Supporting Information
for
Permeable Environmental Leaching Capsules (PELCAPs) for In Situ Evaluation of Contaminant Immobilization in Soil

B. P. Spalding* and S. C. Brooks
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box 2006
Oak Ridge, Tennessee 37831
*Corresponding author: phone (865)-574-7265; fax (865)-576-8543; e-mail spaldingbp@ornl.gov

Published in *Environmental Science & Technology*

Prepared: August 29, 2005

Summary (4 Tables, 6 Figures, 12 pages)

Supporting information is provided for the summarized measurements presented in the main text. Table SI-1 lists the average fractions (± one standard error) of both ^{85}Sr and ^{134}Cs sequentially extracted from soils with and without PELCAPs. Table SI-2 is a complete list of the measured cation exchange capacities of the soils with and without PELCAPs. Table SI-3 lists the average and range of stream and ground water chemical characteristics during the periods when PELCAPs were deployed; this data supports the summary characterization of both the surface and ground waters as relatively hard calcium/magnesium bicarbonate types. Significantly more ^{90}Sr was dissolved in the Core Hole #8 groundwater than in the Northwest Tributary stream water. Table SI-4 summaries the activities of ^{90}Sr in the various sequential extracts of PELCAPs after deployment for six months in CH8 with its relatively high ^{90}Sr activity. The unheated soil, with its higher cation exchange capacity (CEC), adsorbed more ^{90}Sr than the heated soil with its lower CEC. PELCAPS with either heated or unheated soil adsorbed more ^{90}Sr than PELCAPs without soil. Full charts of the retention of ^{85}Sr and ^{134}Cs, by all nine types of PELCAPs, are presented in Figured SI-1 and SI-2 for the NWT and CH8 sites, respectively, during their deployments over six months. The sequential extractive behavior of residual ^{85}Sr and ^{134}Cs in PELCAPs after six months of in situ water exposure are presented in Figure SI-3; this normalized activity of each isotope does not include the activity of ^{85}Sr or ^{134}Cs leached during the previous six months of exposure. The sequential extractive behavior of ^{90}Sr in PELCAPs from CH8 after six months deployments is depicted in Figure SI-4. The unheated soil, presumably due to its higher cation exchange capacity, adsorbed more ^{90}Sr than the heated soil or PELCAPs without soil. Residual ^{85}Sr or ^{134}Cs did not interfere with the ^{90}Sr assay as evidenced by the small and non-significant differences between the various isotope spikes (^{85}Sr, ^{134}Cs, or none). Figure SI-5 depicts the relatively small temporal variability in the activity of ^{90}Sr in both the CH8 and NWT waters in grab samples over the six month deployment interval of the PELCAPs. Figure SI-6 depicts the sequential extractive behavior of ^{85}Sr and ^{134}Cs from soils with and without PELCAPs using the original extraction intervals of 16 hours for the initial extract followed by four 1-hour intervals for each subsequent extract type (water, 0.1 *N* $CaCl_2$, and 0.2 *N* HCl). Use of these shorter extraction intervals (compared to the 24-hour intervals for all extractions actually used in Figure 2 of the main text) removed less isotope from soil contained in PELCAPs than from soil not contained in PELCAPs. The longer extraction intervals presented in the main text exhibited similar magnitudes for isotope removal for each extractant presumably because the longer interval allowed sufficient time for the isotope to diffuse from the PELCAP into each extract solution.

Soil cation exchange capacity method

Cation exchange capacity (CEC) of both the untreated and thermally-treated soil was measured using a standard ^{85}Sr-labeled 0.1 *N* $SrCl_2$ (*15*) for both unencapsulated and encapsulated soil. The net amount of Sr in milliequivalents (+) adsorbed from this saturating solution, after correcting for residual solution retained in a soil or in a soil plus polymer matrix, was computed as the CEC. Cation exchange capacity (CEC) of both the untreated and thermally-treated soil was measured using a standard ^{85}Sr-labeled 0.1 *N* $SrCl_2$ (*15*) containing sufficient ^{85}Sr to achieve 950 cpm/mL under the assay conditions. Newly constituted PELCAPs were placed in triplicate in previously weighed 50-mL polycarbonate Oak Ridge centrifuge tubes. A second group of triplicate soil samples without PELCAP encapsulation were placed in centrifuge tubes as were triplicate samples of neat PELCAPs and triplicate samples of reagent blanks (no soil or PELCAPs). A precise volume of 20.00 mL of 0.1 *N* $SrCl_2$ was pipetted into each centrifuge tube which was capped, weighed, and shaken overnight. After centrifuging at 3,500 × *g* for 10 minutes, supernatant was decanted into previously weighed 20-mL polyethylene scintillation vials which were capped and weighed to determine the amount of extract recovered; care was exercised not to disturb the soil pellet in the centrifuge tube and complete supernatant liquid recovery was not attempted. The counts in each vial were assayed as described above and all extracts were normalized to the average of triplicate 20-mL volumes of the starting 0.1 *N* Sr(^{85}Sr)Cl_2 solution placed directly in scintillation vials. The fraction of the spiked ^{85}Sr counts recovered in each sample was computed. Net counts in excess of the liquid volume contained by a sample (i.e., PELCAPs with and without soil), which was determined from the initial and recovered weights of liquid in each sample, were interpreted as exchangeable cations and computed in milliequivalents (meq) (+) of Sr^{2+} based on the counts/meq in the starting 0.1 *N* $SrCl_2$ solution and correction for dilution of water in the starting PELCAPs. The adsorbed meq (+) of Sr^{2+} was divided by the weight of soil in the sample to compute its cation exchange capacity (in meq (+)/100g). Because neat PELCAPs contained no soil, their CEC was simply expressed as meq (+)/PELCAP. Triplicate samples of the non-spiked PELCAPs, deployed at the NWT site for six months, were measured for CEC as described above to determine if CEC had changed for either soil or whether neat PELCAPs exhibited any CEC.

