

**CHEMICAL PROPERTIES OF PORE WATER AND SEDIMENT AT THREE WET-  
LAND SITES NEAR THE F- AND H-AREA SEEPAGE BASINS, SAVANNAH RIVER  
SITE**

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## Executive Summary

In 1980, vegetative stress and arboreal mortality in wetland plant communities down-gradient from the F- and H-Area seepage basins were detected using aerial imagery. By 1988, approximately six acres in H-Area and four acres in F-Area had been adversely impacted. Today, wetland plant communities have become well established at the H-Area tree-kill zone. At the F-Area tree-kill zone, however, phytotoxicological conditions remain and wetland flora are either nonexistent or marginally surviving. Despite numerous studies and monitoring activities in these areas, none have comprehensively sampled and analyzed the interstitial water and substrate from these areas. The objectives of this investigation were to (1) characterize the pore water and sediment within the tree-kill zones and a control, (2) qualitatively assess the environmental health and recovery of the wetlands, and (3) identify ecological stressors associated with vegetative stress and mortality.

Concentrations of Al, Ba, Cd, Ca, Co, Mg, Mn, Na, Ni, Tl, Zn, and nitrate-nitrite in pore water were significantly ( $P < .01$ ) higher in the F-Area tree-kill zone than in H-Area or the control. With the exception of Ba, Ca, Mg, and Tl, concentrations of these constituents in sediment were also significantly elevated in F-Area. Acidity, specific electrical conductance, and water hardness were also significantly higher in F-Area pore water than the other locations. Although aluminum has been previously thought to be the primary toxicant, the high concentrations of other constituents suggest that multiple toxicants or synergistic interactions may play a role in inhibiting plant growth. In pore water there were no significant differences in concentrations of As, Be, Cu, Cyn, and ammonia nitrogen between locations. In sediment, there were no significant differences in concentrations of Ba, Ca, Cr, Hg, Mg, Pb, V, and ammonia nitrogen between locations. These constituents do not appear to affect the establishment of native flora. Most of the target compound list (TCL) volatile and semivolatile organic compounds were not detected in pore water or sediment. For the few organic compounds that were detected, concentrations were not significantly higher in F-Area than the other locations. Low pH, metals, and nitrate appear to be the principal ecological stressors in the F-Area tree-kill zone. One of the most logical explanations for these conditions is acid leachate migration that resulted from the deposition of contaminants in the F- and H-Area seepage basins.

## INTRODUCTION

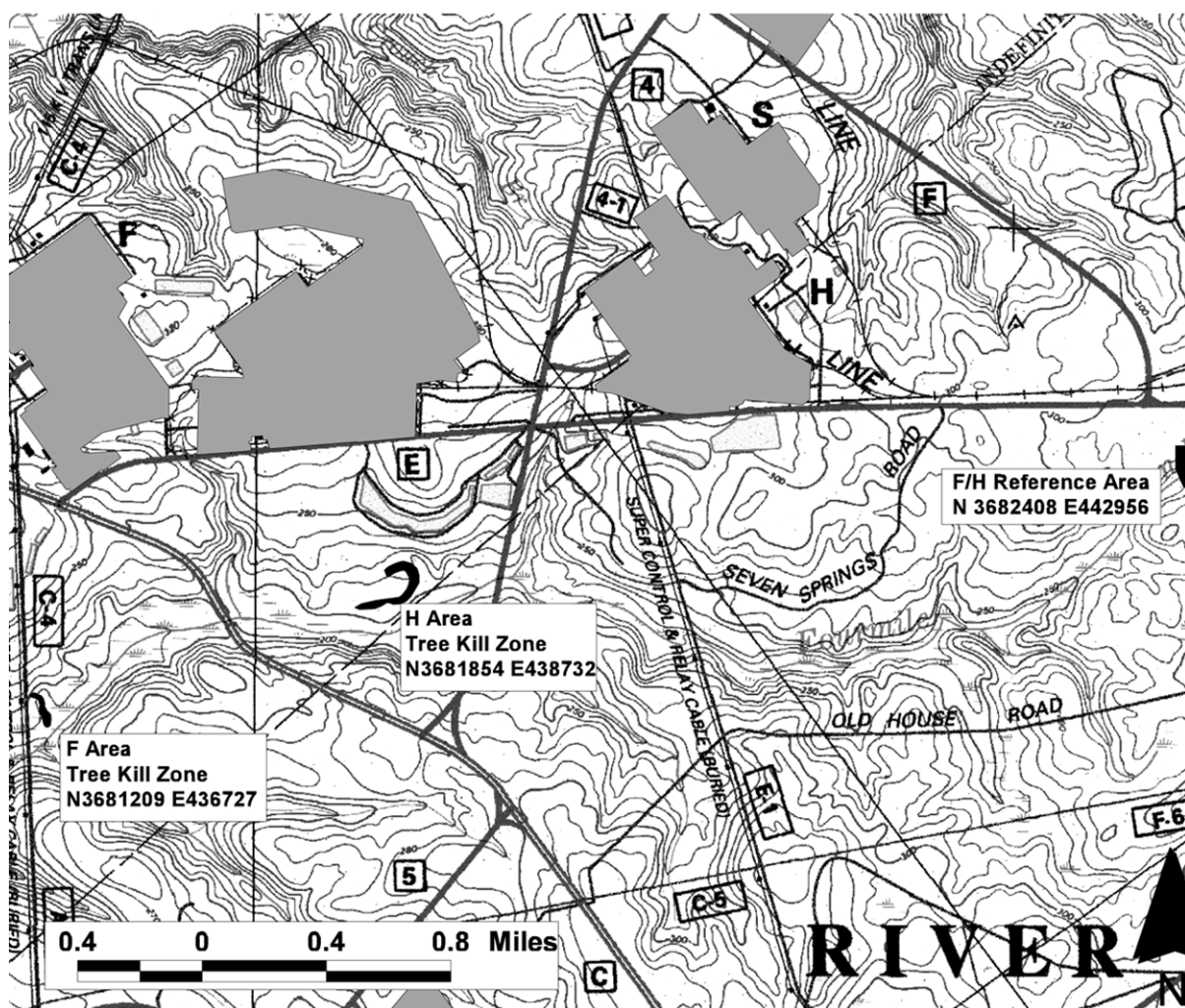
The Savannah River Site (SRS) was constructed in the early 1950's to produce nuclear materials for the nation's defense. From 1955 to 1988, the F- and H-Area separation facilities discharged hazardous chemicals into seven seepage basins, contaminating the underlying soils and groundwater between the basins and Fourmile Branch, a tributary of the Savannah River. In 1979, signs of vegetative stress in the riparian wetlands between the basins and Fourmile Branch were detected using aerial photography. By 1988, approximately ten acres downgradient from the seepage basins had experienced vegetative stress or arboreal mortality. Today, vegetation has become re-established in H-Area, but the F-Area tree-kill zone supports only a depauperate flora and some areas are devoid of vegetation. Although these wetlands have been the subject of several investigations and continue to be monitored as part of environmental compliance activities at the SRS, little is known about the chemistry of the substrate and its associated interstitial water. This has resulted in a poor understanding of which ecological stressors are associated with arboreal mortality and vegetative stress. The objectives of this investigation were to (1) characterize the pore water and sediment within the tree-kill areas and a reference area, (2) assess the environmental health and recovery of the wetlands, and (3) identify ecological stressors associated with vegetative mortality.

