

IN-SITU SAMPLE PREPARATION FOR RADIOCHEMICAL ANALYSES OF SURFACE WATER

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A new method for radionuclide sample analysis of surface water has been demonstrated at the Savannah River Site, a U.S. Department of Energy manufacturing facility, currently in standby. The method makes use of selective solid phase extraction (SPE) disks being placed in a modified portable aqueous sampler. The analytes currently measured by this in-situ preparation are ⁹⁹Tc, ⁹⁰Sr, ¹³⁷Cs and ^{58,60}Co. The SPE disks are placed singly or in series in an automatic sampler; water is passed through the SPE disks at the time of collection. The disks are then returned to the laboratory for counting; no additional chemical separation is performed prior to analysis. The modified automatic samplers have been placed at several different locations around the Savannah River Site along side traditional samplers. The traditional samplers were used to collect water which was analyzed for the same analytes using standard laboratory methods. Most of the sample results were less than five times the method detection limit, thus a mean difference statistic was used to compare the data. Within the uncertainties of the methods, there was no statistical difference in the ⁹⁹Tc results, although a slight negative bias was observed for the in-situ ⁹⁰Sr results versus the lab method. The in-situ method produces a dissolved (<0.45µm) and particulate ¹³⁷Cs result, whereas the traditional laboratory method measures total activity in the sample. As expected, a negative bias was found between the dissolved in-situ result and the laboratory total ¹³⁷Cs result, and a positive bias between the in-situ total (dissolved plus particulate) and laboratory total ¹³⁷Cs result.

Technetium-99, ⁹⁰Sr, ¹³⁷Cs and ^{58,60}Co are fission and activation products that were produced from the uranium in the nuclear reactors at the Savannah River Site (SRS). During the production of nuclear materials at the SRS in Aiken SC, for the U.S. Department of Energy (DOE), these isotopes have been released to the environment in small quantities. (Strontium-89 and ¹³⁴Cs were

also produced, however they have decayed to insignificant levels at the SRS.) To ensure the public safety, an extensive environmental monitoring program has been in place at the SRS since it began operation. A similar program is in place at all DOE facilities, resulting in the collection and analysis of millions of samples per year. Typical matrices include surface water, groundwater, soil, vegetation, air filters, local biota and crops, as well as bioassay samples. Typical analytes of interest at the SRS include U, Pu, radiostrontium, radiocesium and tritium, with analyses of radioiodine, ^{99}Tc , ^{14}C , radiocobalt, americium/curium and neptunium performed less frequently; in the past, analyses of ^{32}P , ^{51}Cr , ^{65}Zn , ^{95}Zr , ^{95}Nb , $^{103,106}\text{Ru}$, and $^{141,144}\text{Ce}$ have also been performed. A similar list of routine and infrequent analytes and matrices can be accumulated at every DOE facility. Thus any new techniques that can reduce the cost of analyses, or provide faster or better quality results, can have a significant impact on the environmental monitoring budget of the DOE.

Recently, the 3M Company, St. Paul MN, USA, introduced a line of solid phase extraction (SPE) disks specific for radiochemical analyses. The disks contain ion selective resins enmeshed in a Teflon support. When an aqueous sample is passed through the SPE disk, the specific analyte is extracted by the resin in the disk¹. The SPE disk is selective enough to require little sample pretreatment or additional sample clean up prior to counting. The three SPE disks used in this study were: the 3M Empore™ Technetium RAD disk, containing the GD-1 adsorbent, for the analysis of ^{99}Tc in solution; the 3M Empore™ Strontium RAD disk, containing the AnaLig™ adsorbent particles, for the analysis of ^{90}Sr ; and the 3M Empore™ Cesium RAD disk, containing potassium cobalt ferrocyanide (KCFC), for the analysis of ^{137}Cs and radiocobalt in solution.

These three SPE disks were placed in a modified automatic sampler as described in BEALS et al.² During an initial field test, samples were collected at routine environmental monitoring

locations, however the sampling frequency and specific analytes measured were not the same by both this new in-situ sample processing method and the routine environmental monitoring measurements, allowing only general conclusions to be drawn about the precision and bias of the field method. A second study was therefore designed, modifying the sample collection frequency, analytes measured and detection limit (the lab method detection limit had to be lowered to meet the field method due to larger samples processed by the in-situ method) to provide directly comparable results. The results of this second, more detailed, study are described herein.

Experimental

Laboratory Methods: Technetium-99 is not routinely measured at the SRS therefore a contract laboratory was used to provide independent sample results. An 8 liter sample was provided to General Engineering Laboratories of Charleston SC for analysis. Briefly, a ^{99m}Tc tracer was added to the sample. The sample and tracer were equilibrated by heating in the presence of hydrogen peroxide; this also serves to ensure the technetium is in the oxidized form. The sample was heated to near dryness. If any color was present, the sample was passed first through an amberlite resin column to remove the organics, and then through a column containing TEVA® resin (EiChroM Industries, Darien IL) for the selective extraction of technetium. After washing with dilute nitric acid the resin was added directly to a vial containing liquid scintillation cocktail. The ^{99m}Tc was counted by gamma spectrometry to determine the chemical recovery, and then the ^{99}Tc counted by liquid scintillation spectrometry after the decay of the ^{99m}Tc . Typical detection limits reported were about 0.5 pCi/l.

The ^{90}Sr and ^{137}Cs measurements were made by the Environmental Monitoring Section at the SRS. The routine methods were modified to improve the method detection limits. A 2 liter sample was used for the ^{90}Sr analysis, as opposed to the routine 1 liter sample aliquot. The samples were acidified with nitric acid and then heated to near dryness. After wet ashing with concentrated nitric acid and hydrogen peroxide a strontium carrier was added and the sample centrifuged to remove any undissolved residue. The strontium was purified by a series of precipitations and finally precipitated as the carbonate. The precipitate was transferred to a stainless steel planchet, weighed to determine chemical recovery, and counted on a gas flow proportional alpha/beta detector. The method detection limit was approximately 1 pCi/l by this method and sample volume.

For the ^{137}Cs determination, a 1 liter sample of unfiltered water was measured into a 1 liter Marinelli beaker and counted on a high purity germanium gamma spectrometry detector (HPGe) for 1000 minutes, as opposed to the routine 100 minutes. The 661 keV gamma-ray of ^{137}Cs was monitored to calculate sample activity. This results in a total (dissolved plus particulate) ^{137}Cs detection limit of about 2.5 pCi/L.

In-Situ Field Method: Based on laboratory studies¹ the SPE disks were placed in the following series: Sr first, followed by Cs, and lastly Tc. All three disks were placed in a single filter housing allowing the water to pass sequentially through the disks. 3M Co. now has prepared a "RLS" (rapid liquid sampler) housing which seals each disk in a housing with luer-lok inlet and outlet fittings. The RLS disks can be assembled in series without the different disks in actual contact, improving upon this early design.