Solution to Diffusion Equation Employed for Modeling PELCAP Isotope Retention

The solution to the diffusion equation describing the average residual concentration in a finite cylinder (as a fraction of the initial loading) presented by Anders et al. (1978):

$$F = 4\left[\frac{1}{R_1^2}\exp\left(-\left(\frac{Dt}{r^2}\right)R_1^2\right)+\frac{1}{R_2^2}\exp\left(-\left(\frac{Dt}{r^2}\right)R_2^2\right)+\ldots\right]\times$$
$$\frac{8}{\pi^2}\left[\exp\left(-\left(\frac{Dt}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right)+\frac{1}{9}\exp\left(-9\left(\frac{Dt}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right)+\frac{1}{25}\exp\left(-25\left(\frac{Dt}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right)+\ldots\right]$$

F = average residual fraction remaining in the cylinder relative to initial loading.
D = diffusion constant (cm^2/s).
r = radius (cm).
a = one-half the height of cylinder (cm).
R_1, R_2, etc = roots of the zero-order Bessel function of first kind $J_0(r)$.
t = time elapsed since the beginning of the leaching process (s).

For reasonable accuracy the indicated summation series must include around 200 terms.

Reference:

Anders O. U., Bartel J. F., and Altschuler S. J. (1978) Determination of the leachability of solids. Anal. Chem. **50**(4), 564-569.

Table SI-1. Summary of extractable and residual forms of ^{85}Sr and ^{134}Cs in fresh and aged PELCAPs with and without test soils using a 15-step sequential extraction protocol (*13*).

Sequential Extraction of PELCAPs With & Without Soils Compared to Soils Without PELCAPS

	Unheated Soil Without PELCAPs		1000°C Heated Soil Without PELCAPs	
	^{85}Sr	^{134}Cs	^{85}Sr	^{134}Cs
Water Soluble	0.0375 ± 0.0006	0.0047 ± 0.0007	0.0008 ± 0.0004	0.0001 ± 0.0001
Cation Exchangeable	0.8816 ± 0.0016	0.0001 ± 0.0008	0.0006 ± 0.0005	0.0002 ± 0.0003
Acid Soluble	0.0583 ± 0.0014	0.0014 ± 0.0009	0.1441 ± 0.0008	0.0046 ± 0.0002
Suspended	0.0001 ± 0.0002	0.0205 ± 0.0011	0.0040 ± 0.0003	0.0049 ± 0.0007
Residual	0.0086 ± 0.0005	0.9628 ± 0.0015	0.8461 ± 0.0002	0.9905 ± 0.0006
Total	0.9861 ± 0.0021	0.9895 ± 0.0035	0.9956 ± 0.0012	1.0003 ± 0.0015

	Unheated Soil With PELCAPs		1000°C Heated Soil With PELCAPs	
	^{85}Sr	^{134}Cs	^{85}Sr	^{134}Cs
Water Soluble	0.1018 ± 0.0008	0.0000 ± 0.0000	0.0002 ± 0.0001	0.0002 ± 0.0002
Cation Exchangeable	0.7623 ± 0.0026	0.0001 ± 0.0001	0.0006 ± 0.0005	0.0002 ± 0.0001
Acid Soluble	0.0892 ± 0.0021	0.0042 ± 0.0003	0.1100 ± 0.0002	0.0031 ± 0.0001
Suspended	0.0000 ± 0.0000	0.0004 ± 0.0004	0.0008 ± 0.0005	0.0014 ± 0.0012
Residual	0.0164 ± 0.0002	0.9907 ± 0.0019	0.8765 ± 0.0048	0.9935 ± 0.0028
Total	0.9696 ± 0.0024	0.9955 ± 0.0027	0.9880 ± 0.0056	0.9983 ± 0.0041

	PELCAPs Without Soil		Reagent Blanks (No Soil or PELCAPs)	
	^{85}Sr	^{134}Cs	^{85}Sr	^{134}Cs
Water Soluble	0.3433 ± 0.0046	0.7513 ± 0.0091	0.8058 ± 0.0120	0.9464 ± 0.0053
Cation Exchangeable	0.6583 ± 0.0034	0.2004 ± 0.0062	0.2085 ± 0.0053	0.0213 ± 0.0053
Acid Soluble	0.0051 ± 0.0033	0.0485 ± 0.0026	0.0014 ± 0.0052	0.0357 ± 0.0050
Suspended	0.0000 ± 0.0000	0.0003 ± 0.0002	NA	NA
Residual	0.0012 ± 0.0006	0.0006 ± 0.0002	NA	NA
Total	1.0079 ± 0.0039	1.0011 ± 0.0030	1.0157 ± 0.0052	1.0034 ± 0.0050

