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WSRC-TR-93-129
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February 1993

Results of the Second Quarter Tritium Survey of the F- and H-Area Seeplines: September 1992 (U)

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Prepared for the U.S. Department of Energy under contract no. DE-AC09-89SR18035

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The Environmental Sciences Section (ESS) established a quarterly monitoring program of the Four Mile Creek seepine down gradient from the F- and H-Area seepage basins. The program surveys and tracks changes in tritium, specific conductivity, and pH for the seepine water. Measurements from the second quarter survey (September 1992) showed lower tritium and conductivity measurements and more natural pH values (pH 5 - 6) than measurements from previous studies. The results of the first two quarterly surveys suggest that infiltration of rainfall may be diluting and flushing the contaminants from the groundwater system. More measurements are needed to confirm these trends.

Executive Summary

In September 1992 the Environmental Sciences Section (ESS) surveyed the Four Mile Creek seepine down gradient from the F- and H-Area seepage basins for tritium, specific conductivity, and pH. The survey was the second of eight quarterly surveys for monitoring the movement of contaminants from the basins since closure. Surface-water samples were collected from 51 locations along the seepine; Haselow et al. (1990) sampled 44 of the locations and 7 were newly established on the seepine south of 643-E, which is a decommissioned area in the Solid Waste Disposal Facility.

Results indicate that rainfall may be diluting the contaminant plume that leached from the seepage basins and washing the plume out of the shallow groundwater of the wetland systems below the basins. ESS found tritium activities in the F- and H-Area seepines significantly lower than the activities measured by Haselow et al. (1990). Conductivity measurements exhibited the same trends as tritium activities in both areas, indicating that salt ions are also being removed from the wetland system. Concentrations of hydrogen ion also decreased in both areas, which indicates that conditions are changing from acidic to more natural pH values (pH 5 - 6).

The seepine south of 643-E appears to be influenced by tritium from the burial grounds. Tritium activities ranged from 26 to 1010 pCi/ml, and conductivity values were near background levels. That is consistent with the wastes introduced into 643-E, which contained low levels of salt ions compared to the F- and H-Area basins. This suggests that seepine tritium in this area emanates from 643-E.

The results suggest that contaminant concentrations are decreasing at the F- and H-Area seepines and are consistent with first quarter results (Dixon and Rogers, 1992). Areas of stressed vegetation are showing signs of recovery as contaminant concentrations decrease and pH increases. Aluminum concentrations measured along the seepine in 1989 (Haselow et al., 1990) were high enough to be potentially toxic to plants. Increases in pH (to about neutral) will reduce the solubility of aluminum and thereby reduce this as a possible source of plant toxicity. Field observations indicate that several stressed areas show signs of recovery, particularly at the H-Area seepine.

Introduction

Seepage basins in the F and H Area of SRS received low-level radioactive-waste effluent from the chemical separation processes in the General Separation Areas (GSA). The basins retained the effluent to delay its release to the environment. The waste effluent consisted principally of sodium hydroxide, nitric acid, low levels of various radionuclides, and some metals (Killian et al., 1985a and b). Discharges of tritiated water to the seepage basins account for most of the radioactivity (Fenimore and Horton, 1972).

The Savannah River Laboratory (now the Savannah River Technology Center) conducted an extensive study aimed at characterizing the shallow groundwater outcropping into Four Mile Creek and its associated seepine in 1988 and 1989 (Haselow et al., 1990). As a part of this study, Haselow et al. surveyed for tritium, pH, and conductivity. Researchers measured low pH values, elevated conductivity, and tritium values along the seepines and determined that contaminants leaching from the F- and H-Area seepage basins were impacting the areas.

SRS stopped discharges to the seepage basins in 1988 and capped and sealed the basins in 1990 to reduce the release of the contaminants. Scientists hypothesized that after eliminating the contaminant source, annual rainfall amounts and natural groundwater flow would dilute and flush the remaining contaminant plume out of the shallow groundwater over time. After the contaminant plume in the shallow groundwater is diluted and flushed out, the wetland systems below the basins will recover.

To investigate this hypothesis, a quarterly sampling program was established. ESS sampled 44 of the seepage locations sampled by Haselow et al., 1990) for tritium, pH, and specific conductivity. This sampling program is intended to complement semiannual sampling of the seepage for selected Resource Conservation Recovery Act Appendix IX characterization, which began in July 1992.