An ISCO Inc., Lincoln NE, 3710 automatic portable sampler was used to collect and process the sample water. A modification was provided by ISCO (now commercially available as the SPX

option) to allow the incorporation of the SPE disks and provide in-situ sample processing at the time of sample collection.² Briefly, the 3710 sampler is programmed to collect a small aliquot of surface water at predetermined intervals. For this study, 30 mL aliquots were collected at either 30 minute or 60 minute intervals. The ISCO uses a peristaltic pump to bring the water to the sampler. The water is pumped through a Gelman GWV high capacity, in-line groundwater filter, 0.45µm particle size, and into a sealed pressure chamber. (Of the three analytes measured during this study only cesium is expected to have a significant portion of the total associated with suspended particulate material.) The air pressure is then used to push the water through the SPE disks. The processed water is collected in a jug in the base of the unit for exact volume determination. Typical sample volumes were 8-10 liters of water.

Once a week, or once every other week, depending on the sample location, the particle filter and filter housing containing the SPE disks were returned to the lab for counting. The SPE filter housing was opened and the three disks separated. The Technetium and Cesium disks were simply air dried for a few hours and then finished drying in an oven set at 70°C for 20 minutes. The Strontium disks were mounted on a filter flask and rinsed with 20 mL of 2M HNO₃ to wash any ⁹⁰Y from the disk. The time of the acid rinse was noted to make a correction for the ingrowth of ⁹⁰Y from the time of separation (acid rinse) to time of counting. The disks were then rinsed with a few mL of DI water to remove the excess acid, and dried as the other disks.

The Technetium and Strontium disks were counted by alpha/beta gas flow proportional counting in the Environmental Monitoring Counting Facility, for 20 minutes each, within a few days of return to the lab (within several hours for the Strontium disks). Several of the Strontium disks were recounted a few weeks later, at full ⁹⁰Y ingrowth, to confirm the lack of interference by this method (Figure 1). The Cesium disks and particle filters were counted overnight by HPGe

in the Savannah River Technology Center's Underground Counting Facility (UCF); the UCF has a very low and stable background thus affording very low limits of detection. The Cesium disks were sealed in 47 mm petri dishes for counting, using this filter geometry for calibration. The nipples on the top and bottom of the particle filters were cut off so that the particle filter could fit into another standard counting geometry vial. The filter was placed upside down in the counting vial with the total height of the filter being used to determine the counting efficiency. This could cause a positive bias in the calculated activity if all the activity was concentrated in the upper part of the filter capsule. Several filters were counted in this upside down geometry and again right side up; within the uncertainties of the measurement no significant difference in calculated activity was observed.

Prior to implementing the in-situ sample processing, several tests were completed in the lab using spiked SRS stream water to determine the extraction efficiency of the individual disks. One test, designed to determine the breakthrough of the analyte of interest, indicated that for sample volumes up to 10 liters, the extraction of ^{99}Tc and ^{137}Cs from solution was greater than 99% and 95%, respectively.¹ Cobalt is also extracted by the Cesium disk with greater than 90% extraction efficiency over the volumes tested.³ The Strontium disk, however, does have a limited capacity based on the concentration of strontium in the water. Strontium-90 was added to SRS surface water, and then pumped through two Strontium SPE disks in series. The percent breakthrough versus sample volume is shown in Figure 2¹. The regression curve was calculated by the SigmaPlot computer program. The ^{90}Sr results have all been corrected for extraction efficiency based on the volume processed and the regression curve calculated in Figure 2.

3M Co. recommends that for routine sample processing a sample be made 2M in nitric acid prior to extraction by the Strontium disk.⁴ Acidification of the sample is used to reduce the

affinity of other metals for the Strontium disk. In the field sampler, the water cannot be acidified prior to processing. Based on the agreement between the first and second sample counts (Figure 1) there does not appear to be any significant interference extracted by the SPE disks from these waters. In other studies at the SRS, radium was noted to be co-extracted by the Strontium disk. This was especially important in groundwaters where the radium activity is often much higher than the ^{90}Sr . Evidence of this contaminant may be observed by noting the alpha counts identified by the gas flow detector. Radium has two alpha emitting isotopes, 224 and 226, and one beta emitting isotope, 228; all are ubiquitous in natural waters although the ratio may vary by strata type. If the alpha counts are above background for the Strontium disk, there is also the potential the beta counts may be positively biased. Repeated rinsing of the Strontium disk with dilute nitric acid may remove some of the radium. For these surface water samples, co-extraction of radium did not appear to be a problem based on the alpha count rate.

Sample Locations: The SRS (total area of 300 square mile) has several streams within its boundaries. The Fourmile Branch (4MC) originates near the center of the Site, coursing past the separation canyons and the C reactor, prior to entering the Pen Branch Swamp. The 4MC receives discharges along seep lines from contaminated groundwater⁵ thus making it an ideal location to test field sampling and monitoring equipment. Three locations were chosen for this study: 4MC-1C, near the headwaters of the creek, only receiving surface water discharges; 4MC-2, midway down the creek, influenced by seeps from the H area seepage basin groundwater; 4MC-A7, furthest point down the creek, below the F area seepage basins and C reactor seepage basins. Typical water quality parameters are shown in Table 1.

Two ISCO automatic samplers were placed at each of the three chosen locations. One sampler was used to collect the extra water required for the laboratory analyses and the second sampler

was equipped with the SPX modification containing the three SPE disks. The disks, particle filter and extra water were collected weekly at 4MC-1C and bi-weekly at 4MC-2 and 4MC-A7. The samplers were thus set to collect 30 mL every 30 minutes at 4MC-1C and 30 mL every 60 minutes at the other two locations. This should result in a 10 liter sample being processed over the sampling period; the ISCO will collect a maximum of 15 liters per sampling period. The samplers were installed for a total of 16 weeks during the summer of 1997 resulting in eight data points per analyte at 4MC-2 and 4MC-A7 and 16 points at 4MC-1C.

Results and Discussion

The results of all of the sample analyses are shown in Figures 3, 4 and 5 (note the difference in scale between sampling locations). The error bars are the 2 sigma counting error only for the field result and the 2 sigma propagated error for the lab result. The ^{99}Tc and ^{90}Sr results appear to agree in most cases while the agreement is not as evident for the ^{137}Cs results since one technique measures total activity (lab method) and the other measures the dissolved and particulate activities separately (in-situ field method).

Figure 6 shows all the ^{99}Tc results from this study; the lab results versus the field results. All the results are less than five times the method detection limits thus a mean difference statistic, which propagates the uncertainty in the measurement, was used to determine the precision of the results. The mean difference is calculated as the absolute value of the difference in the results divided by the square root of the sum of the squared 2 sigma errors, as shown below:

$$\text{MD} = |R_1 - R_2| / (s_1^2 + s_2^2)^{1/2}$$

where R_1 and R_2 , and s_1 and s_2 , are the result and 2 sigma error of the field and lab result, respectively. A value of less than 1.96 indicates the results are precise. The results of the mean difference calculation are shown in Figure 7; all fall below the acceptance criteria of 1.96 indicating no difference in the lab and field based results.

