ disks; the processed water is collected in the sample jug in the base of the ISCO unit.

The Empore™ RAD disks are selective for specific elements. Two commercial RAD disks and one experimental disk were field tested during this study: the commercial Tc RAD disk (for Tc-99 determinations), the commercial Sr RAD disk (for Sr-89,90 determinations), and a disk containing potassium cobalt ferrocyanide (KCFC; Boni, 1966) for the selective extraction of Cs from solution (Cs RAD disk; for Cs-137 determinations).

To measure several radionuclides in a single sample, the water would have to be passed through the different disks sequentially. In addition to the lab tests described in Beals, et al. (submitted) a few additional tests were performed to ensure that stacking the Empore™ RAD disks did not decrease their uptake efficiency for the selected radionuclide. The decontamination factors determined for each disk are shown in Table 2 (from Beals, et al., submitted). Based on these results it was decided to place the Sr RAD disk first in series, followed by the experimental Cs RAD disk, and lastly the Tc RAD disk. A laboratory study was then performed in which deionized (DI) water and river water spiked with Tc-99, Sr-90 and Cs-137. The solutions were then passed through the disks in the order determined above; all three disks were placed in contact with each other in a single filter housing.

Table 2. Results of Decontamination Studies for Empore™ RAD Disks.
Numbers in the table are decontamination factors given as:
1-(amount found/amount added)*100%]

interference	Tc-99	Sr-90	Cs-137
RAD Disk			
Tc RAD	NA	98.6%	>99.9%
Sr RAD	>99.98%	NA	98.5%
Cs RAD	>99.9%	83.7%	NA

As seen in Table 3, the observed beta count rate measured was nearly the same as the expected count rate indicating the lack of interference between the various radioisotopes when analyzed in this manner. Cesium-137 was quantified by gamma spectrometry, for which there is no interference potential from Tc-99 or Sr-90, thus the Cs RAD disk was not counted in this test

Table 3. Results of Stacked Disk Study Using Empore™ RAD Disks

	isotope	expected cpm	actual cpm
Deionized water	Sr-90	55	54.3
	Cs-137	133	--
	Tc-99	1200	1235.9
river water	Sr-90	55	60.95
	Cs-137	133	--
	Tc-99	1200	1129.0

A final test was completed examining the potential for breakthrough when high volume samples were processed through the stacked Empore^{TM} RAD disks. Unfiltered river water was used for this study. Sample sizes were varied from 1-10 liters, as shown in Table 4.

Table 4. Sample Volume versus Extraction Efficiency of Empore™ RAD Disks

sample volume (liters)	Tc-99 (cpm) first disk	Tc-99 (cpm) second disk	Tc-99 (cpm) % breakthru	Sr-90 (cpm) first disk	Sr-90 (cpm) second disk	Sr-90 (cpm) % breakthru	Cs-137 (pCi) first disk	Cs-137 (pCi) second disk	Cs-137 (pCi) % breakthru
1	5392.9	-0.5	-0.01	67.25	0.05	0.07	58.6	<0.6	<1
2.5	7696.2	-0.7	-0.01	67.25	-0.20	-0.30	56.8	<0.4	<0.7
5	11592.9	0.2	0.00	48.80	1.05	2.11	63.0	0.4	0.58
7.5	7755.9	27.9	0.36	47.75	5.90	11.00	41.9	1.2	2.83
10	8148.0	26.2	0.32	46.25	11.95	20.53	38.0	1.3	3.31

Each aliquot of water was spiked with Tc-99, Sr-90 and Cs-137. The solution was mixed and then pumped through a 0.45μm particle filter followed by two filter holders, each containing all three RAD disks in the predetermined order. As seen in Table 4, less than 0.5% of the Tc-99 and only a few percent of the Cs-137 was observed on the back up disk even at volumes of 10 liters. Breakthrough of the Sr-90 began to occur between 5 and 7.5 liters of sample processed, with 11% breakthrough at 7.5 liters and 20% at 10 liters. The particle filter was also counted for the 7.5 and 10 liter samples by gamma spectrometry. Only a few percent of the Cs-137 was found to have been removed by the particle filter.