## STUDY AREA

The F- and H-Areas are located within the General Separations Area (GSA) of the Savannah River Site (Figure 1). Three basins covering approximately seven acres were built in F-Area whereas four basins covering 16 acres were constructed in H-Area. The nearest stream, Fourmile Branch, is located approximately 1300 ft from the H-Area Basins and approximately 2000 ft from the F-Area Basins. The Savannah River is located approximately eight miles from the basins.

The F- and H-Area Seepage Basins were constructed and began operations in 1955. The F-Area Seepage Basins consisted of three unlined basins that were hydraulically connected by vitrified clay process sewers. The seepage basins received process waste water from the F-Area Separations Facilities for a period of 33 years. The major sources of waste were cooling water from tritium facilities, nitric acid recovery overheads, general purpose evaporator overheads, and retention basin transfers (Killian et al., 1987a). Discharges to the basins ceased in November 1988, and closure caps were placed over the basins to minimize infiltration through the basin sediments in 1990.

The H-Area Seepage Basins also consisted of three unlined basins that were constructed in 1955. In 1962, however, one basin was made inactive and replaced by a fourth basin. The basins received process waste water from the H-Area Separations Facilities until 1988. The main sources of waste water included those listed for the F-Area Seepage Basins, overheads from the two H-Area Tank Farm evaporators, and liquids from the Receiving Basin for Offsite Fuels Facility (Killian et al., 1987b). Discharges to the basins terminated in November 1988. Closure caps placed over the seepage basins to minimize infiltration through the basin sediments were completed in 1991.



**FIGURE 1. General location of the F- and H-Area tree-kill zones and reference site, Savannah River Site.**

The F/H-Area occupies approximately 194 acres on a nearly flat divide between Upper Three Runs Creek to the north and Fourmile Branch to the south. Ground surface elevations range from approximately 270 feet above mean sea level (msl) to approximately 300 feet above msl. The surface topography generally slopes to the south. A mixture of brushland, sparse forest, and grassland occupies areas to the east, north, and west of the F/H-Area. The environment in the vicinity of the seepage basins provides habitat for a diverse flora and fauna. Immediately downslope from the basins is old field herbaceous/scrub brush habitat which transitions into upland forest. The upland forest intergrades into bottomland hardwood forest at the seepage line. It is at the seepage line where groundwater surfaces and flows into the wetlands. The wetland habitat also includes the Fourmile Branch stream community.

Vegetation stress in the wetlands downgradient from the F- and H-Area seepage basins was initially detected by reviewing remote sensing data. Subsequent ground truthing confirmed that mortality within the tree canopy had occurred in areas that were believed to receive outcropping groundwater contaminated by the seepage basins. The affected sites were once nearly pure stands of swamp tupelo (*Nyssa sylvatica* var. *biflora*). Historical photography indicated that the mortality was present as early as 1979. Imagery taken in 1998 shows that approximately 5.7 acres was affected below H-Area and 3.6 acres was impacted below F-Area (Figure 1). This represents about 0.07% of the 13,824 acres of bottomland hardwood forest on the SRS (Halverson et al. 1997).

## METHODS

Sediment and pore water samples were collected in July and December 2000, respectively, from three wetland locations on the Savannah River Site. These included two areas exhibiting vegetative stress and mortality downgradient from the F- and H-Area seepage basins, and a reference site (i.e., control) having historically similar soil type and vegetation. The procedures and equipment used to collect sediment and pore water were consistent with the guidelines contained in the WSRC Procedure Manual 3Q5, U.S. Environmental Protection Agency standard operating procedures, and the American Society for Testing and Materials (ASTM). With the exception of duplicates, splits, trip blanks, field blanks, and rinsates, 10 samples were collected from each location.

Pore water was collected from shallow wells (i.e., piezometers) positioned within the tree-kill zones and reference area. Piezometers were installed to a depth no greater than 3.0 m (10 ft) using a 5.0 cm (2 in.) diameter hand or power auger. Pore water entered the piezometer through a screened opening that extended from 1.0 meter (3 ft) below the surface to the bottom of the piezometer. Pore water which collected within the sample chamber was extracted through a dedicated, sterilized tube using a peristaltic pump. Samples were placed in labeled containers and put in iced coolers for shipment to the laboratory.

Sediment samples were collected with a stainless steel hand corer. Prior to use, the coring device was washed with a non-phosphate detergent and rinsed with deionized water. Samples were collected by twisting the corer into the sediment to a depth of 30 cm, bringing the corer to the surface and emptying the cored material into a sample container. Aliquots of sediment slated for organic analyses were taken using a modified syringe. Pore water and sediment samples were placed in labeled containers, and all samples were placed on ice in coolers and transported to the laboratory for analysis.

### ***Analytical Analyses***

Pore water and sediment samples were analyzed at four laboratories using EPA methods (Tables 1-4). Target compound list (TCL) volatile and semivolatile organic compounds were analyzed on-site at the GEL mobile lab (ML). Target analyte list (TAL) inorganics and other constituents including, cyanide, pH, chloride, sulfate and others were analyzed in Charleston, South Carolina at GEL. Radiological analyses for tritium were conducted by General Physics (GP), Charleston, South Carolina. Duplicates and splits were analyzed by RCRA Laboratories, Lionville, Pennsylvania.

### ***Statistical Analyses***

Data were initially examined by evaluating the frequency of detection by EPA qualifying codes (e.g., J, JU, R, and U). Unless constituents had frequencies of detection greater than 10%, they were excluded from further analyses. A listing of these constituents and maximum concentrations are presented later in this report. For all other constituents, concentration values less than the method detection limit were divided by two and retained for the analyses of variance.

Statistical tests were performed with SPSS 9.0. Normal and detrended normal Q-Q plots were prepared to test the assumptions of parametric analyses. The distribution of the data were also evaluated using the Shapiro-Wilk normality test and the Leven test for homogeneity of variance. For constituents having normal distributions and homogeneity of variance, a one way analysis of variance (anova) was performed to test the null hypothesis of no significant difference between mean concentrations. When a significant difference was found, the least significant difference (lsd) was used as a multiple comparisons procedure. For constituents whose data were not normally distributed or the variances were not homogeneous, the Kruskal-Wallis nonparametric anova was used. The Dunn test was used to compare differences in populations.