Another way to compare the results is to calculate the bias of the field method compared to the standard lab method, bias being calculated as:

$$\text{Bias} = (\text{field result} - \text{lab result}) / \text{lab result}$$

The result of the bias calculation for all samples having a positive result are shown in Figure 8. The mean bias of the ^{99}Tc results is insignificant within the errors of these measurements and within the standard deviation of the calculated mean.

Figure 9 shows all the ^{90}Sr results from this study; the lab results versus the field results. In this data set there does appear to be a bias in the results as the calculated regression line is well below unity with an r^2 of 0.73; the slope is calculated to be 0.75 with a calculated intercept of 0.012. As only six results are greater than five times the method detection limits the mean difference statistic was again applied to the whole data set. The results are shown in Figure 10. Several sample results failed the mean difference criteria indicating a significant difference in the results by the two methods. The bias was calculated for all these sample results as above and is shown in Figure 8. The mean bias of the field method compared to the lab method is 23% low, nearly identical to that estimated from the slope of the regression line in Figure 9.

Three of the five samples that greatly exceeded the mean difference criteria were from sample point 4MC-2. In determining the extraction efficiency for volume versus breakthrough of ^{90}Sr , water was used from the Upper Three Runs Creek on the SRS and from the Savannah River, which is adjacent to the SRS. If the Fourmile Branch strontium concentration is significantly different from the tested waters, the regression curve could be biased. The curve appears satisfactory for the 4MC-1C and 4MC-A7 locations but possibly not for this location. Further testing will be performed to test this hypothesis.

Alternatively, the stream bottom at 4MC-2 is very sandy as opposed to the rock and fine silt that are at 4MC-1C and 4MC-A7. Strontium usually exists in the dissolved phase, not associated with particle surfaces, but perhaps at this location (4MC-2) there is some ^{90}Sr associated with the sandy bottom material. During rain events, which would stir up the bottom, this particulate ^{90}Sr would be suspended and picked up by the two samplers. The particulate ^{90}Sr would be removed on the particle filter by the in-situ sample processing and not be counted; the particulate ^{90}Sr would be released to solution during the acidification step of the lab method and therefore be counted by this method. Two of the three outliers from 4MC-2, and the one outlier from 4MC-A7, did have a large calculated particulate ^{137}Cs concentration in the same period that the in-situ ^{90}Sr result was biased low (Figure 4 and 5).

Figure 11a and 11b show the comparison of the in-situ sample results with the lab results for ^{137}Cs ; Figure 11a shows the in-situ processed dissolved ^{137}Cs concentration versus the total lab measured ^{137}Cs and 11b shows the total (dissolved plus particulate) in-situ processed ^{137}Cs concentration versus the total lab measured ^{137}Cs . As expected, the calculated (in-situ processed) dissolved ^{137}Cs concentration was less than the measured total ^{137}Cs concentration by the lab (Figure 11a). Unexpectedly, the total ^{137}Cs concentration measured by the in-situ processing was

much higher than determined by the lab (Figure 11b). This can also be seen in Figure 8; the mean bias of the field dissolved result is low compared to the lab total result, while the mean bias of the field total result is very high compared to the lab result.

Some of the bias in the total results may be due to an overestimation of the particulate ^{137}Cs concentration by the field method due to the counting configuration used, as mentioned earlier. However, in the samples tested orientation of the filter capsule on the HPGe did not seem to have a great effect. Another possibility is that when the sample is returned to the lab for analysis, it often sits in the collection carboy for several days prior to being poured up for analysis. During this time the sample is not acidified, which may allow some of the fine particulate ^{137}Cs to adhere to the sides of the carboy, and does allow some of the suspended sediment to settle to the bottom of the carboy. When the sample (a 1 liter aliquot out of 10-12 liters) is poured up for analysis, the carboy may not be completely mixed prior to taking an aliquot, thus biasing the total activity measurement. Also, once the sample is measured into the Marinelli beaker for counting, it may sit for several days prior to being put on the detector. Visible solids can be seen that settle to the bottom of the Marinelli beaker; these solids are below the view of the detector thus are not counted.

An EPA Office of Water October 1993 policy memorandum states that the *dissolved* metal concentration in water should be used to set and measure compliance with water quality standards. The disparity in the ^{137}Cs results presented here suggest that this policy may be appropriate for radionuclide measurements as well. According to the EPA guidance, the sample is filtered, unacidified, through a $0.45\mu\text{m}$ particle filter prior to any analyses being completed. This is completed using the in-situ sample processing presented in this paper.

Conclusions

Surface water samples were collected and processed automatically in the field using a programmable sampler and ion selective solid phase extraction disks. Weekly, or bi-weekly, the SPE disks were returned to the lab for counting of the specific radionuclide activity. At the same time, water was collected for return to the lab for routine analysis. Statistical analysis of the paired results showed no discernible bias in the ^{99}Tc results by the lab and field methods. The ^{90}Sr in-situ results were biased low compared to the lab results; this may be due to the in-situ sample being filtered or due to an incorrect uptake calibration curve being used. Because the in-situ sample is filtered and the lab sample is not, comparing the ^{137}Cs data is not as straight forward as for the other two analytes. However, the in-situ processing does appear to provide reasonable results when compared to the lab results.

Sample results were available within a few days for the in-situ processed samples as no additional sample preparation was required prior to counting. Results from routine analyses took weeks to become available, especially for the ^{99}Tc results which had to be sent to an offsite contract lab for analysis. The reduced sample handling resulted in a significant time and hard dollar cost savings. Due to processing samples in the field, a larger sampler volume was used as compared to routine laboratory procedures, resulting in a lower detection limit for the in-situ method. Overall, this technique holds significant promise to provide equivalent or better results, faster and cheaper than laboratory based methods, thereby reducing the overall cost of environmental monitoring at nuclear facilities.

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Table 1. Typical Water Quality Parameters for Fourmile Branch⁶

parameter	units	4MC-A7
water volume	L	0.84-2.8 E09
pH		6.0-7.1
dissolved oxygen	mg/l	5.1-15.9
alkalinity	mg/l	7-24
total organic carbon	mg/l	ND-8.4
suspended solids	mg/l	1-13
chloride	mg/l	3-7
nitrogen (nitrate)	mg/l	2.0-4.6

Figure 1.