Field Study

The samplers were placed in the field in early July 1996 and continued in operation through October. The samplers were programmed to collect a 30 mL grab sample every 30 minutes; this was passed through the RAD disks at the time of collection. Once a week a technician performed routine service on the samplers. Weekly, the 0.45μm particle filters and the filter holder housing the Empore^{TM} disks were changed. The processed water volume was measured and the water discarded. The filter housings containing the three Empore^{TM} disks were returned to the lab unopened. Biweekly the tubing in the pump was changed.

In the lab, the technician opened the Empore^{TM} holders and separated the disks. The Sr RAD disk was placed in a Millipore filter assembly and washed with 20 mL of 2M HNO_3 to remove the Y-90 (daughter of Sr-90). All the disks were then allowed to air dry for a few hours. Stainless steel rings were used to hold the edges of the disk flat while air drying. The disks were then dried in an oven set at 70^{o}C for 15-20 minutes. The Tc and Sr RAD disks were loaded onto two-inch stainless steel planchetts and counted by gas flow beta proportional counting for 20 minutes each. The Cs RAD disks were loaded into caplugs and counted by gamma spectrometry for 100 minutes each. Some of the particle filters were also counted by gamma spectrometry.

RESULTS

The calculated radionuclide concentrations in the streams for the samples collected and processed during this study are shown in Tables 5-10 and in Figures 3-8. Sample concentrations were calculated by subtracting the detector background from the sample count rate; the net count rate (cpm) is converted to activity (dpm or pCi) by dividing by the detector efficiency for the isotope. The Sr RAD disk was counted as soon as practical after the Y-90 removal (2M HNO_3 wash) to minimize any Y-90 ingrowth; no correction was made for ingrowth for this data set. The reported errors for this data are counting errors only.

Results of routine EMS laboratory based analyses are also shown in Tables 5-10 and Figures 3-8; the errors given for this data are propagated errors. The EMS Sr-89,90 results are on a monthly composite sample (the data have been corrected for radiochemical yield and Y-90 ingrowth); the Cs-137 results are on a bi-weekly composite; no Tc-99 samples were analyzed at these locations for the year. Routine EMS laboratory analyses process a one-liter sample for each analyte. Samples are counted by beta proportional counting for 20 minutes each for Sr-89,90; 100 minutes each by gamma spectrometry for Cs-137. Most EMS sample activities reported here are less than or equal to the EMS detection limits of about 2.5 pCi/L for Sr-89,90 and about 10 pCi/L for Cs-137. Even though values less than the detection limit are reported here they are not considered statistically significant.

Many of the Tc-99 results and some of the Sr-90 and Cs-137 results produced by this study are shown as not detected (ND) in the tables. This is indicated in cases where the count rate measured for the Empore™ disk is less than or equal to the detector background. If the sample volume processed was less than one liter for the week the data is considered not significant; it is marked as "no sample" (NS). The Cs RAD disks did not get counted from the first two weeks of the study (NC). No experimental Cs RAD disks were available (NR) for two sample locations during the week of 10/16-23. The Sr RAD disk from 4MC-1C duplicate was damaged thus uncountable ("lost") for the week of 7/18-24.

Over the course of the study only 9 of a possible 96 samples were not collected (NS; less than one liter of water collected). In tables 5-10, a code letter is listed if there was a problem in sample collection. These problems are described below. For the week ending 8/14 at SC, the inlet tube of the pump had gotten buried in mud and thus was unable to draw up a sample (problem code A). Problem code A was also noted at 4MC-1C primary, when a stick got stuck in the sample inlet tube the first week of sampling, and when at the same location the inlet tube got above the creek water level the week ending 8/21.

After not collecting a sample at SC for the week ending 9/11, the rollers in the pump housing were cleaned (problem code B) and the sampler returned to normal operation. During the week of 9/25-10/2 we had several rainy days. Samplers at the SRS are battery powered, with solar panels to regenerate the batteries. The sampler location at SC is the most heavily shaded of all the sampling locations studied here. During the above week, the battery wore down (problem code C). A five-liter sample was collected suggesting the battery failed toward the end of the week long sampling period. As there was still no sun, the sampler did not get restarted until 10/9.

After cleaning the pump rollers on the 4MC-1C primary sampler on 9/11, the sampler was rechecked on 9/12 to confirm it was again working properly. Unfortunately, only a few hundred milliliters of water had been collected. The sampler appeared to be working properly however the tubing from the pump to the particle filter kept blowing off (problem code D). After several days of diagnosis, we discovered that some oil had apparently gotten sucked up by the sampler, coating the one way valve thus preventing water from being processed. All parts of the sampler were cleaned and it was returned to service on 9/19.