**TABLE 1. Listing of inorganic constituents and analytical methods used to characterize pore water and sediment chemistry.**

<b>Constituent</b>	<b>Method</b>
Aluminum	6010B
Antimony	6010B
Arsenic	6010B
Barium	6010B
Beryllium	6010B
Cadmium	6010B
Calcium	6010B
Chromium	6010B
Cobalt	6010B
Copper	6010B
Cyanide	6010B
Iron	6010B
Lead	6010B
Magnesium	6010B
Manganese	6010B
Mercury	7470A/7471A
Nickel	6010B
Potassium	6010B
Selenium	6010B
Silver	6010B
Sodium	6010B
Thallium	6010B
Vanadium	6010B
Zinc	6010B
<b>Miscellaneous</b>	
Ammonia	350.1
Chloride	300.0
Nitrate-nitrite	353.1
Phosphate (total)	365.4
Sulfate	300.0
Total Organic Carbon	415.1
Hardness	Std. Method 2340B
pH	150.1



**TABLE 2. Listing of target compound list (TCL) volatile organics.**

<b>Constituent</b>	<b>Method</b>
1,1,1-Trichloroethane	EPA8260B
1,1,2,2-Tetrachloroethane	EPA8260B
1,1,2-Trichloroethane	EPA8260B
1,1-Dichloroethane	EPA8260B
1,1-Dichloroethene	EPA8260B
1,2-Dichloroethane	EPA8260B
1,2-Dichloropropane	EPA8260B
2-Butanone (MEK)	EPA8260B
2-Hexanone	EPA8260B
4-Methyl-2-pentanone	EPA8260B
Acetone	EPA8260B
Benzene	EPA8260B
Bromodichloromethane	EPA8260B
Bromoform	EPA8260B
Bromomethane (Methyl bromide)	EPA8260B
Carbon disulfide	EPA8260B
Carbon tetrachloride	EPA8260B
Chlorobenzene	EPA8260B
Chlorodibromomethane	EPA8260B
Chloroethane	EPA8260B
Chloroform	EPA8260B
Chloromethane (Methyl chloride)	EPA8260B
cis-1,3-Dichloropropene	EPA8260B
Dichloromethane (Methylene chloride)	EPA8260B
Ethylbenzene	EPA8260B
Styrene	EPA8260B
Tetrachloroethene	EPA8260B
Toluene	EPA8260B
trans-1,3-Dichloropropene	EPA8260B
Trichloroethene (TCE)	EPA8260B
Vinyl chloride	EPA8260B
Xylenes (total)	EPA8260B

**TABLE 3. Listing of target compound list (TCL) semivolatile organics.**

Constituent	Method
1,2,4-Trichlorobenzene	8270C
1,2-Dichlorobenzene	8270C
1,3-Dichlorobenzene	8270C
1,4-Dichlorobenzene	8270C
2,4-Dichlorophenol	8270C
2,4-Dimethyl phenol	8270C
2,4-Dinitrophenol	8270C
2,4-Dinitrotoluene	8270C
2,4,5-Trichlorophenol	8270C
2,4,6-Trichlorophenol	8270C
2,6-Dinitrotoluene	8270C
2-Chloronaphthalene	8270C
2-Chlorophenol	8270C
2-Methyl-4,6-dinitrophenol	8270C
2-Methylnaphthalene	8270C
2-Nitroaniline	8270C
2-Nitrophenol	8270C
3,3'-Dichlorobenzidine	8270C
3-Nitroaniline	8270C
4-Bromophenyl phenyl ether	8270C
4-Chloro-3-methylphenol (p-chloro-m-cresol)	8270C
4-Chloroaniline	8270C
4-Chlorophenyl phenyl ether	8270C
4-Nitroaniline	8270C
4-Nitrophenol	8270C
Acenaphthene	8270C
Acenaphthylene	8270C
Anthracene	8270C
Benzo(a)anthracene	8270C
Benzo(a)pyrene	8270C
Benzo(b)fluoranthene	8270C
Benzo(g,h,i)perylene	8270C
Benzo(k)fluoranthene	8270C
Bis(2-chloroethoxy) methane	8270C
Bis(2-chloroethyl) ether	8270C
Bis(2-chloroisopropyl) ether (2,2'-oxybis(1-chloropropane)	8270C
Bis(2-ethylhexyl) phthalate	8270C
Butyl benzyl phthalate	8270C

**TABLE 3. Listing of target compound list (TCL) semivolatile organics.**

<b>Constituent</b>	<b>Method</b>
Carbazole	8270C
Chrysene	8270C
Dibenzo(a,h)anthracene	8270C
Dibenzofuran	8270C
Diethyl phthalate	8270C
Dimethyl phthalate	8270C
Di-n-butyl phthalate	8270C
Di-n-octyl phthalate	8270C
Fluoranthene	8270C
Fluorene	8270C
Hexachlorobenzene	8270C
Hexachlorobutadiene	8270C
Hexachlorocyclopentadiene	8270C
Hexachloroethane	8270C
Indeno(1,2,3-c,d)pyrene	8270C
Isophorone	8270C
m-cresol (3-methylphenol)	8270C
Naphthalene	8270C
Nitrobenzene	8270C
N-Nitrosodi-n-propylamine	8270C
N-Nitrosodiphenylamine	8270C
o-cresol (2-methylphenol)	8270C
p-cresol (4-methylphenol)	8270C
Pentachlorophenol	8270C
Phenanthrene	8270C
Phenol	8270C
Pyrene	8270C

## Previous Investigations

### *Vegetative Stress and Mortality*

Observations of arboreal mortality in bottomland hardwoods between the seepage basins and Fourmile Branch have been documented by Mackey (1988), Loehle and Gladden (1988), LeBlanc and Loehle (1990), Greenwood et al. (1990), Loehle (1990 a,b,c), and others. Mackey (1988) examined aerial photography taken from 1961 through 1987 and found no signs of vegetative stress for 1979. September 1980 imagery however, showed canopy thinning and tree mortality. He concluded that effects to the vegetation occurred in 1979 or 1980, and that expansion of the die-off areas continued through 1987.

Loehle and Gladden (1988) conducted a preliminary assessment to evaluate factors that may have been responsible for the vegetation damage identified by Mackey (1988). They concluded that the most likely causes of tree mortality were low pH and elevated concentrations of aluminum, sodium, and conductivity.

Loehle (1990a) reported the results of a laboratory study in which contaminated soils from the F-Area seepage line were collected and leached with rainwater. After six leachings the leachate was observed to be non-toxic to lettuce seedlings, whereas untreated soil water was toxic. These results suggest that the contaminant responsible for plant toxicity is relatively soluble and that leaching could be a feasible remediation technique. Loehle (1990b) also correlated climate changes with the timing of tree stress, and cited high levels of sodium in soils and aluminum in root and leaf tissues.