Sequential Extraction of PELCAPs After Field Deployment For 180 Days

	Unheated Soil With PELCAPs		1000°C Heated Soil With PELCAPs	
	^{85}Sr	^{134}Cs	^{85}Sr	^{134}Cs
Water Soluble	0.0380 ± 0.0519	0.0001 ± 0.0002	0.0013 ± 0.0002	0.0001 ± 0.0001
Cation Exchangeable	0.0328 ± 0.0467	0.0001 ± 0.0002	0.0008 ± 0.0002	0.0004 ± 0.0003
Acid Soluble	0.3342 ± 0.0377	0.0010 ± 0.0005	0.0351 ± 0.0005	0.0008 ± 0.0003
Suspended	0.0342 ± 0.0093	0.0014 ± 0.0010	0.0020 ± 0.0010	0.0017 ± 0.0004
Residual	0.6084 ± 0.0401	0.9999 ± 0.0032	0.9464 ± 0.0032	0.9911 ± 0.0182
Total	1.0477 ± 0.0871	1.0026 ± 0.0047	0.9856 ± 0.0047	0.9942 ± 0.0189

Table SI-2. Cation exchange capacity (CEC) measurements with unheated and heated test soil with and without encapsualtion in freshly-prepared PELCAPs and in PELCAPs deployed in stream water for six months.

Soil Treatment and Configuration:	CEC (meq/100g ± standard error)
Unheated Soil Without PELCAP	13.3 ± 0.2
Unheated Soil Within Fresh PELCAP	12.7 ± 0.3
Unheated Soil Within PELCAP After Six Months	13.0 ± 0.2
1000°C Heated Soil Without PELCAP	1.9 ± 0.2
1000°C Heated Soil Within Fresh PELCAP	3.8 ± 0.2
1000°C Heated Soil Within PELCAP After Six Months	7.9 ± 0.3

Table SI-3. Summary of chemical characteristics of grab water samples collected at the Northwest Tributary (NWT) and Core Hole 8 (CH8) Sump field sites employed for in situ leaching of PELCAPs.

Northwest Tributary (NWT) Stream Water

Water Property	Units	Average	Range
Temperature	°C	18.2	10.8 - 22.0
pH	-log[H+]	7.3	6.28 - 7.60
Electrical Conductivity	μmhos/cm	399	59 - 526
Hardness	mg $CaCO_3$/L	242	49 - 299
Alkalinity	mg $CaCO_3$/L	209	18 - 259
^{90}Sr	dpm/mL	0.70	0.23 - 1.18

Core Hole 8 (CH8) Groundwater

Water Property	Units	Average	Range
pH	-log[H+]	6.9	6.83 - 7.04
Electrical Conductivity	μmhos/cm	393	350 - 414
Hardness	mg $CaCO_3$/L	202	151 - 219
Alkalinity	mg $CaCO_3$/L	159	136 - 181
^{90}Sr	dpm/mL	4.94	3.96 - 6.27
Na	mM	0.50	0.42 - 0.54
Mg	mM	0.33	0.30 - 0.36
Ca	mM	1.44	1.36 - 1.51
Fe	μM	2.64	2.33 - 2.93
Sr	μM	1.67	1.58 - 1.74

Uptake of ^{90}Sr by PELCAPs

Because of the significant activity of ^{90}Sr present in the CH8 groundwater (Table SI-3), the final uptake of ^{90}Sr by these PELCAPs deployed at the CH8 site was observed by nondestructive Cerenkov emissions from all the sequential extracts of these PELCAPs (Table SI-4). Interestingly, the activity of ^{90}Sr within a given soil extract did not depend on whether the soil was spiked with either ^{85}Sr or ^{134}Cs or how much of either activity remained in the PELCAPs after the final removal; the activity of these gamma emitting isotopes was too low in these extracts to yield any interference with the Cerenkov emissions from a hard beta emitters like ^{90}Sr (and its seqular equilibrated daughter, ^{90}Y). Thus, all PELCAPs with the same soil (unheated or thermally stabilized) were grouped as replicates in Table SI-4. The unheated soil, with its greater CEC, yielded much more ^{90}Sr than the heated soil, particularly in the 0.1 *N* $CaCl_2$ extracts where most exchangeable cations would be expected. The apparent distribution coefficient (K_d) for total ^{90}Sr activity between the unheated soil (349 dpm/g) and the average activity in the groundwater (4.9 dpm/mL) calculated to a value of 70 mL/g which is the same order of magnitude as the R_s calculated for release of ^{85}Sr in the diffusive modeling discussed previously (Table 1, Main Text). However, even the heated soil with its minimal CEC, exhibited greater uptake of ^{90}Sr than neat PELCAPs whose activity of ^{90}Sr likely represented its equilibrated constituent groundwater which amounted to 85% of the neat PELCAP mass. Although ^{90}Sr could not be assayed non-destructively in the residual soil (only in extracts of PELCAPs), its uptake by the PELCAPs indicates how contaminant uptake and release, using different isotopes of strontium, can be assayed simultaneously during in situ field deployment. The complete sequential extraction of ^{90}Sr from PELCAPs after six months deployment in CH8 groundwater is depeicted in Figure SI-4.