Table 5. Radionuclide Concentrations in Upper Three Run Creek at SC Hwy 125

spl dates	volume (mL)	problem code	Tc pCi/L	2s err	Sr pCi/L	2s err	Cs pCi/L	2s err	EMS baseline data: Sr pCi/L	2s err	EMS baseline data: Cs pCi/L	2s err
7/11-7/17	4250		0.16	0.05	1.01	0.20	NC				ND	
7/17-7/24	6775		ND		0.82	0.15	NC					
7/24-7/31	5700		ND		0.62	0.13	ND				ND	
7/31-8/7	8000		0.03	0.01	0.61	0.11	ND					
8/7-8/14	6000		0.08	0.03	0.88	0.16	ND				ND	
8/14-8/21	8000		ND		0.58	0.11	ND					
8/21-8/27	7000		0.08	0.03	0.58	0.12	ND				1.48	2.28
8/27-9/4	9000		0.01	0.00	0.41	0.08	ND					
9/4-9/11	8500		0.08	0.02	0.53	0.10	ND				ND	
9/11-9/18	8000		0.03	0.01	0.89	0.14	ND					
9/18-9/24	8000		0.04	0.02	0.34	0.08	ND				ND	
9/24-10/2	12000		ND		0.31	0.06	ND					
10/2-10/9	7000		0.04	0.02	0.70	0.13	ND		0.01	0.43	ND	
10/9-10/16	7000		0.07	0.02	0.61	0.12	ND					
10/16-10/23	7000		0.02	0.01	0.41	0.09	NR		0.47	0.48	ND	
10/23-10/30	8000		0.03	0.01	0.53	0.10	ND					

historical gross beta (1993) 0.21-3.9 pCi/L
historical Tc-99 (1993-1994) 0.11-0.57
historical Sr-89,90 (1993) 0-0.78

Table 6. Radionuclide Concentrations in Lower Three Run Creek below PAR Pond

Lower Three Runs Creek at Par Pond Dam

spl dates	volume (mL)	problem code	Tc pCi/L	2s err	Sr pCi/L	2s err	Cs pCi/L	2s err	EMS baseline data: Sr pCi/L	2s err	EMS baseline data: Cs pCi/L	2s err
7/10-7/17	7250		ND		0.68	0.13	NC		0.00	0.25		
7/17-7/24	7170		0.01	0.00	0.40	0.09	NC				4.04	4.76
7/24-7/31	7050		0.01	0.01	0.16	0.05	0.60	0.42			1.25	2.66
7/31-8/7	5250		ND		0.31	0.08	2.31	0.85				
8/7-8/14	6000		ND		0.26	0.07	2.35	0.90	0.00	0.19	9.94	3.30
8/14-8/22	8000		0.13	0.04	0.36	0.08	1.26	0.62				
8/21-8/28	5600		0.06	0.02	0.32	0.08	1.84	0.84			3.25	1.65
8/27-9/4	5600		ND		0.19	0.06	2.08	0.83	0.18	0.21		
9/4-9/11	8000		ND		0.25	0.06	1.52	0.64			3.66	2.29
9/11-9/18	7000		0.09	0.03	0.39	0.09	2.06	0.72				
9/18-9/24	7000		ND		0.19	0.05	2.02	0.68			9.90	3.83
9/24-10/2	7000		ND		0.33	0.08	2.26	0.75				
10/2-10/9	7000		0.01	0.00	0.38	0.09	1.97	0.66	0.11	0.23	7.53	1.73
10/9-10/16	7500		0.01	0.00	0.44	0.09	1.95	0.67				
10/16-10/23	7500		0.05	0.02	0.08	0.02	NR				10.30	3.51
10/23-10/30	8000		ND		0.25	0.06	2.01	0.72				

historical gross beta (1993) 1.7-5.5 pCi/L
Tc-99 grab (1994) 0.08-0.32
historical Sr-89,90 (1993) 0-1.3
Cs-137 (single grab, 1995) 1.21