Greenwood et al. (1990) reviewed SRS data and information in the published literature on contaminant chemistry and toxicology in trees in an attempt to determine the cause of tree mortality observed in the F- and H-Areas. The study focused on three possible causes of stress, namely altered hydrology, hazardous chemicals, and nonhazardous chemicals. Greenwood et al. (1990) concluded that severe drought in 1977 played a role in the observed tree stress. Dry conditions may have exacerbated stress caused by chemicals present in the soils by concentrating them further. Salt and heavy metal concentrations were elevated in soil at each impacted site. Aluminum was identified as probably the most toxic metal at F-Area. However, cadmium, manganese, and zinc were present at concentrations high enough to be considered possible causes of tree mortality. Aluminum was thought to be the most likely cause of tree mortality at H-Area.

LeBlanc and Loehle (1990) analyzed tree-rings to determine causes of vegetative stress at the tree-kill zones. Chemical analyses of the cores failed to provide conclusive evidence of temporal changes in the soil chemical environment associated with groundwater contamination. Observed increases in aluminum concentrations during the 1978-1987 period were consistent with the expected effects of acidic contaminants on soil solution chemistry. However, this effect was not corroborated by increases of manganese, also expected as a result of soil acidification. Tree ring analysis indicated that severe droughts occurred in 1977 and 1986.

Dames and Moore (1991) characterized wetland vegetation near Fourmile Branch using stratified plots, but this study did not include the tree-kill areas in the vicinity of the seepage basins. Loehle (1990c) performed a cluster analysis using the Dames and Moore (1991) data but failed to identify any contamination patterns. Vegetative stress and low species richness, however, were reported.

### ***Seed Germination Studies***

Eaton and Murphy (1993) also tested the toxicity of F-Area seepage line soil leachate using lettuce seedlings. Their study, which was designed to evaluate changes in toxicity from those reported by Loehle (1990a), revealed no significant differences in germination between the treatments but radicle length was markedly reduced by the first extraction from seepage soils. Continued seed germination studies have shown that extracts of wetland soils generally reduce seed vigor.

In a subsequent study by Nelson and Westbury (1994), the growth response, as measured by seed germination and root elongation, to leachates (first and sixth water washings) from the impacted soils of F-Area were compared to uncontaminated wetland soils and distilled water. This study showed a greatly reduced toxic effect of the leachate from F-Area seepage soil samples over time on lettuce seed germination and growth as compared to control samples from an uncontaminated site. As part of this effort, additional water chemistry collection showed that the seepage water entering the tree-kill areas was less toxic than the water within the area but more toxic than the background wetland area. This indicated the presence of residual effects within the tree-kill zones that have not been completely reduced, as well as effects from continuing inputs from the seepage into the system.

Westbury (1998), using root elongation testing, found the toxicity of water from the F-Area tree-kill zone to be significantly greater than water from the seepage. He also concluded that aluminum was not responsible for observed reductions in root elongation. Seaman (2000) analyzed grab samples of surface water and soil from the F-Area tree-kill zone to identify possible environmental factors responsible for plant mortality and inability of native species to revegetate. He reported that manganese and other potentially toxic metals within the tree-kill zone were elevated, but levels of aluminum, sodium, and nitrate were lower than concentrations reported by Greenwood et al. (1990).

### ***Vegetative Structure and Revegetation Studies***

In 1993, wetland vegetation in the F- and H-Area tree-kill zones was examined by Nelson and Irwin (1994) to evaluate the type and extent of revegetation. Vegetation within the tree-kill zones in both F- and H-Areas was sparse. Mortality of the canopy approached 100% and only a few live trees remained. The sparse vegetation of the F- and H-Area tree-kill areas was in stark contrast to the adjacent forest. The species composition was similar, but the structure differed. Unlike a relatively undisturbed forest, the tree-kill areas were not stratified. The species normally associated with canopy, subcanopy, and shrub layer were present in the F-Area, but as sickly seedlings perched above the substrate on stumps, logs, and piles of debris.

The vegetation characterization plots were revisited in June of 1994 to determine if any improvement had occurred (Westbury and Nelson 1994). Results showed that saturated sediments in the F-Area tree-kill zone were not being re-colonized by wetland plants, whereas the plant community had largely recovered at the H-Area tree kill-zone. The F-Area site exhibited minimal plant community development and virtually all plants were rooted out of the saturated sediments.

In 1994, Nelson and Rogers (1995) initiated efforts to re-establish native vegetation in several of the tree kill areas. In an effort to reestablish the climax species of the area, swamp tupelo seedlings were planted in four of the impacted areas. Survival of swamp tupelo seedlings after the first growing season was excellent at all sites. During the second growing season, two sites which had less severe original impacts showed good survival rates and seedling condition. The two sites that experienced the greatest mortality also had good over-winter survival. However, the vegetative health of the seedlings deteriorated throughout the growing season, and the re-establishment of the original flora was unsuccessful.

Nelson (2000) re-examined the vegetation plots in F- and H-Area tree kills in August 2000. He found that flora in the F-Area tree kill zone continued to exhibit toxicity or stress conditions, and noted a shifting from normally hydrophytic species as a possible result of dry conditions. The H-Area site exhibited robust vegetative development associated with successional recovery.

## RESULTS AND DISCUSSION

### Pore Water

The principal constituents detected in pore water were metals and other inorganics. Of the 32 volatile and 65 semivolatile TCL organic compounds in the analytical suite, four were detected. Pentachlorophenol was detected in a single sample from F-Area (41 µg/L) and 4-nitrophenol (9.6 µg/L) was detected once from the control. Bis-(2-ethylhexyl) phthalate was detected in 6 of 30 samples, five of which occurred in H-Area. A single detect was recorded in the control and no detects were found in F-Area. The maximum concentration of bis-(2-ethylhexyl) phthalate was 153 µg/L. Toluene was detected in 13 of 30 samples. Eight detects for toluene occurred in H-Area, whereas the control had four and F-Area had one. The maximum concentration of toluene was 10.6 µg/L. Concentrations of bis-(2-ethylhexyl phthalate) and toluene in F- and H-areas were not significantly different from the control.

Nineteen metals were identified in pore water samples (Table 4). Concentrations of dissolved aluminum, barium, cadmium, calcium, cobalt, magnesium, manganese, nickel, nitrite-nitrate, phosphate, sodium, thallium, and zinc were significantly higher in the F-Area tree kill zone than in H-Area or the control. The mean concentration of dissolved aluminum in F-Area (16,922 µg/L) was orders of magnitude greater than H-Area (1,862 µg/L) or the control (248 µg/L). Levels of total recoverable aluminum, total organic carbon, chloride, chromium, iron, lead, and vanadium were significantly higher in the H-Area tree kill zone than the other locations. Concentrations of nitrite-nitrate and water hardness were significantly higher at F-Area than H-Area and the control. Both pH and sulfate was significantly lower at F-Area than H-Area or the control. There was no significant difference between locations for concentrations of arsenic, beryllium, copper, cyanide, and ammonia nitrogen.