Table SI-4. Summary of sequential extractions of ^{90}Sr taken up by PELCAPs after six months deployment in a ^{90}Sr-contaminated groundwater at the ORNL corehole 8 collection sump.

Extractable Phase	Unheated Soil (dpm)	Heated Soil (dpm)	No Soil (dpm)
Water Soluble	47.5 ± 8.3	38.2 ± 3.6	31.0 ± 2.4
Cation Exchangeable	423.2 ± 27.3	97.4 ± 16.8	52.5 ± 5.1
Acid Soluble	226.4 ± 41.6	40.1 ± 31.4	26.0 ± 8.6
Total	697.1 ± 77.3	175.7 ± 51.8	109.5 ± 16.1

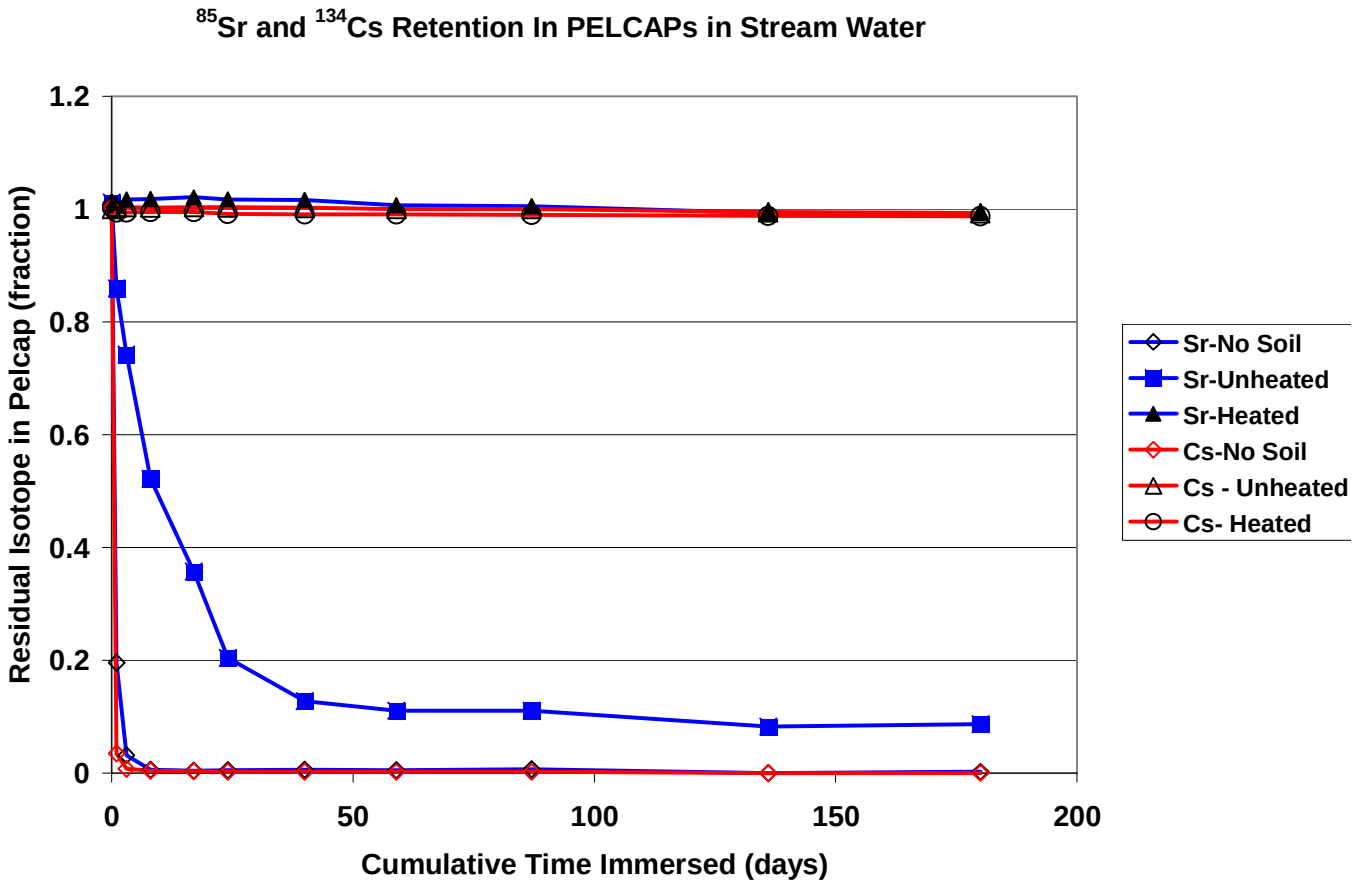

Figure SI-1. Normalized retention of ^{85}Sr and ^{134}Cs in PELCAPs, with and without soil, during six months of suspension in stream water of the Northwest Tributary (NWT) of White Oak Creek, Oak Ridge National Laboratory.