Table 7. Radionuclide Concentrations in Steel Creek above L Lake

Steel Creek above L Lake (SC-2A)

spl dates	volume (mL)	problem code	Tc pCi/L	2s err	Sr pCi/L	2s err	Cs pCi/L	2s err	EMS baseline data Sr pCi/L	2s err	EMS baseline data Cs pCi/L	2s err
7/10-7/17	2515		ND		0.54	0.15	NC		0.00	0.28	0.95	2.32
7/18-7/24	9800		ND		0.28	0.06	NC					
7/24-7/31	5500		ND		0.28	0.07	2.43	0.90			4.12	2.60
7/31-8/7	2600		0.16	0.05	0.37	0.11	2.02	1.55	0.10	0.20		
8/7-8/14	150	A	NS		NS		NS				1.41	2.00
8/14-8/22	8000		0.04	0.02	0.40	0.09	1.52	0.66				
8/21-8/28	6000		ND		0.32	0.08	1.35	0.72			3.99	2.31
8/27-9/4	6000		ND		0.22	0.06	1.44	0.80	0.24	0.22		
9/4-9/11	500	B	NS		NS		NS				3.84	1.62
9/11-9/18	8000		0.12	0.03	0.42	0.09	1.98	0.55				
9/18-9/24	8000		ND		0.28	0.07	1.49	0.53			3.90	2.12
9/24-10/2	5000	C	0.04	0.01	0.12	0.04	ND					
10/2-10/9	0	C	NS		NS		NS		0.03	0.22	5.44	3.10
10/9-10/16	5000		ND		0.37	0.10	ND					
10/16-10/23	1000		ND		1.75	0.45	ND				<9.64	
10/23-10/30	0	C	NS		NS		NS					
histroical gross beta (1990) 3-9 pCi/L												
Tc-99 grab sample (1994)			0.14									
historical Sr-89,90 (1993)					0-0.8							
historical Cs-137 (1993)							9-20					

Table 8. Radionuclide Concentrations in Fourmile Branch, sample point 1C (primary)

Fourmile Branch at Road 1C (primary)

spl dates	volume (mL)	problem code	Tc pCi/L	2s err	Sr pCi/L	2s err	Cs pCi/L	2s err	EMS baseline data Sr pCi/L	2s err	EMS baseline data Cs pCi/L	2s err
7/11-7/17	6260		ND		1.47	0.21	NC				3.42	1.49
7/17-7/24	15950		0.04	0.01	3.60	0.22	NC		0.55	0.46	2.42	2.33
7/24-7/31	13300		0.02	0.01	0.52	0.08	0.53	0.28			<1.87	
7/31-8/7	14500		0.02	0.01	1.34	0.14	1.28	0.40			4.15	1.36
8/7-8/12	4000		0.13	0.04	1.58	0.27	2.26	0.95			1.94	1.26
8/14-8/21	2050	A	0.12	0.04	1.79	0.37	3.04	2.36	0.73	0.40	2.55	2.11
8/21-8/27	2925		0.07	0.02	5.01	0.59	2.25	0.96			2.40	2.40
8/27-9/4	6000		0.01	0.00	1.20	0.19	1.42	0.74			3.38	2.43
9/4-9/11	500	B	NS		NS		NS				4.41	1.42
9/11-9/18	140	D	NS		NS		NS		1.01	0.44	1.11	1.78
9/18-9/24	8000		ND		1.65	0.20	2.76	0.69			15.60	3.02
9/24-10/2	7000		ND		2.40	0.27	0.96	0.64			13.70	3.08
10/2-10/9	9000		ND		1.56	0.19	0.83	0.59			1.79	2.39
10/9-10/16	10000		ND		1.50	0.17	1.23	0.44	0.67	0.55	4.06	1.31
10/16-10/23	10000		ND		1.51	0.18	0.77	0.35			<2.37	
10/23-10/30	9000		0.04	0.01	2.00	0.21	1.17	0.55			2.84	2.21
historical gross beta (1990) 7-103 pCi/L												
histroical Sr-89,90 (1990)					0-1.3							

DISCUSSION

The only location to have measurable Tc-99 was the 4MC-A7 site (Table 10, Figure 8) with the results determined by this study being consistent with grab sample results from previous years. The highest Sr-90 measured was also at 4MC-A7, as expected from the historical data. The Cs-137 was found to average between 1-4 pCi/L at both 4MC sampling points and on L3R, slightly lower on SC, and nondetectable on U3R.