Concentrations of dissolved oxygen were not significantly different between F- and H-Area tree-kill zones (Table 4). Levels of dissolved oxygen at the control, however, were significantly lower than both tree-kill zones. Specific electrical conductance was significantly higher in F-Area (789 µS/cm) than H-Area (163 µS/cm) or the control (75 µS/cm). Water hardness was significantly higher at F-Area (76 mg/L CaCO<sub>3</sub>) than H-Area (16 mg/L CaCO<sub>3</sub>) or the control (20 mg/L CaCO<sub>3</sub>).

Radioactivity of tritium, the sole radioisotope that was included in pore water analyses, ranged from 718 pCi/mL at the control to 6,980 pCi/mL at the F-Area tree kill zone (Table 4). Mean tritium radioactivities at F-Area (4,719 pCi/mL) and H-Area (1,757 pCi/mL) were significantly higher than the control site (1.6 pCi/mL).

## Sediment

The constituents identified in sediment were similar to those found in pore water. The most frequently detected constituents were metals and other inorganics. Two metals and 14 organic compounds were screened from further analyses because of low frequencies of detection (Table 5). Over half of these constituents had single detects in the H-Area tree-kill zone. Diethyl phthalate, 1,1-dichloroethylene, and selenium were detected twice, and three detects were recorded for bis-(2-ethylhexyl) phthalate and pyrene. There were no detections of the other volatile and semivolatile compounds in sediment.

Mean concentrations in sediment of Al, As, Cd, Co, Cu, Cyn, Fe, Mn, Ni, nitrate-nitrite, K, sulfate, Sn, and Zn were significantly higher in F-Area than H-area or the control (Table 6). The mean concentration of aluminum in F-Area (41,200 mg/kg) was significantly greater than levels in H-Area (6,474 mg/kg) or the control (9,458 mg/kg). Concentrations of beryllium, chloride, total organic carbon, total phosphates, and sodium were also significantly higher in F-Area than the control. There were no significant differences in concentrations of barium, calcium, chromium, lead, magnesium, mercury, and ammonia nitrogen between locations. The pH of sediment in H-Area (5.6) was significantly higher than the pH in F-Area (4.8) or the control (4.5). There was no significant difference in pH levels between F-Area and the control (Table 6).

Organic compounds having frequencies of detection greater than 10% included acetone, dichloromethane (methylene chloride), methyl ethyl ketone, and toluene. Concentrations of acetone and methyl ethyl ketone were markedly higher in F- and H-Areas than the control (Table 6). Dichloromethane was detected in 5 of 30 samples, all of which were from the H-Area tree-kill zone. Concentrations of dichloromethane ranged from 6.0 to 23.8 µg/kg. There was no significant difference in the mean concentration of toluene between locations.

## Comparison of Pore Water and Sediment

A comparison of pore water and sediment chemistry for selected constituents including pH is shown using boxplots (Figure 2). Observations between the 25th and 75th percentile (50% of the cases) are contained within the box. The horizontal line within the box is the median, and the largest and smallest values that are not outliers are represented by the lines extending from the top and bottom of the box, respectively.

Concentrations of aluminum, cadmium, cobalt, manganese, nickel, nitrate-nitrite, sodium, and zinc were significantly elevated in the F-Area tree-kill zone as compared to the other locations. The pH of both pore water and sediment were lower in the F-Area tree-kill zone than in H-Area or the control. A comparison of concentrations resulting from this study with those conducted previously is presented in Table 7. Data from Greenwood et al. (1990), Koch (1999), and Koch and Friday (1999) show that concentrations declined from 1988 to 1998 at the seepage down-gradient from the F-Area seepage basin. Based on the results of surface water samples taken from Fourmile Branch during the third quarter of 2000, the concentrations of selected constituents are lower than those found at the seepage (Table 7). Results presented by Seaman (2000) were taken from the F-Area tree-kill zone, and his data closely approximate the findings of this investigation.

**TABLE 4. Means, standard errors, and results of parametric (F) and non-parametric (H) analysis of variance (ANOVA) for constituents in pore water from three locations, Savannah River Site.**

Constituent	Location <sup>a</sup>	n <sup>b</sup>	Mean	Std. Error	ANOVA <sup>c</sup>
Total Dissolved	F-Area❖	10	16,922	3,793	H=17.2 (P<.001)
Aluminum (µg/L)	H-Area◆	10	1,862	594	
	Control◆	10	248	63	
Total Recoverable	F-Area❖	10	24,700	4,420	F=12.8 (P<.001)
Aluminum (µg/L)	H-Area◆	10	82,840	13,132	
	Control❖	10	28,280	7,583	
Total Recoverable	F-Area❖	10	1.3	1.1E-17	H=2.2 (P=0.33)
Arsenic (µg/L)	H-Area❖	10	2.8	1.01	
	Control❖	10	2.8	1.03	
Bis-(2-ethylhexyl)	F-Area❖**	10	2.1	8.3E-17	H= 7.9 (P=0.02)
phthalate (µg/L)	H-Area◆	10	40	18	
	Control◆**	10	15	13	
Total Recoverable	F-Area❖	10	430	84	F=9.9 (P<.001)
Barium (µg/L)	H-Area◆	10	199	38	
	Control◆	10	97	19	
Total Recoverable	F-Area❖	10	3.5	0.8	H=4.5 (P=.11)
Beryllium (µg/L)	H-Area❖	10	1.8	0.4	
	Control❖	10	3.6	0.5	
Total Recoverable	F-Area❖	10	10.2	2.2	H=22.3 (P<.001)
Cadmium (µg/L)	H-Area◆	10	0.5	0.1	
	Control◆	10	0.7	0.4	
Total Recoverable	F-Area❖	10	21,427	5,834	H=15.0 (P=.001)
Calcium (µg/L)	H-Area◆	10	2,628	954	
	Control◆	10	3,220	544	
Total Organic	F-Area❖	10	5.0	0.8	F=8.6 (P=.001)
Carbon (mg/L)	H-Area◆	10	59	18	
	Control❖	10	6.3	0.8	
Chloride (mg/L)	F-Area❖	10	2.7	0.3	F=12.8 (P<.001)
	H-Area◆	10	16.6	3.7	
	Control❖	10	3.5	0.7	
Total Recoverable	F-Area❖	10	14.5	5.7	F=12.5 (P<.001)
Chromium (µg/L)	H-Area◆	10	73.6	9.5	
	Control❖	10	37.9	9.4	
Total Recoverable	F-Area❖	10	185	36	H=19.1 (P<.001)
Cobalt (µg/L)	H-Area◆	10	5.4	0.7	
	Control◆	10	8.7	4.4	



**TABLE 4. (Continued) Means, standard errors, and results of parametric (F) and non-parametric (H) analysis of variance (ANOVA) for constituents in pore water from three locations, Savannah River Site.**