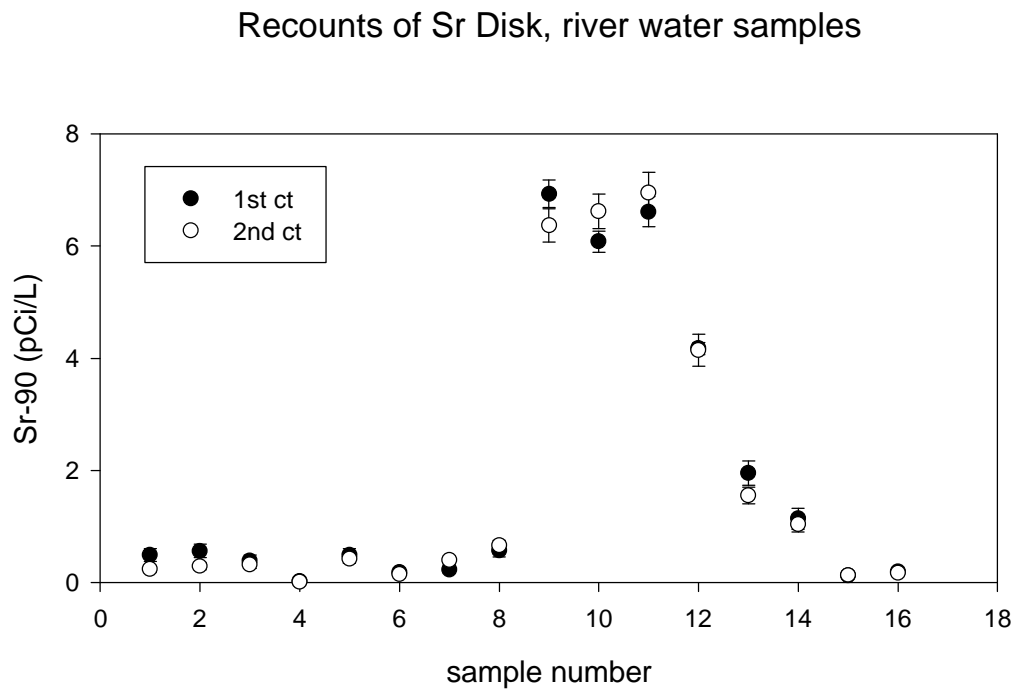


Figure 2.

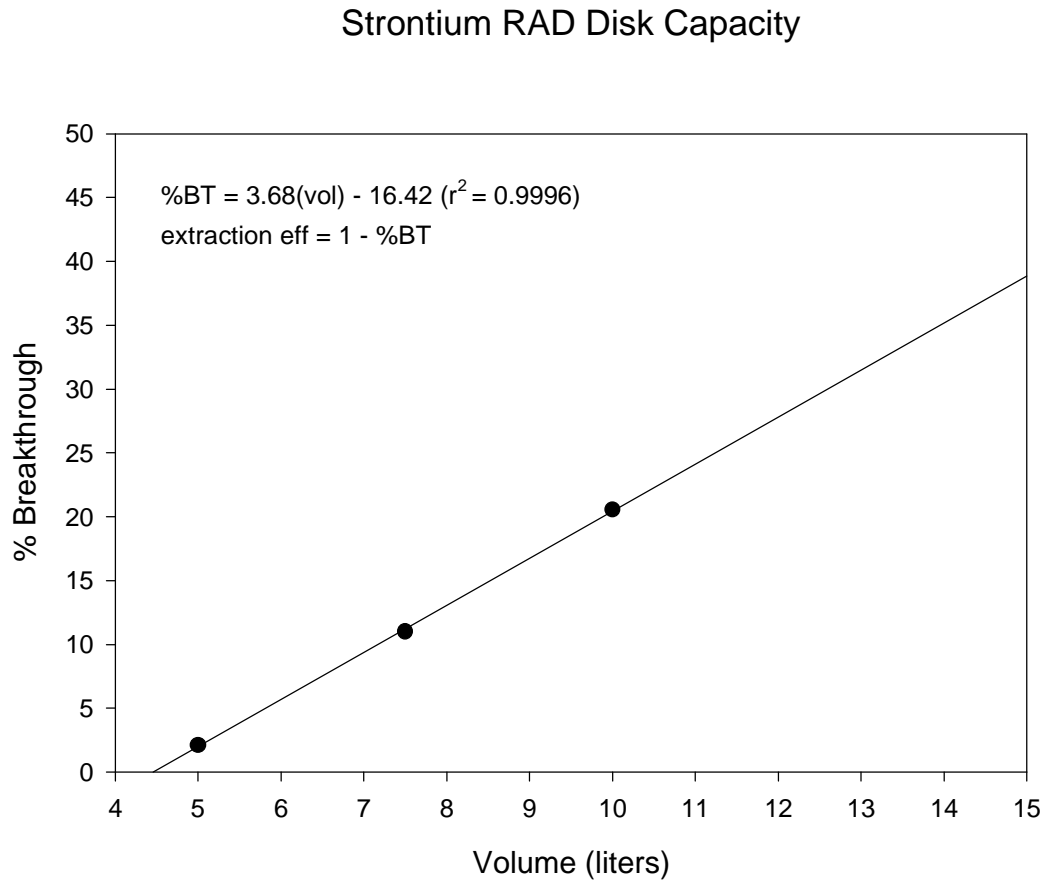


Figure 8.

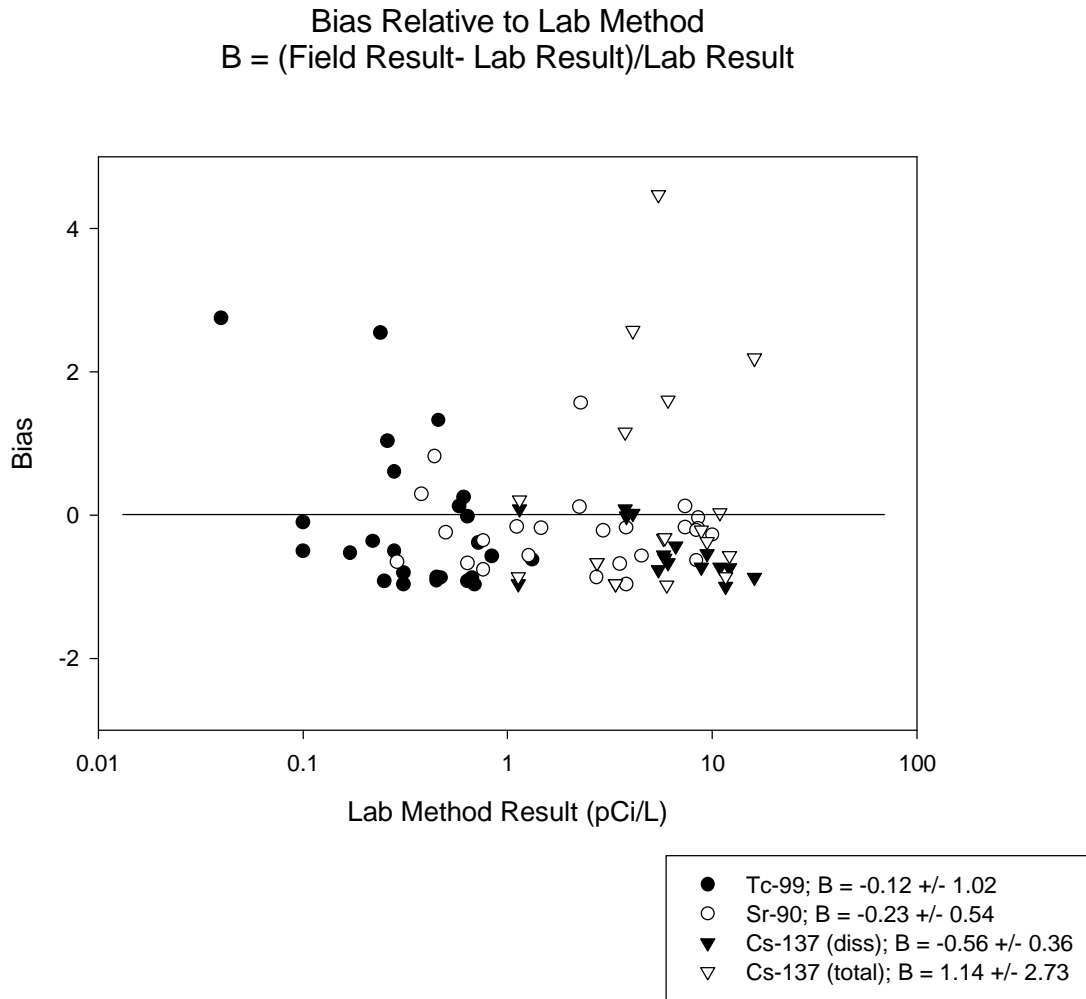


Figure 6.