The Environmental Protection Department expressed concern about possible seepage of tritium and other contaminants from 643-E. To investigate this possibility, seven new locations on the H-Area seepage south of 643-E were established and have been incorporated into the quarterly sampling plan.

Methods

ESS conducted the second round of sampling in the quarterly tritium survey in September 1992. Sampling locations were selected that, according to 1989 data, exhibited high and low values for the three variables of concern. Attempts were made to establish even ground coverage along both seepages. ESS collected 51 samples along the seepages in F and H Area—22 along the F-Area seepage, 22 along the H-Area seepage, and 7 locations on the H-Area seepage south of 643-E. Figures 1 and 2 show the sampling locations.

Prior to sampling for the first quarter, the Health Protection Department (HPD) collected and monitored soil samples from several locations along both seepages for gamma radioactivity. HPD did not detect measurable levels of gamma radiation, and protective clothing was chosen based on the findings. During sampling operations in the seepage areas, protective clothing consisted of rubber boots and disposable rubber gloves. These measures were intended to prevent dermal contact with seepage water.

Seepage sampling locations were marked and labeled previously with PVC stakes. Water samples were collected within a 3-ft radius of the PVC stake by boring a hole into the soil with a 3.5 in. soil auger until water was reached. Polyethylene sample containers (25 ml) were dipped into the water until full and then capped to collect water for tri-

tium analysis. The outside of each container was then rinsed with deionized water and sealed in a small polyethylene bag to minimize the possibility of contamination. The small bags were then placed in a large polyethylene bag, which was sealed for analysis. The Environmental Monitoring Section (EMS) performed tritium analysis. EMS counted aliquots of 5 ml for 20 minutes, which yielded a lower detection limit of 1.3 pCi/ml (WSRC-3Q1-4, 1992).

ESS measured specific conductivity and pH *in situ* with conductivity and pH electrodes (WSRC-L14.1, 1992a and 1992b). The electrodes were rinsed with deionized water after each sampling and all sampling equipment was thoroughly rinsed with water at the end of each day.

Results and Observations

Concentrations of variables measured at seepage sampling locations fluctuate throughout the year. Climate, especially rainfall, influences measured concentrations. Low rainfall for a few months prior to sampling could concentrate constituents, and high rainfall amounts could dilute the constituents in the shallow groundwater at the seepage intercept. Rainfall measured at SRS at the weather station in F Area from January through August 1992 was 97.33 cm. Long-term rainfall records were available for F Area, but not for H Area. The average rainfall from 1960 to 1991 through the month of August for F Area was 92.32 cm. This indicates that for the second quarter tritium survey, rainfall amounts in F and H Areas may be above normal. This should be considered when interpreting the survey results.

Figures 3 through 8 show comparisons of 1989 and 1992 tritium, conductivity, and pH measurements. Figures 9 through 11 show the data for the new locations on the seepage south of 643-E in H Area. These sampling locations were assigned the identification prefix FHB.

Tritium Measurements

F Area

Tritium values in the F-Area seepage ranged from 10 to 12,700 pCi/ml (see Table 1 and Figure 3). Of the 22 sampling locations in F Area, only 3 had tritium activities that exceeded the 1989 measurements by more than 10%. No values exceeded the maximum value recorded in 1989 of 14,000 pCi/ml. The graphs in Figure 3 show that the tritium activity in most sampling locations either decreased significantly or remained relatively unchanged. These results are generally consistent with the first quarter results.

To investigate the hypothesis that the September 1992 tritium activities are significantly less than in 1989, ESS conducted a Wilcoxon signed-rank test. The Wilcoxon signed-rank test uses the sign and the magnitude of the rank of the differences between pairs of measurements to compare nonparametric data. This test was chosen because it allows comparisons of paired data without assumptions of normality. The results showed that the September 1992 concentrations were significantly less ($P=0.005$) than the 1989 concentrations.

Generally, the locations with the greatest decrease in tritium activity are closest to the seepage basins. In contrast, those further away show little change or even an increase (FSP035) in tritium activities. These changes indicate that the bulk of the tritium plume in the wetland system has passed the locations closest to the seepage basins and is exiting the wetland system at the points closest to Four Mile Creek. This supports the general hypothesis that annual rainfall amounts would dilute the remainder of the contaminant plume emanating from the seepage basins. Due to the complex hydrologic system present in the basin areas, it is difficult to draw final conclusions at such an early point in the study about why tritium activities are exhibiting these trends. Final conclusions should not be drawn until after further sampling has been completed and seepage data has been compared to groundwater data.