Constituent	Location <sup>a</sup>	n <sup>b</sup>	Mean	Std. Error	ANOVA <sup>c</sup>
Total Recoverable	F-Area❖	10	12.3	2.3	F=0.074 (P=.929)
Copper (µg/L)	H-Area❖	10	13.3	1.6	
	Control❖	10	12.3	2.7	
Cyanide (µg/L)	F-Area❖	10	2.1	0.37	H=1.34 (P=.51)
	H-Area❖	10	1.6	0.24	
	Control❖	10	2.1	0.41	
Hardness as CaCO <sub>3</sub>	F-Area❖	10	76	13	F=16.6 (P<.001)
(mg/L)	H-Area♦	10	16	15	
	Control♦	10	20	3	
Total Recoverable	F-Area❖	10	1,103	379	H=16.6 (P<.001)
Iron (µg/L)	H-Area♦	10	11,460	1,794	
	Control♦	10	7,507	1,913	
Total Recoverable	F-Area❖	10	5.4	1.3	F=14.3 (P<.001)
Lead (µg/L)	H-Area♦	10	51	10	
	Control❖	10	16	4.1	
Total Recoverable	F-Area❖	10	9,049	2,518	F=6.6 (P=.005)
Magnesium (µg/L)	H-Area♦	10	2,488	629	
	Control♦	10	2,227	321	
Total Recoverable	F-Area❖	10	3,683	637	H=19.0 (P<.001)
Manganese (µg/L)	H-Area♦	10	257	63	
	Control♦	10	300	99	
Total Recoverable	F-Area❖	10	36	7.0	F=9.2 (P=.001)
Nickel (µg/L)	H-Area♦	10	18	2.1	
	Control♦	10	10	5.3	
Ammonia nitrogen	F-Area❖	10	1.27	0.33	H=4.1 (P=.13)
(mg/L)	H-Area❖	10	0.84	0.16	
	Control❖	10	0.45	0.09	
Nitrate-nitrite (mg/L)	F-Area❖	10	111	15	H=23.1 (P<.001)
	H-Area♦	10	1.8	1.0	
	Control♦	10	0.015	0.009	
Dissolved Oxygen (mg/L)	F-Area❖	10	6.0	0.81	F = 9.1 (P=.001)
	H-Area❖	10	4.5	0.61	
	Control♦	10	2.4	0.21	
pH (unitless)	F-Area❖	10	4.47	0.145	H=9.18 (P=.01)
	H-Area♦	10	5.15	0.159	
	Control♦	10	4.91	0.102	

**TABLE 4. (Continued) Means, standard errors, and results of parametric (F) and non-parametric (H) analysis of variance (ANOVA) for constituents in pore water from three locations, Savannah River Site.**

Constituent	Location <sup>a</sup>	n <sup>b</sup>	Mean	Std. Error	ANOVA <sup>c</sup>
Total Phosphates (as P) (mg/L)	F-Area❖	10	0.093	0.025	H=15.7 (P<.001)
	H-Area◆	10	0.769	0.177	
	Control❖◆	10	0.311	0.110	
Total Recoverable Selenium (µg/L)	F-Area❖	10	1.5	0.27	H=11.0 (P=.004)
	H-Area◆*	10	4.5	0.58	
	Control❖*	10	3.2	0.96	
Total Recoverable Sodium (µg/L)	F-Area❖	10	88,850	6,468	F=25.3 (P<.001)
	H-Area◆	10	44,270	8,845	
	Control*	10	12,896	7,252	
Specific Electrical Conductance (mS/cm)	F-Area❖	10	789	95	F=46.8 (P<.0001)
	H-Area◆	10	163	23	
	Control*	10	75	6	
Sulfate (mg/L)	F-Area❖*	10	6.2	2.8	H=8.8 (P=.012)
	H-Area◆*	10	14.8	5.0	
	Control◆	10	22.4	3.2	
Total Recoverable Thallium (µg/L)	F-Area❖	10	3.8	0.61	H=12.8 (P=.002)
	H-Area◆	10	2.0	0.013	
	Control◆	10	2.2	0.259	
Toluene (µg/L)	F-Area❖	10	0.69	0.07	H=9.4 (P=.009)
	H-Area◆	10	2.32	0.93	
	Control❖◆	10	1.71	0.71	
Tritium (pCi/mL)	F-Area❖	10	4,719	436	H=23.7 (P<.001)
	H-Area❖	10	1,757	559	
	Control◆	10	1.6	0.5	
Total Recoverable Vanadium (µg/L)	F-Area❖	10	5.2	1.2	F=9.1 (P=.001)
	H-Area◆	10	88	19	
	Control*	10	46	15	
Total Recoverable Zinc (µg/L)	F-Area❖	10	115	21	F=11.6 (P<.001)
	H-Area◆	10	50	7	
	Control*	10	31	4	

a. Any two locations having the same symbol do not have significantly different (P<.05) mean or median concentrations as determined by the least significant difference (lsd) or Dunn's test.

b. n = number of samples

c. F values represent one-way analysis of variance; H values represent the Kruskal-Wallis non-parametric analysis of variance.

**TABLE 5. List of constituents in sediment having frequencies of detection not greater than 10%.**

Constituent	FOD <sup>a</sup>	No. Detects by Location			Maximum (mg/kg)
		F-Area	H-Area	Control	
1,1-Dichloroethylene	2/30	0	1	1	.002
1,3-Dichlorobenzene	1/30	0	1	0	.41
1,4-Dichlorobenzene	1/30	0	1	0	.41
2,4,5-Trichlorophenol	1/30	0	1	0	1.0
2,4,6-Trichlorophenol	1/30	0	1	0	1.0
2,4-Dichlorophenol	1/30	0	1	0	1.0
2,4-Dimethyl phenol	1/30	0	1	0	1.0
2,4-Dinitrophenol	1/30	0	1	0	2.0
2,4-Dinitrotoluene	1/30	0	1	0	.41
2-Hexanone	3/30	2	0	1	.05
Antimony	2/30	2	0	0	1.2
Bromomethane	1/30	0	1	0	.002
Bis-(2-ethylhexyl) phthalate	3/30	0	2	1	4.7
Diethyl phthalate	2/30	0	1	1	3.5
Pyrene	3/30	0	0	3	1.1
Selenium	2/30	0	1	1	1.5

a. Frequency of detection.