All Fourmile Branch Results

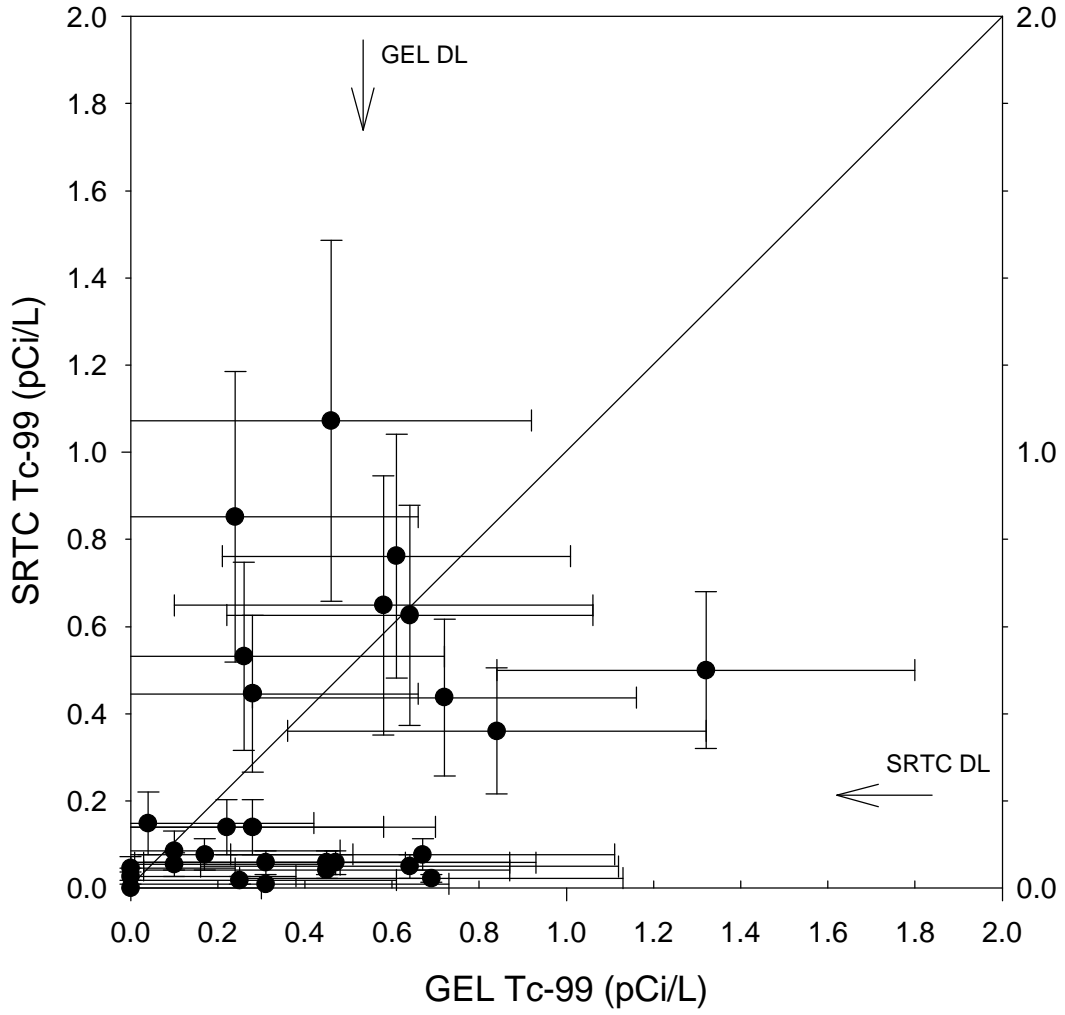


Figure 11a.

All Fourmile Branch Cs-137 Results

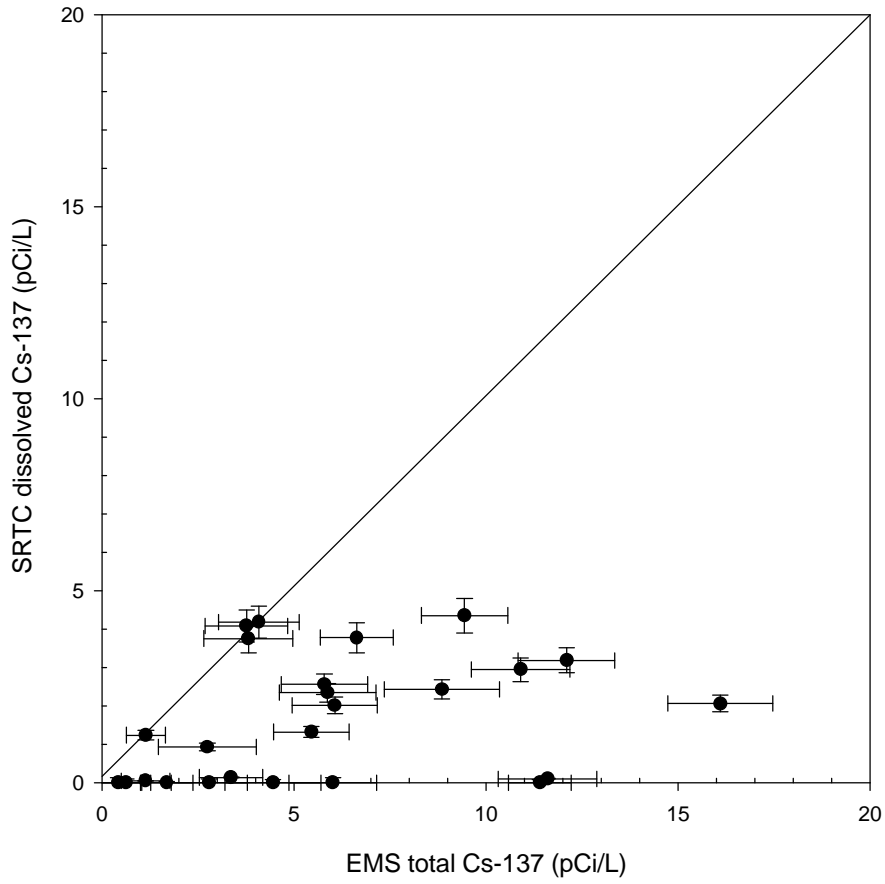


Figure 10.