H Area

Tritium values in the H-Area seepage line ranged from 63 to 12,700 pCi/ml (see Table 2 and Figure 4). Of the 22 sampling locations, tritium activities in only 3 locations exceeded the 1989 values. The graphs in Figures 5 and 6 show that most locations have either decreased or have remained relatively unchanged. These results are generally consistent with the first quarter results.

To investigate the hypothesis that September 1992 tritium activities are significantly less than in 1989, ESS conducted a Wilcoxon signed-rank test. This test was chosen because it allows comparisons of paired data without assumptions of normality. The results showed that the September 1992 concentrations were significantly less ($P=0.002$) than the 1989 concentrations.

ESS found the tritium activities in H-Area sampling locations nearest to seepage basin exhibited the greatest decrease. The activity at locations further away had a less significant decrease or increased. These changes indicate that the bulk of the tritium plume in the wetland system has passed the locations closest to the seepage basins and is exiting the wetland system at the points closest to the creek. Again, due to the complex hydrologic system

present in the basin areas, it is difficult to draw final conclusions at such an early point in the study about why tritium activities are exhibiting these trends. Final conclusions should not be drawn until after further sampling has been completed and seepage data has been compared to groundwater data.

Conductivity Measurements

F Area

Conductivity measurements in the F-Area seepage line ranged from 35 to 1525 $\mu\text{S}/\text{cm}$ (see Table 1 and Figure 5). Due to the extreme variability of conductivity measurements, ESS only considered differences of 100 $\mu\text{S}/\text{cm}$ or more to be significant. Of the 22 sampling locations in the F-Area seepage line, only 3 had measurements of more than 100 $\mu\text{S}/\text{cm}$ above the 1989 measurements. One of the locations coincided with a location where the tritium activity was elevated above the 1989 measurements. At the other two locations with elevated tritium activities, neither location had conductivity values exceeding the 1989 values; however, conductivity was elevated considerably above background at one location. A comparison of the graphs in Figures 3 and 5 suggests that conductivity follows the same general trends as the tritium activities. Using a Spearman rank correlation test for nonparametric data, it was found that the probability that tritium and conductivity exhibited independent trends was $P<0.001$. The rank correlation coefficient was found to be $r_s = 0.87$, suggesting that the two parameters are exhibiting the same trends. This similarity was expected because tritium traces the movement of the contaminant plume from the basins (Haselow et al., 1990). These results suggest that the salt ions are also exiting the wetland system in F Area.

H Area

Conductivity measurements in the H-Area seepage line ranged from 35 to 461 $\mu\text{S}/\text{cm}$ (see Table 2 and Figure 6). Of the 22 sampling locations, no location had a measurement of more than 100 $\mu\text{S}/\text{cm}$ above the 1989 measurements. However, two of the three locations where elevated tritium activities were observed exhibited conductivity values that were slightly elevated above the 1989 measurements. Observation of Figures 4 and 6 suggest that conductivity and tritium are following the same general trends. The Spearman rank correlation test for nonparametric data was used to investigate the correlation of H-Area tritium activities and conductivity values also. Again, it was found that the probability that the two parameters exhibited independent trends was $P<0.001$. The rank correlation coefficient, $r_s = 0.79$, for H Area was slightly lower than in F Area but still suggested a strong correlation.

Conductivity measurements at sampling location HSP103 in May 1992 remained relatively unchanged and were at background levels; however, tritium activities were elevated. In September 1992, conductivity was at background and tritium had decreased considerably compared to the May 1992 value. This may represent seasonal variation in concentrations and further exemplifies the need to analyze the data over more quarters. The tritium activity measured in May suggested that this area of the seepage line may be influenced by tritium leaching from wastes deposited in 643-E as suggested by Haselow et al. (1990). This observation will need to be assessed further based on data collected from future surveys.

pH Measurements

F-Area pH values ranged from 3.7 to 6.3 with an average value of 5.2 (Table 1 and Figure 7). H-Area pH values ranged from 5.0 to 6.8 with an average of 6.0 (Table 2 and Figure 8). The pH for the entire seepage line (F and H Areas combined) averaged 5.6. The average increased 0.7 units over the 4.9 average in 1989 (Haselow et al., 1990). While the average pH remains in the acidic range, the fivefold decrease further indicates that the contaminant plume is exiting the system. The increase in pH will affect the solubility of metals in the soil profile, which will enhance the recovery of wetlands potentially stressed by low pH. Aluminum concentrations measured along the seepage line in 1989 (Haselow et al., 1990) were high enough to be potentially toxic to plants. Increases in pH (to about neutral) will reduce the solubility of aluminum and thereby reduce this as a possible source of plant toxicity. Field observations of the stressed areas support this conclusion.