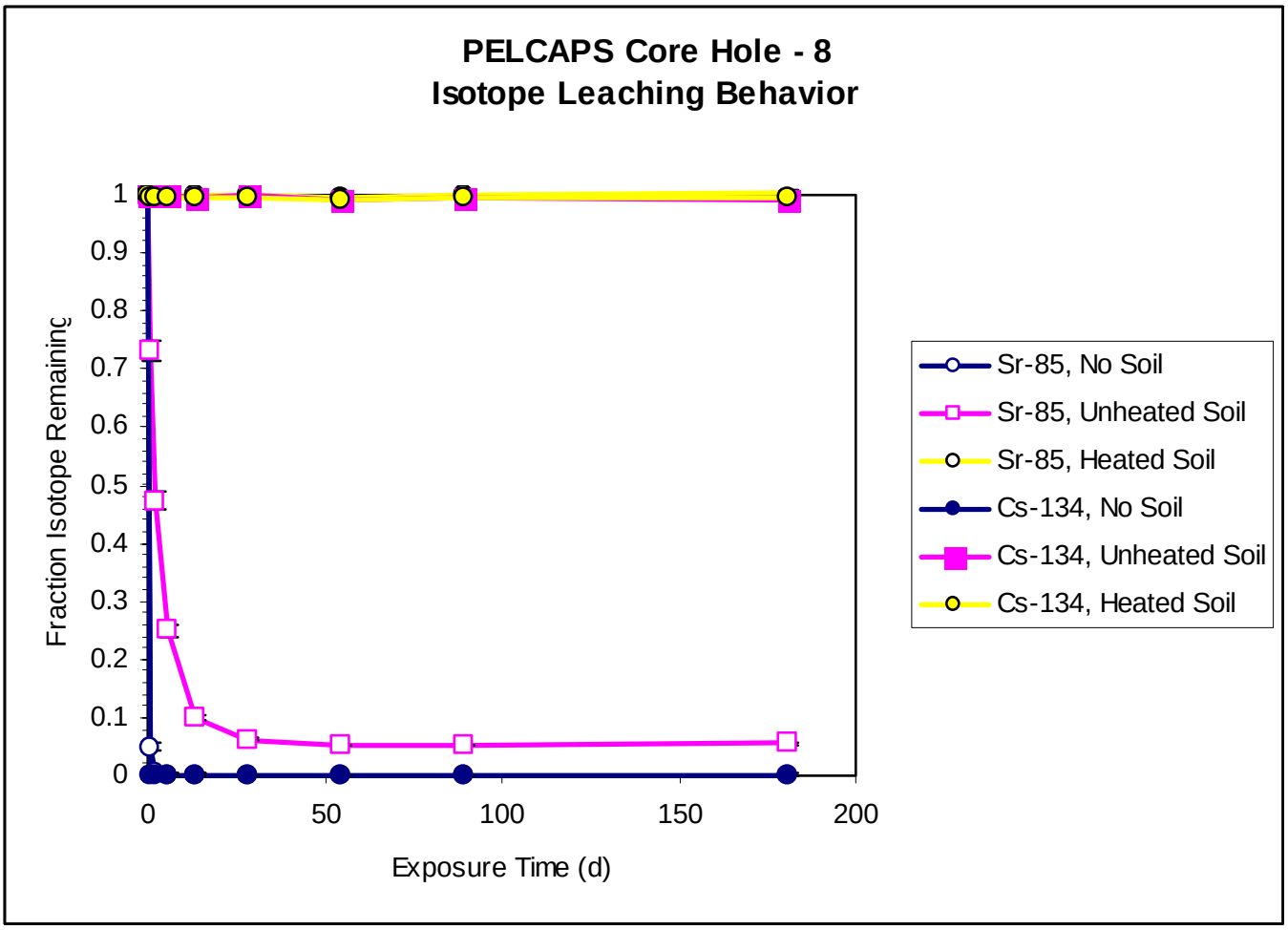

Figure SI-2. Normalized retention of ^{85}Sr and ^{134}Cs in PELCAPs, with and without soil, during six months of suspension in groundwater within the sump of core hole #8 (CH8) at Oak Ridge National Laboratory, Oak Ridge, Tennessee.