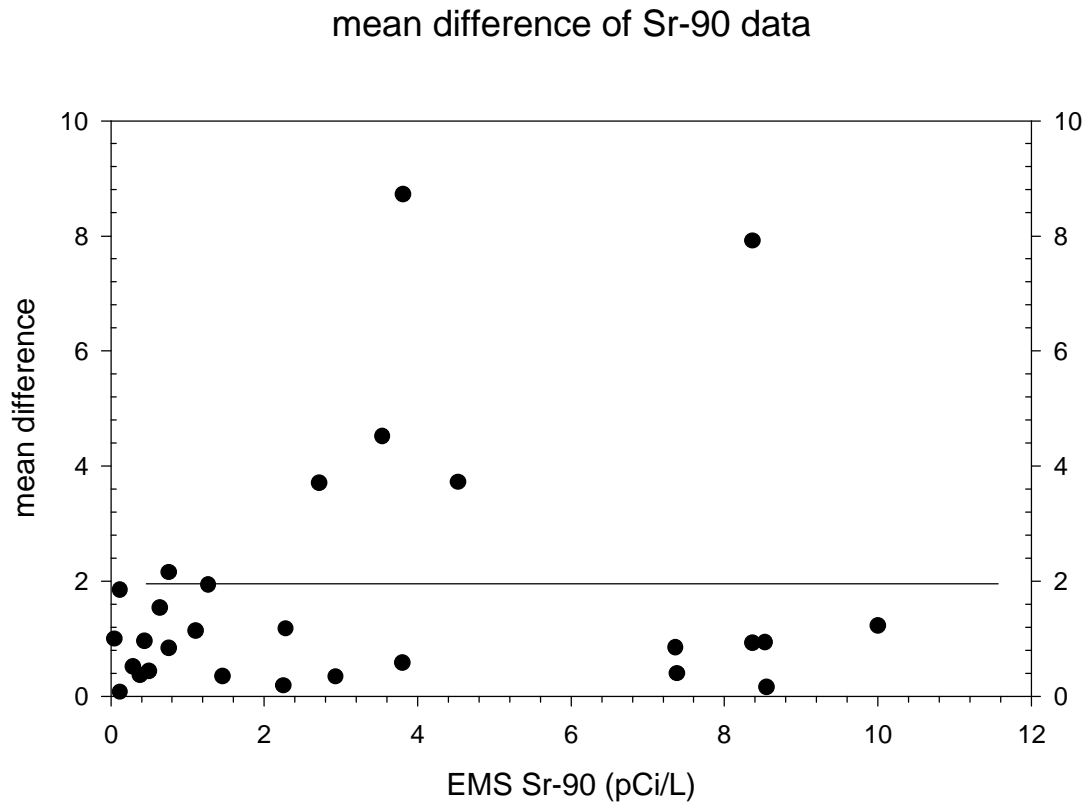


Figure 7.

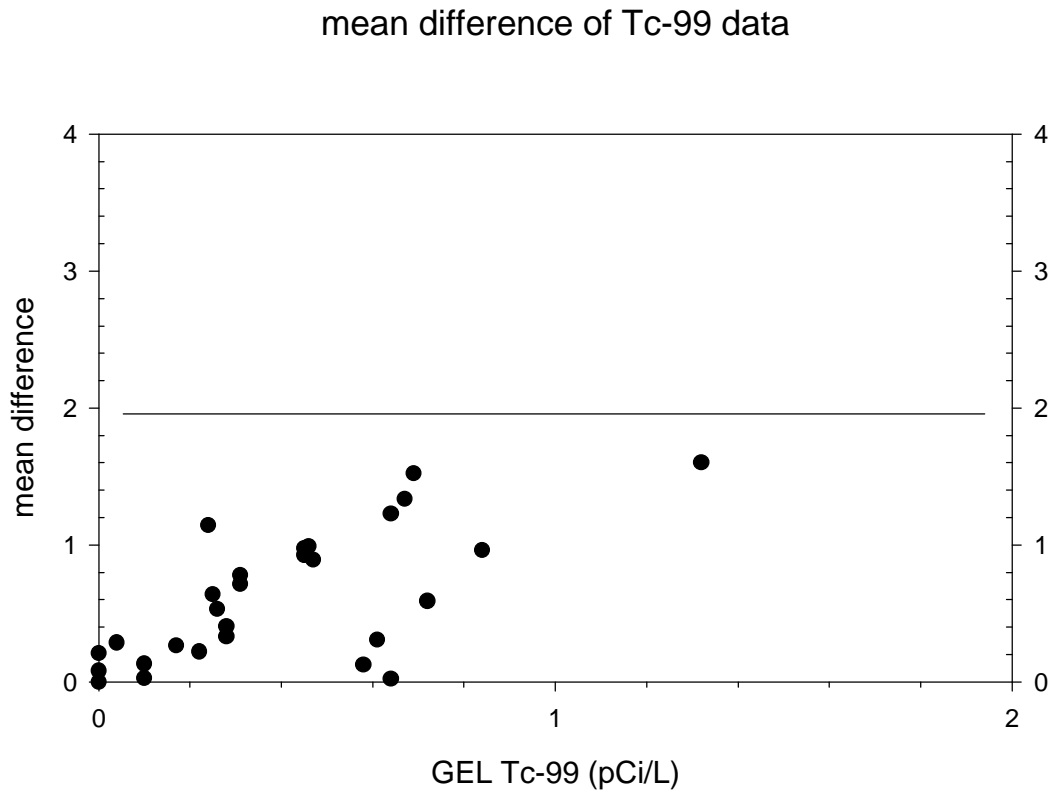


Figure 9.