Solid Waste Disposal Facility (643-E Old Burial Ground) Seepage Results

The graphs in Figures 9 through 11 show tritium, conductivity, and pH values for the new seepage line sampling locations south of 643-E, which is within the Solid Waste Disposal Facility. Table 3 provides the data used in the figures.

Tritium activities for the area range from 26 to 1010 pCi/ml. While the tritium activities are slightly elevated, they are generally not as high as most F- and H-Area seepage line concentrations.

Conductivity measurements ranged from 25 to 55 $\mu\text{S}/\text{cm}$. This range is near background levels and instrument detection limits. No correlation ($r_s = 0.32$) was found to exist between conductivity and tritium for these locations using the Spearman rank correlation test. Values of pH ranged from 5.2 to 5.8 with an average of 5.4.

These results are consistent with the Haselow et al. (1990) results for the western portion of the H-Area seepage line, particularly near location HSP103. Haselow et al. (1990) found that conductivity values down gradient of 643-E were near background while tritium concentrations were elevated. This was attributed to tritiated wastes deposited in 643-E. Tritium survey results and Haselow et al. (1990) results suggest that this area of the seepage line is being influenced by seepage from 643-E. Several new sampling locations have been established on the seepage line and the branch channel-way, which is a few feet east of the canal that drains effluent from F-Area Separations and runoff from the west end of area 643-E.

Conclusions

Results from the second quarter tritium survey indicate that the contaminant plume migrating from the F- and H-Area seepage basins is beginning to exit the wetland system down gradient from the basins. These results are consistent with the first quarter results. ESS attributes this to the closure and capping of the basins. This eliminated the hydraulic head driving the contaminants out of the basin, thereby eliminating the source of the contaminants. WSRC scientists hypothesized that after the basins were capped, annual rainfall amounts would dilute and flush out the remaining contaminant plume. The first and second quarter tritium survey results appear to support this hypothesis; however, due to the complex hydrologic system present in the basin areas, it is difficult to draw final conclusions at such an early point in the study. Additional collections of seepage line data combined with groundwater data will be used to fully assess the trends.

Evaluation of data from several new seepage line locations south of the 643-E facility indicates that tritium seepage from 643-E is impacting the seepage line slightly. However, tritium activities measured on the seepage line are well below maximum May and September 1992 concentrations measured for both the F- and H-Area seepage lines.

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Figure 1. Location of F-Area Seepage Basins and Seepage Sampling Points

Figure 2. Location of H-Area Seepage Basins and Seepage Sampling Points

Figure 3. Comparison of March 1989, May 1992, and September 1992 Tritium Concentrations for selected F-Area Seepage Locations

Figure 4. Comparison of March 1989, May 1992, and September 1992 Tritium Concentrations for selected H-Area Seepage Locations

Figure 5. Comparison of March 1989, May 1992, and September 1992 Conductivity Measurements for selected F-Area Seepage Locations

Figure 6. Comparison of March 1989, May 1992, and September 1992 Conductivity Measurements for selected H-Area Seepage Locations

Figure 7. Comparison of March 1989, May 1992, and September 1992 pH Measurements for selected F-Area Seepage Locations

Figure 8. Comparison of March 1989, May 1992, and September 1992 pH Measurements for selected H-Area Seepage Locations

Figure 9. Comparison of May 1992 and September 1992 Tritium Concentrations for Selected Locations on the Seepline South of 643-E

Figure 11. Comparison of May 1992 and September 1992 pH Measurements for Selected Locations on the Seepline South of 643-E

Figure 10. Comparison of May 1992 and September 1992 Conductivity Measurements for Selected Locations on the Seepline South of 643-E

Tables

Table 1. Comparison of F-Area Seepage Measurements of Tritium, Conductivity, and pH in March 1989 and September 1992