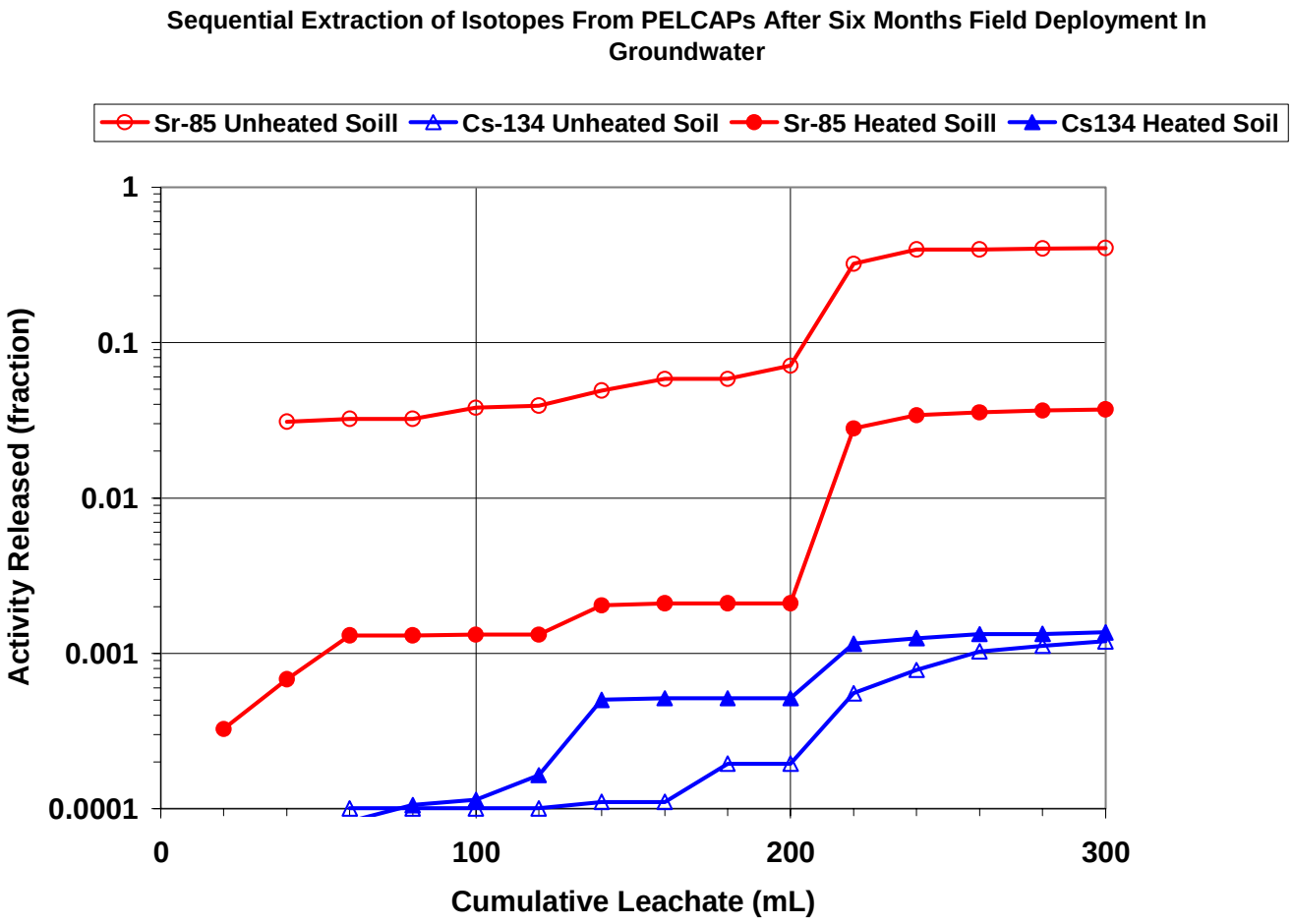

Figure SI-3. Sequential extraction of residual ^{85}Sr and ^{134}Cs from PELCAPs containing heated or unheated soil after six months of suspension in groundwater in the sump of Oak Ridge National Laboratory Core Hole #8 (CH8).