All Fourmile Branch Results

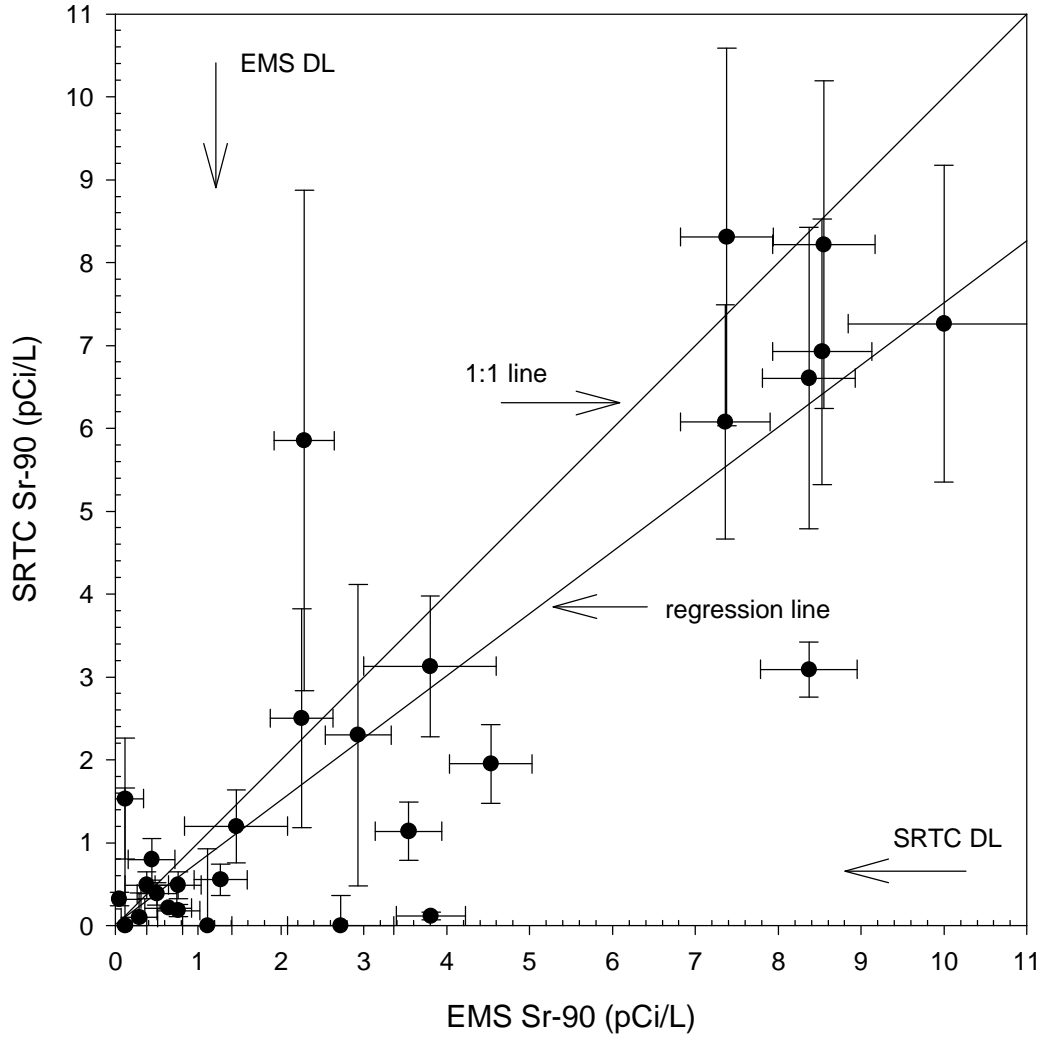
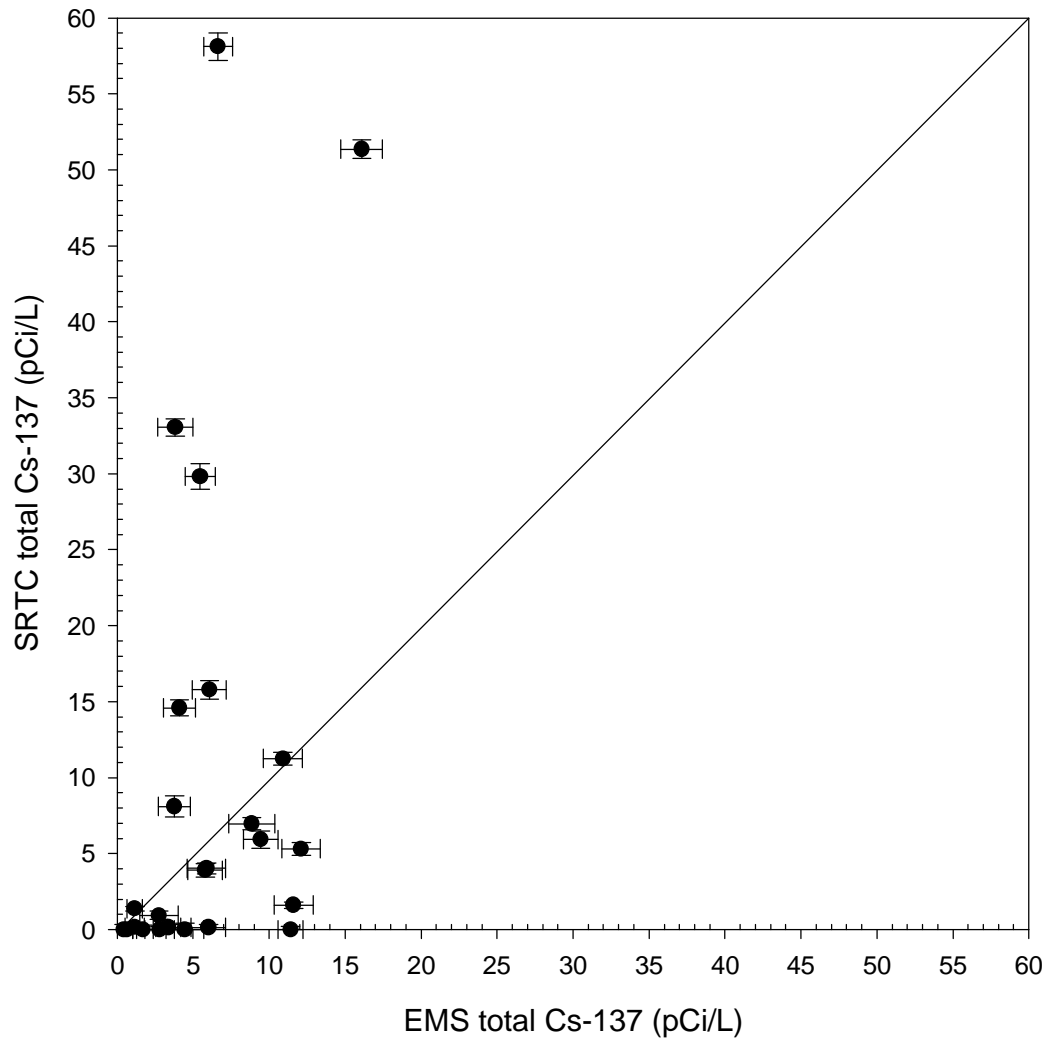
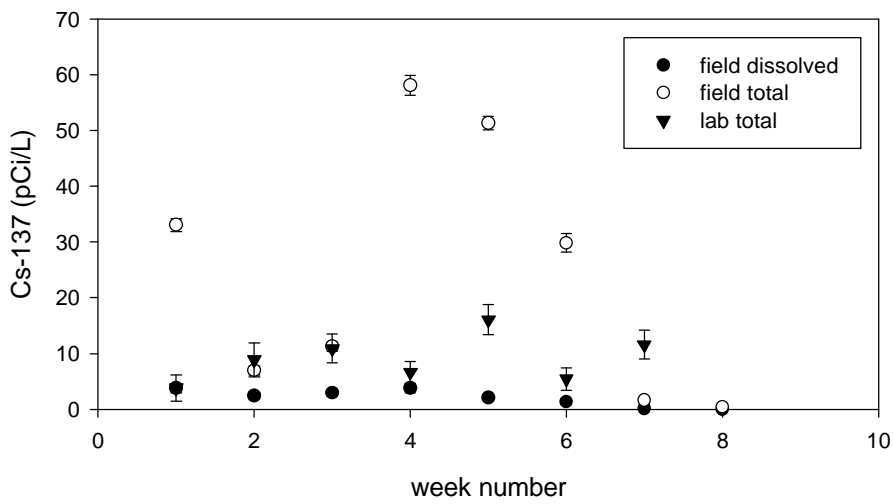
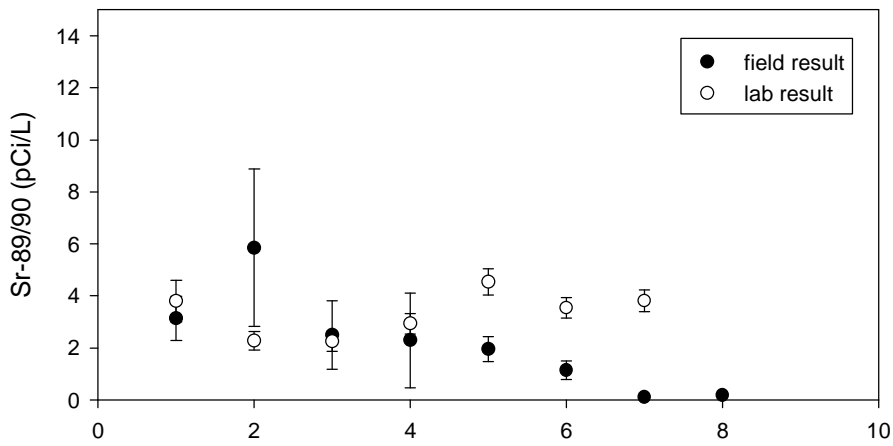
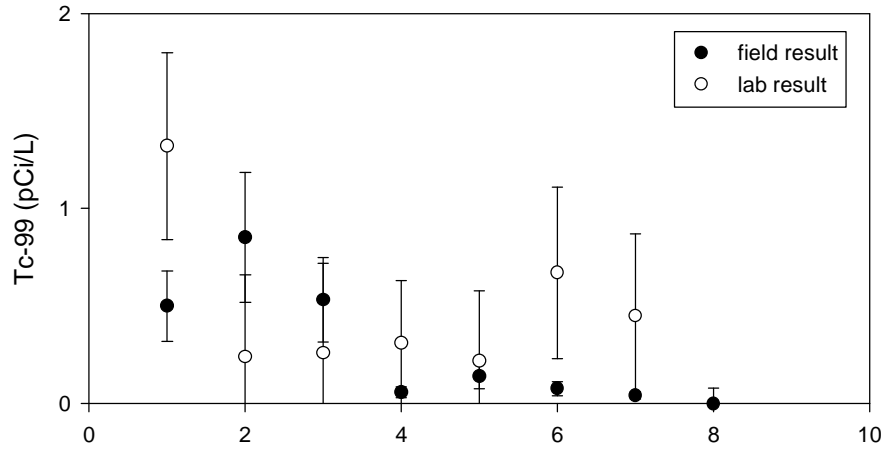