As seen in Tables 5-10, the data reported here generally agree within the error with the data obtained by the routine EMS laboratory based methods. The large uncertainties associated with most of the EMS results can be attributed to the lack of sensitivity of the routine EMS methods. Because much larger sample volumes were processed in the field, the detection limits for the field samples are lower than for the lab based methods, providing more precise results.

Table 9. Radionuclide Concentrations in Fourmile Branch, sample point 1C (duplicate)

Fourmile Branch at Road 1C (duplicate)

									EMS baseline results			
spl dates	volume (mL)	problem code	Tc pCi/L	2s err	Sr pCi/L	2s err	Cs pCi/L	2s err	Sr pCi/L	2s err	Cs pCi/L	2s err
7/11-7/12	380	A	NS		NS		NS				3.42	1.49
7/18-7/24	6475		ND		lost		NC		0.55	0.46	2.42	2.33
7/24-7/31	7900		ND		0.36	0.08	ND				<1.87	
7/31-8/7	15000		0.07	0.02	1.83	0.16	1.65	0.36			4.15	1.36
8/7-8/12	15000		0.00	0.00	0.22	0.05	1.96	1.80			1.94	1.26
8/14-8/21	0	A	NS		NS		NS		0.73	0.40	2.55	2.11
8/21-8/27	2250		0.14	0.05	5.43	0.69	1.92	2.04			2.40	2.40
8/27-9/4	8500		ND		1.61	0.20	1.34	0.74			3.38	2.43
9/4-9/11	8500		0.05	0.02	2.03	0.22	1.45	0.51			4.41	1.42
9/11-9/18	8000		ND		2.24	0.24	0.60	0.52	1.01	0.44	1.11	1.78
9/18-9/24	8000		0.13	0.04	5.98	0.40	32.60	2.93			15.60	3.02
9/24-10/2	6000		0.03	0.01	2.49	0.29	1.59	0.83			13.70	3.08
10/2-10/9	4000		ND		2.18	0.32	2.03	1.16			1.79	2.39
10/9-10/16	12700		ND		1.52	0.16	1.50	0.42	0.67	0.55	4.06	1.31
10/16-10/23	0	D	NS		NS		NS				<2.35	
10/23-10/30	15000		0.02	0.01	1.75	0.16	0.69	0.28			2.84	2.21
historical gross beta (1990) 7-103 pCi/L												
historical Sr-89,90 (1990)					0-1.3							

Table 10. Radionuclide Concentrations in Fourmile Branch at Road A-7

Fourmile Branch at Road A-7

									EMS baseline data			
spl dates	volume (mL)	problem code	Tc pCi/L	2s err	Sr pCi/L	2s err	Cs pCi/L	2s err	Sr pCi/L	2s err	Cs pCi/L	2s err
7/11-7/17	5400		0.61	0.13	17.96	0.86	NC		8.41	0.72		
7/17-7/24	7020		0.43	0.09	17.53	0.75	NC					
7/24-7/31	3700		0.62	0.15	20.10	1.09	3.85	1.25			1.25	2.66
7/31-8/7	5500		1.14	0.19	10.00	0.63	3.29	0.81	7.28	0.66		
8/7-8/14	1450		0.39	0.12	6.56	0.93	3.77	2.17			9.94	3.30
8/14-8/21	6600		0.64	0.12	8.54	0.53	2.63	0.83				
8/21-8/27	15000		0.05	0.02	1.35	0.14	2.87	2.54			3.25	1.65
8/27-9/4	8500		0.72	0.12	7.90	0.45	2.82	0.70				
9/4-9/11	7000		0.64	0.12	13.31	0.65	2.61	0.71	9.16	0.76	3.66	2.29
9/11-9/18	5000		0.57	0.13	12.49	0.74	3.26	0.95				
9/18-9/24	7000		0.45	0.10	9.07	0.53	2.48	0.75			9.90	3.83
9/24-10/2	8000		0.55	0.10	9.05	0.50	2.99	0.69				
10/2-10/9	8000		0.63	0.11	7.95	0.47	3.78	0.72			7.53	1.73
10/9-10/16	5500		0.30	0.08	5.12	0.45	3.28	0.76	11.00	1.23		
10/16-10/23	6000		0.65	0.13	7.70	0.53	3.49	0.94			10.30	3.51
10/23-10/30	7000		0.52	0.10	8.05	0.50	3.39	0.78				
historical Tc-99 (1992-1994)			0.57-3.1									
historical Sr-89,90 (1993)					10-15							
histroical Cs-137 (1993)							8.8-19					