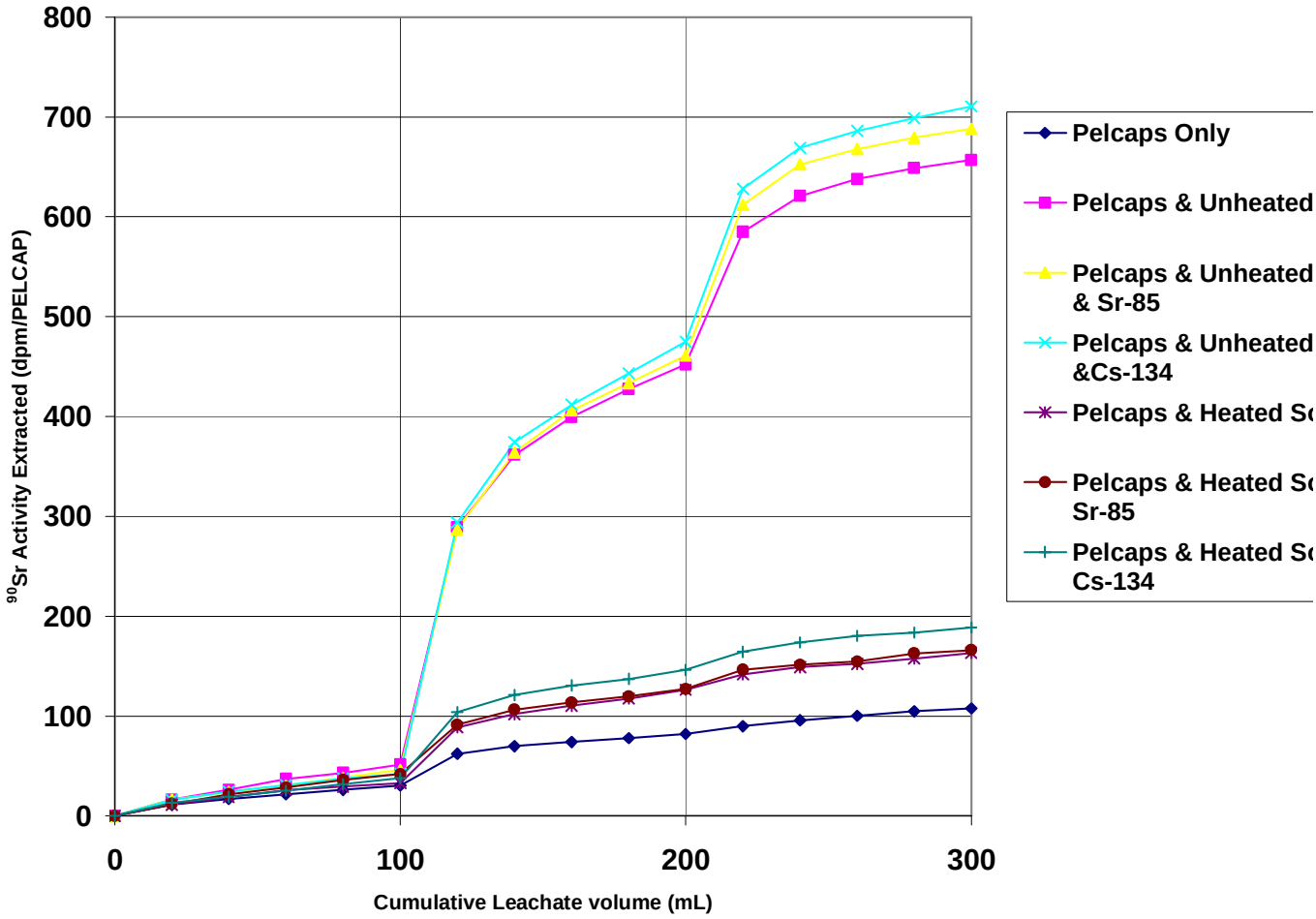

Figure SI-4. Sequential extraction of ^{90}Sr from PELCAPs, with and without soil, after six months of suspension in groundwater in the sump of Core Hole #8 (CH8) at Oak Ridge National Laboratory.