Figure 11b.

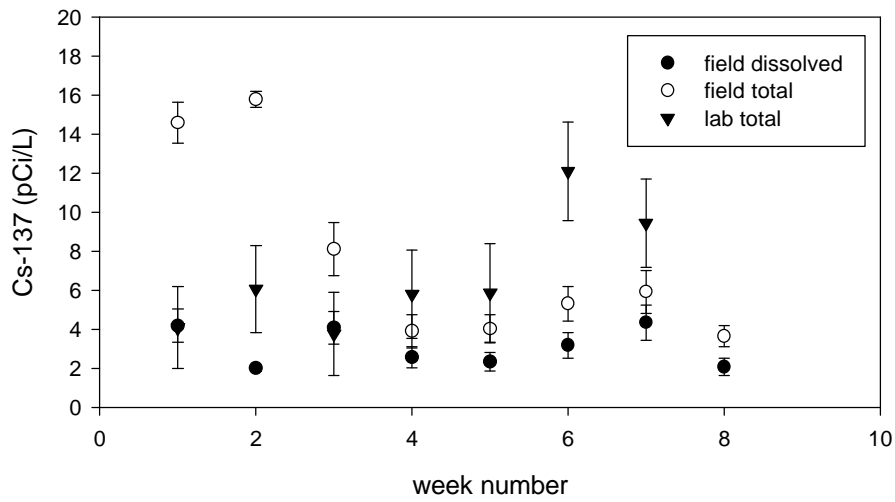
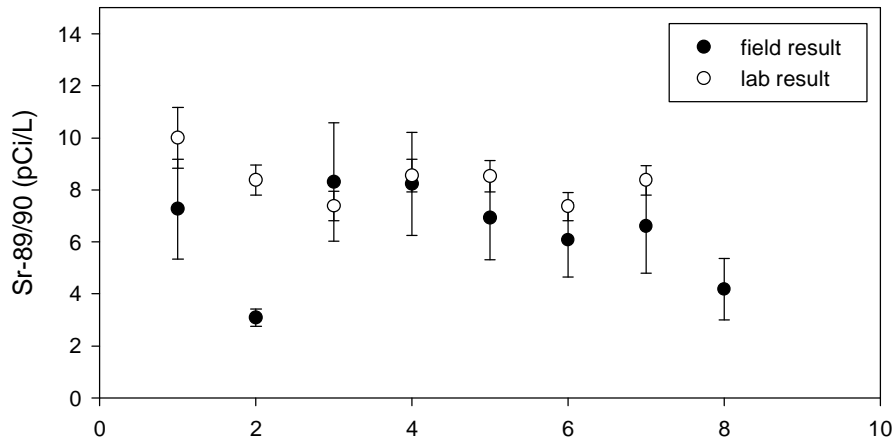
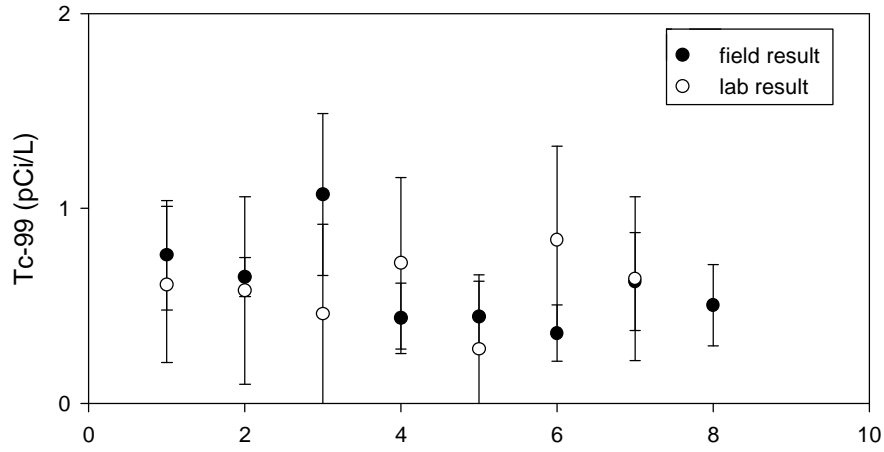
All Fourmile Branch Cs-137 Results



Fourmile Branch, sample point 2



Fourmile Branch at Road A7



Fourmile Branch at Road 1C