Location	Tritium (pCi/mL)			Conductivity ($\mu\text{S/cm}$)			pH (- log H)		
	Mar 89	May 92	Sep 92	Mar 89	May 92	Sep 92	Mar 89	May 92	Sep 92
2	520	186	290	94	70	80	5.6	5.8	5.7
7	3400	1311	845	681	255	267	5.4	5.9	6.0
12	260	45	43	30	58	219	5.3	5.4	6.1
14	14000	323	2250	666	243	360	4.2	4.2	4.0
19	4900	6017	4380	1424	1107	1118	4.2	4.1	4.0
26	4400	5888	2810	1095	1314	620	6.5	5.8	6.3
32	3600	824	631	174	138	139	5.0	4.3	4.3
34	14000	5096	4520	810	539	639	3.8	2.9	3.7
35	11000	7937	12700	1100	913	1525	3.9	3.6	3.7
40	7800	9359	6630	900	1454	867	5.2	3.4	4.1
47	100	556	84	52	125	179	4.7	4.6	5.7
56	19	11	10	34	37	60	4.5	4.5	5.3
204	3000	1137	1610	895	311	258	4.4	4.4	5.7
213	2800	697	4340	860	136	684	4.6	5.5	4.6
220	560	560	541	147	138	122	4.8	5.1	5.7
226	1300	968	890	306	147	168	5.1	*NR	6.1
235	580	512	320	84	72	113	5.7	*NR	6.1
241	560	339	246	36	51	92	4.7	4.8	5.3
249	580	94	142	84	61	44	4.4	4.7	5.0
256	400	608	408	56	127	103	5.1	5.5	6.2
270	40	33	42	50	46	35	4.1	4.4	5.1
290	35	51	47	49	28	47	3.6	4.8	5.2

Table 2. Comparison of H-Area Seepage Measurements of Tritium, Conductivity, and pH in March 1989 and September 1992

Location	Tritium (pCi/mL)			Conductivity ($\mu\text{S/cm}$)			pH (- log H)		
	Mar 89	May 92	Sep 92	Mar 89	May 92	Sep 92	Mar 89	May 92	Sep 92
3	14000	4881	3400	468	176	191	5.2	5.8	6.1
4	11000	3358	1880	292	196	234	5.8	6.5	6.4
8	24000	1074	6440	556	334	333	5.7	5.6	6.8
11	960	48	259	80	57	79	5.1	4.6	5.7
13	12000	1610	1160	592	131	136	6.2	6.4	6.4
15	1000	4681	2140	82	278	176	5.2	6.4	6.1
20	6500	3449	1700	183	166	224	6.2	6.4	6.1
25	3300	2255	1400	135	98	67	4.7	5.8	5.7
29	9200	1567	932	257	234	97	5.2	6.1	5.7
34	5600	1631	7160	331	141	316	5.8	6.0	6.1
38	6500	479	186	227	185	176	4.9	6.4	6.3
43	10000	9865	5160	413	294	325	5.3	6.2	6.4
46	11000	13076	2740	318	223	246	5.5	6.6	6.6
49	11000	9483	7030	551	115	203	4.4	6.1	6.3
52	20000	14515	12700	699	505	461	4.1	5.6	6.4
57	15000	2930	2250	581	183	141	5.5	5.6	5.5
60	21000	3357	3160	473	274	204	5.9	5.6	5.9
64	320	121	63	38	62	40	4.7	5.3	5.2
71	450	338	232	40	36	35	5.1	5.5	5.5
76	400	7	416	146	162	144	5.7	5.9	6.1
97	1100	2265	3110	37	120	134	4.3	6.0	6.0
103	510	9885	361	43	45	41	4.4	4.9	5.0

Table 3. Comparison of Seepage below 643-E Measurements of Tritium, Conductivity, and pH in March 1989 and September 1992

Location	Tritium (pCi/mL)		Conductivity ($\mu\text{S/cm}$)		pH (- log H)	
	May 92	Sep 92	May 92	Sep 92	May 92	Sep 92
1	173	111	51	55	4.6	5.8
2	35	26	46	40	4.7	5.2
3	1280	826	57	42	4.7	5.4
4	1306	947	42	51	4.8	5.5
5	555	1010	39	47	4.9	5.4
6	273	243	32	46	4.7	5.4
8	281	177	28	25	5.0	5.2

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