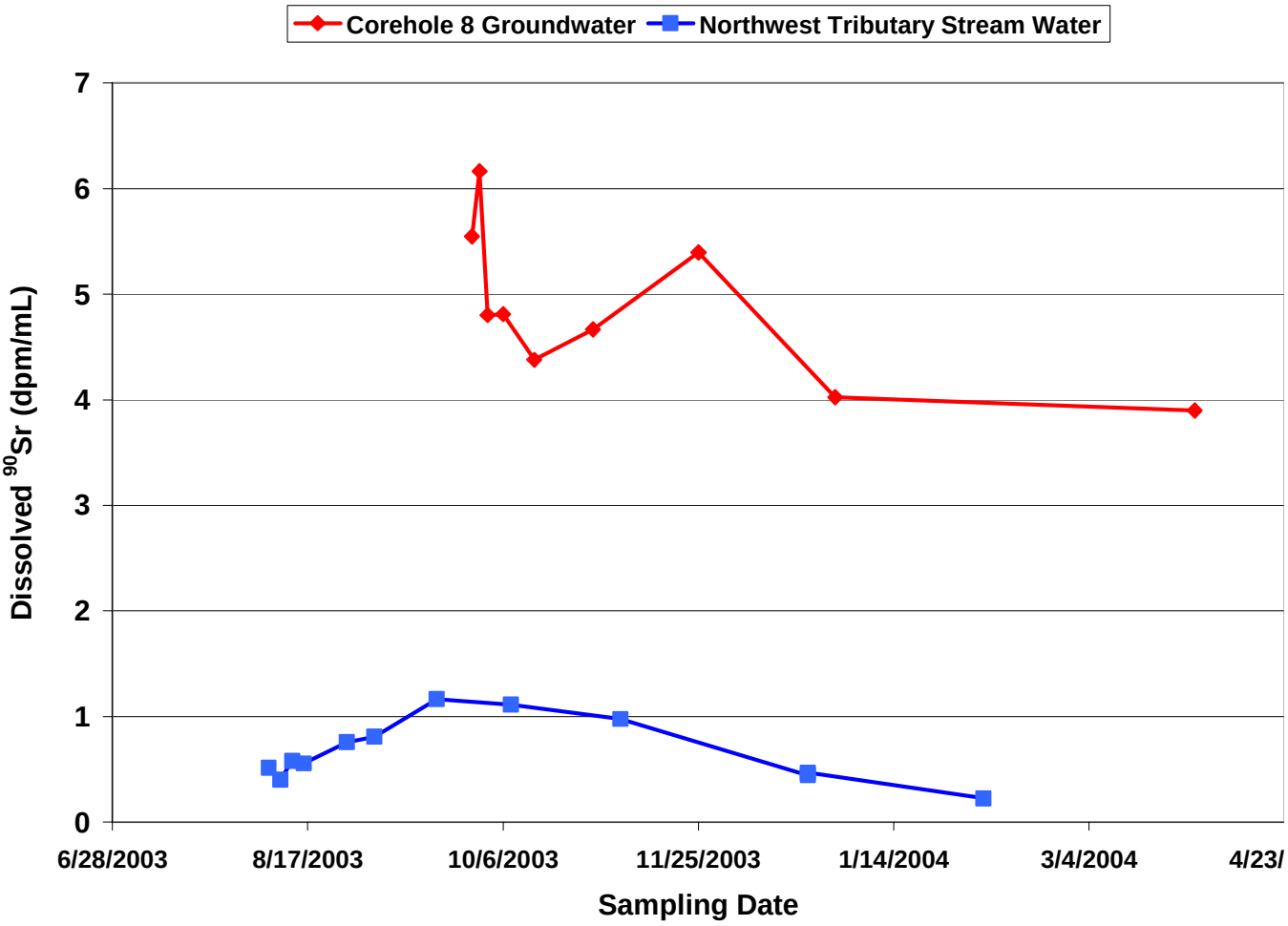

Figure SI-5. Activity of ^{90}Sr in water samples taken during the six month periods when PELCAPs were suspended in either Core Hole #8 (CH8) or the Northwest tributary of White Oak Creek, Oak Ridge National Laboratory.

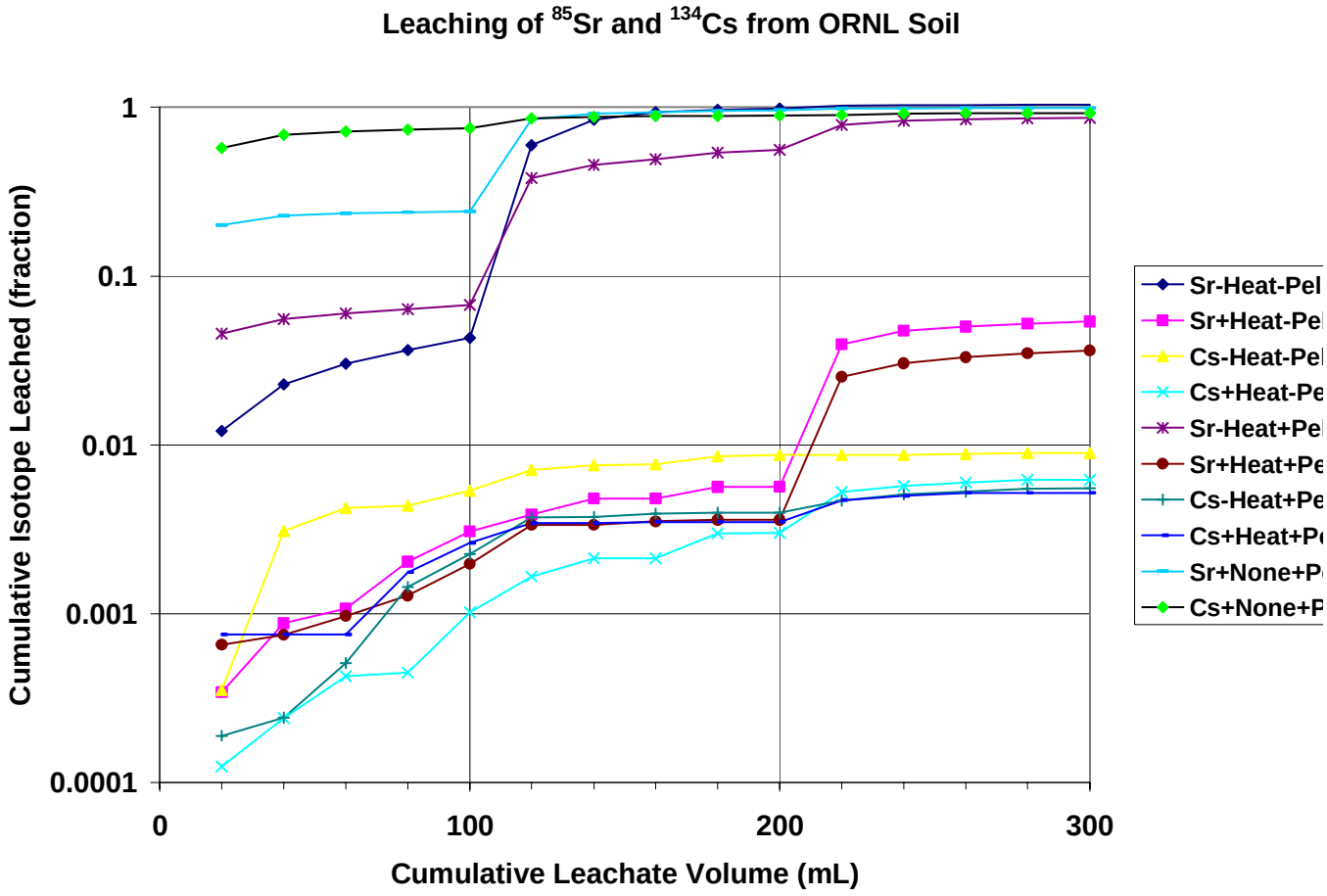

Figure SI-6. Sequential extraction of ^{85}Sr and ^{134}Cs from PELCAPs, with and without heated or unheated soil, in laboratory tests using an initial 16-hour extraction interval followed by four one-hour intervals for each extractant.