The only obvious difference in the data sets, this study versus EMS, is the Cs-137 results from 4MC-A7 (Table 10). The field results from this study appear to be lower than the historical values and lower than the current EMS results. The 0.45µm particle filters were counted for the last three weeks of this study. 5.0±1.2 pCi/L of Cs-137 was found on the particle filter from 4MC-A7 for the week ending 10/16, 4.4±1.1 pCi/L for the week ending 10/23, and 3.6±0.9 pCi/L for the week ending 10/30. The EMS samples are not filtered; thus this may account for the lower reported RAD disk values obtained by this study when compared to the EMS values. The only other particle filter to have measurable Cs-137 was collected at SC for the week ending 10/23; 6.4±1.9 pCi/L of Cs-137 was measured. The remaining particle filters counted from SC and from all three weeks at the other locations were found to have less than 0.3 pCi/L of Cs-137.

A comparatively low Sr-90 value is reported from 4MC-A7 for the week ending 8/27 (Table 10). The sample volume processed this week was 15 liters. The laboratory studies suggest that breakthrough of Sr-90 may occur in the 7-10 liter sample size range, thus the low sample result may by due to a less than quantitative extraction at this volume. This may also account for the apparently low result reported at 4MC-1C duplicate for the week ending 8/12 (Table 9). An apparently high Sr-90 result is reported for SC for the week ending 10/23 (Table 7). Due to the small sample size, this is approaching the detection limit of this sample. Both samplers (Tables 8 and 9) confirm the higher Sr-90 for the week ending 8/27 at 4MC-1C.

One result that is less easily explained is the Cs-137 measured at 4MC-1C for the last two weeks of September (Tables 8 and 9). The EMS samples were collected from 9/16-9/23 and 9/23-9/30. If a small release occurred on 9/23, the activity may have been split between the two EMS collections; this study would have collected the entire release signal in the 9/18-9/24 sample. It is unclear why the spike was not detected in the primary sampler but was observed in the duplicate sampler at this location. The Sr-90 measured by the primary sampler was also lower than that measured by the duplicate sampler, for the same sample size. The sampler inlet tubes for the EMS ISCO sampler and the two modified samplers were within a few feet of each other, but possibly the creek water was not well mixed at the sampling point such that the two modified samplers sampled different water.

FUTURE WORK

A second field trial is planned at the SRS. Samplers will again be placed at routine monitoring locations, concentrating only on the Fourmile Branch system. Even with the lower limits of detection by the SPE field method, only the samples collected on Fourmile Branch showed consistently measurable radionuclide activity for ease of data comparison. Sample collection will be adjusted such that the ISCO-SPE sample will be collected for the same time period as the routine sample. All the particle filters will be counted for Cs-137 to determine if this is the cause of the bias in the Cs-137 data observed at 4MC-A7 in this first study. Routine EMS procedures will be modified during the study period, increasing sample volume and/or increasing counting times, to try to improve the laboratory based detection limits to the same level as the field based method.

SUMMARY

ISCO 3700 series automatic portable field samplers were modified by the manufacturer to collect surface water samples and process them in the field through 3M Empore^{TM} RAD solid phase extraction disks. The modified samplers were field tested at the Savannah River Site for a period of four months. The analytes studied were Tc-99, Sr-90 and Cs-137. Results obtained during this study compare favorably with historical data as well as with results obtained by the routine EMS sample collection and analyses performed at the same locations.

Radionuclide concentration data were available based on the field sampler method within one week of sample collection as opposed to the typical 45 day turnaround for routine monitoring programs. One technician was able to prepare samples for counting for three different analyses within a few hours as opposed to multiple technicians being required to perform separate lengthy chemical separations for each analyte. Also, the new method resulted in a lower detection limit as larger samples can be processed in the field, several liters (field) as opposed to only one liter (lab). The sample analysis cost is reduced by processing samples in the field, eliminating the need for multiple technicians performing lengthy laboratory methods. Overall, this new method results in the desired "faster, better, cheaper" analysis protocols.

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