**TABLE 6. Means, standard errors, and results of parametric (F) and non-parametric (H) analysis of variance (ANOVA) for constituents in sediment collected from three locations, Savannah River Site.**

Constituent	Location <sup>a</sup>	n <sup>b</sup>	Mean	Std. Error	ANOVA <sup>c</sup>
Acetone (µg/kg)	F-Area❖	10	494	67	H=10.6 (P=.005)
	H-Area❖♦	10	304	80	
	Control♦	10	101	32	
Total Recoverable	F-Area❖	10	41,200	2,499	F=115 (P<.001)
Aluminum (mg/kg)	H-Area♦	10	6,474	933	
	Control♦	10	9,458	1,610	
Total Recoverable	F-Area❖	10	4,792	333	F=32.0 (P<.001)
Arsenic (µg/kg)	H-Area♦	10	1,777	444	
	Control♦	10	1,084	236	
Total Recoverable	F-Area❖	10	60	16	F=0.98 (P=.39)
Barium (mg/kg)	H-Area❖	10	57	14	
	Control❖	10	37	7	
Total Recoverable	F-Area❖	10	600	123	H=10.2 (P=.006)
Beryllium (µg/kg)	H-Area❖❖	10	305	91	
	Control♦❖	10	197	43	
Total Recoverable	F-Area❖	10	1,015	502	H=11.2 (P=.004)
Cadmium (µg/kg)	H-Area❖*	10	347	103	
	Control♦*	10	86	13	
Total Recoverable	F-Area❖	10	1,123	592	H=1.9 (P=.38)
Calcium (mg/kg)	H-Area❖	10	1,642	512	
	Control❖	10	220	37	
Total Organic	F-Area❖	10	217,100	14,376	H=9.9 (P=.007)
Carbon (mg/kg)	H-Area❖❖	10	129,052	40,300	
	Control♦❖	10	37,917	10,494	
Chloride (mg/kg)	F-Area❖	10	376	20	H=20.4 (P<.001)
	H-Area❖	10	210	61	
	Control♦	10	31	9	
Total Recoverable	F-Area❖	10	9,847	470	H=2.5 (P=.28)
Chromium (µg/kg)	H-Area❖	10	9,389	2,349	
	Control❖	10	10,771	1,482	
Total Recoverable	F-Area❖	10	37,350	11,874	H=22.7 (P<.001)
Cobalt (µg/kg)	H-Area♦	10	2,295	474	
	Control♦	10	687	112	
Total Recoverable	F-Area❖	10	133,340	9,760	H=19.4 (P<.001)
Copper (µg/kg)	H-Area♦	10	2,925	456	
	Control♦	10	3,123	550	

**TABLE 6. (Continued) Means, standard errors, and results of parametric (F) and non-parametric (H) analysis of variance (ANOVA) for constituents in sediment collected from three locations, Savannah River Site.**

Constituent	Location <sup>a</sup>	n <sup>b</sup>	Mean	Std. Error	ANOVA <sup>c</sup>
Cyanide (µg/kg)	F-Area❖	10	3,334	387	H=18.2 (P<.001)
	H-Area◆	10	506	171	
	Control◆	10	224	69	
Total Recoverable	F-Area❖	10	12,906	1,270	H=12.1 (P=.002)
Iron (mg/kg)	H-Area◆	10	7,605	2,437	
	Control◆	10	4,355	460	
Total Recoverable	F-Area❖	10	15,630	1,128	F=2.2 (P=.125)
Lead (µg/kg)	H-Area❖	10	13,515	3,340	
	Control❖	10	9,006	1,690	
Total Recoverable	F-Area❖	10	420	116	H=5.6 (P=.061)
Magnesium (mg/kg)	H-Area❖	10	557	164	
	Control❖	10	146	26	
Total Recoverable	F-Area❖	10	576	215	H=17.1 (P<.001)
Manganese (mg/kg)	H-Area◆	10	141	38	
	Control◆	10	25	4	
Total Recoverable	F-Area❖	10	36	2.0	H=3.5 (P=.178)
Mercury (µg/kg)	H-Area❖	10	96	26	
	Control❖	10	34	8.0	
Methyl Ethyl Ketone (µg/kg)	F-Area❖	10	28	6	H=6.9 (P=.031)
	H-Area❖	10	38	11	
	Control◆	10	7	2	
Total Recoverable	F-Area❖	10	8,862	1,815	F=7.5 (P=.002)
Nickel (µg/kg)	H-Area◆	10	3,873	743	
	Control◆	10	2,618	444	
Ammonia Nitrogen (mg/kg)	F-Area❖	10	78	4	H=0.124 (P=.94)
	H-Area❖	10	164	49	
	Control❖	10	79	17	
Nitrate-nitrite (mg/kg)	F-Area❖	10	447	78	H=20.7 (P<.001)
	H-Area◆	10	1.3	0.3	
	Control◆	10	0.8	0.4	
pH (unitless)	F-Area❖	10	4.8	0.24	H=11.6 (P=.003)
	H-Area◆	10	5.6	0.21	
	Control❖	10	4.5	0.08	
Total Phosphates (as P) (mg/kg)	F-Area❖	10	679	73	H=12.3 (P=.002)
	H-Area❖*	10	328	100	
	Control◆*	10	167	39	

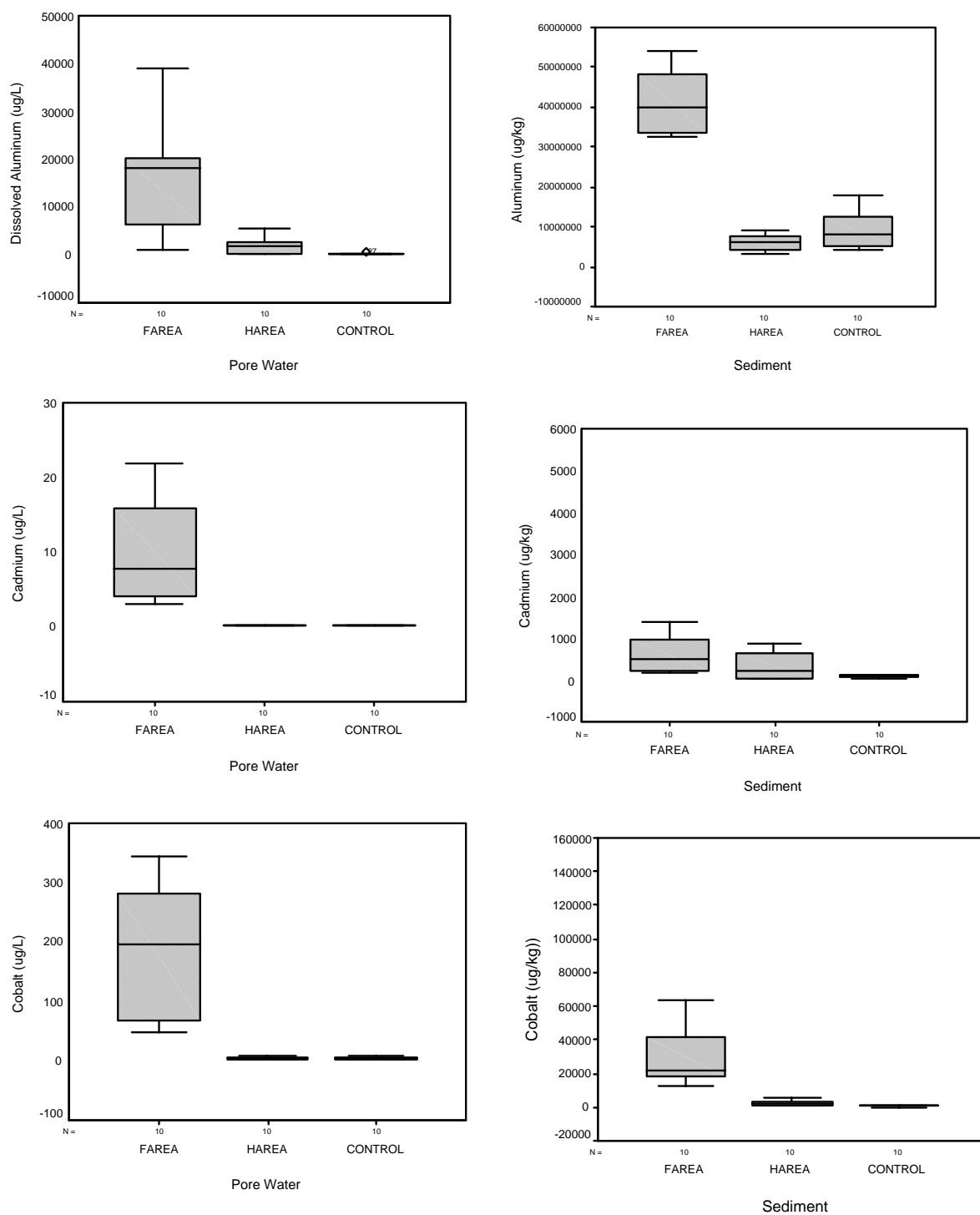
**TABLE 6. (Continued) Means, standard errors, and results of parametric (F) and non-parametric (H) analysis of variance (ANOVA) for constituents in sediment collected from three locations, Savannah River Site.**

Constituent	Location <sup>a</sup>	n <sup>b</sup>	Mean	Std. Error	ANOVA <sup>c</sup>
Total Recoverable	F-Area♣	10	220	21	F=21.9 (P<.001)
Potassium (mg/kg)	H-Area♦	10	81	12	
	Control♦	10	94	15	
Total Recoverable	F-Area♣	10	670	100	H=17.9 (P<.001)
Sodium (mg/kg)	H-Area♣	10	448	150	
	Control♦	10	7.3	2.5	
Sulfate (mg/kg)	F-Area♣	10	61	14	F=5.7 (P=.009)
	H-Area♦	10	23	4	
	Control♦	10	29	5	
Total Recoverable	F-Area♣	10	1,526	221	F=7.8 (P=.002)
Tin (µg/kg)	H-Area♦	10	626	177	
	Control♦	10	651	146	
Toluene (µg/kg)	F-Area♣	10	2.7	0.44	H=1.98 (P=.372)
	H-Area♣	10	50.2	22.7	
	Control♣	10	1.9	0.69	
Total Recoverable	F-Area♣	10	21,560	879	H=3.3 (P=.191)
Vanadium (µg/kg)	H-Area♣	10	19,317	6,638	
	Control♣	10	22,474	3,239	
Total Recoverable	F-Area♣	10	91	8.7	F=81 (P<.001)
Zinc (mg/kg)	H-Area♦	10	11	1.9	
	Control♦	10	9	1.2	

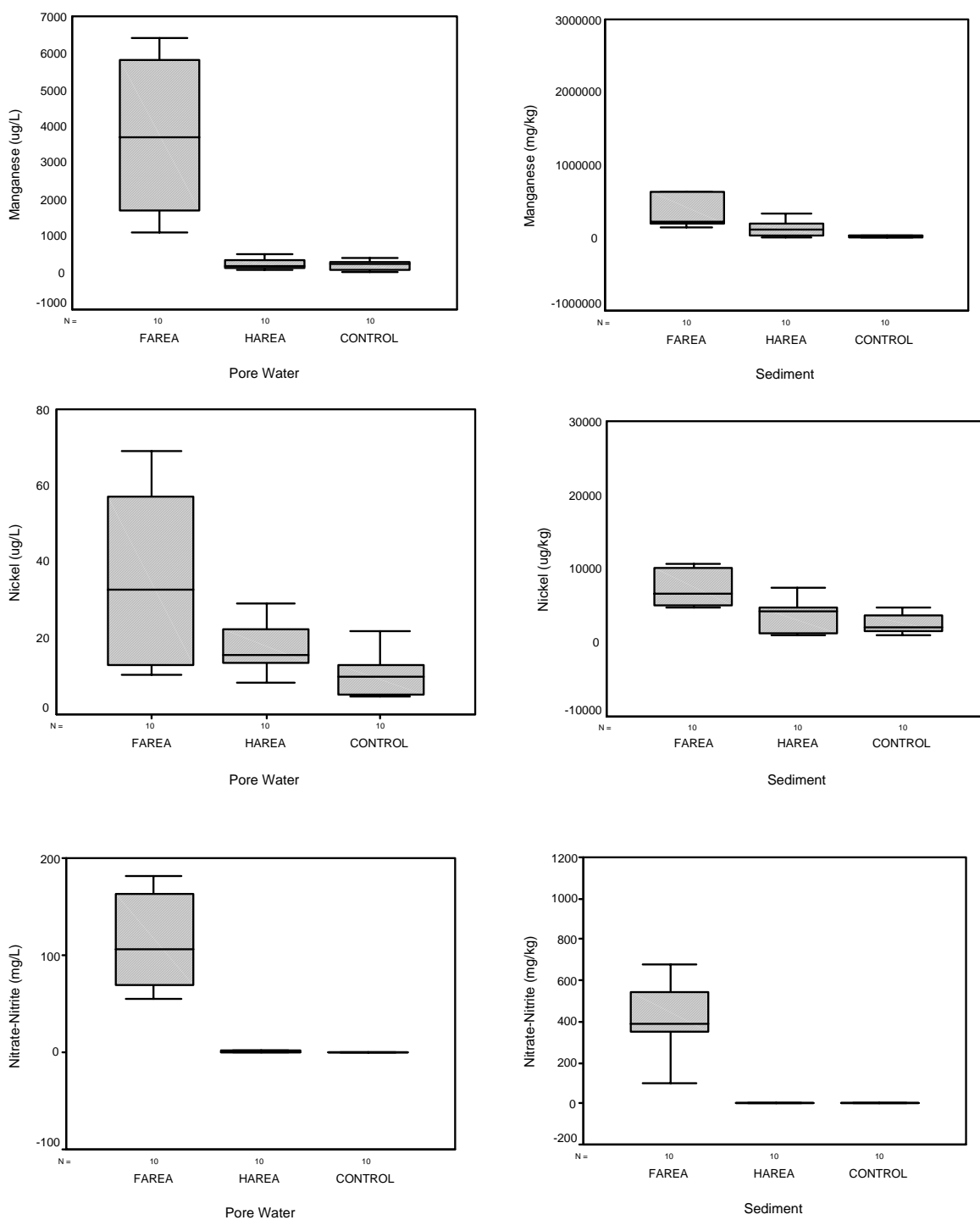
a. Any two locations having the same symbol do not have significantly different (P<.05) mean or median concentrations as determined by the least significant difference (lsd) or Dunn's test.

b. n = number of samples

c. F values represent one-way analysis of variance; H values represent the Kruskal-Wallis non-parametric analysis of variance.

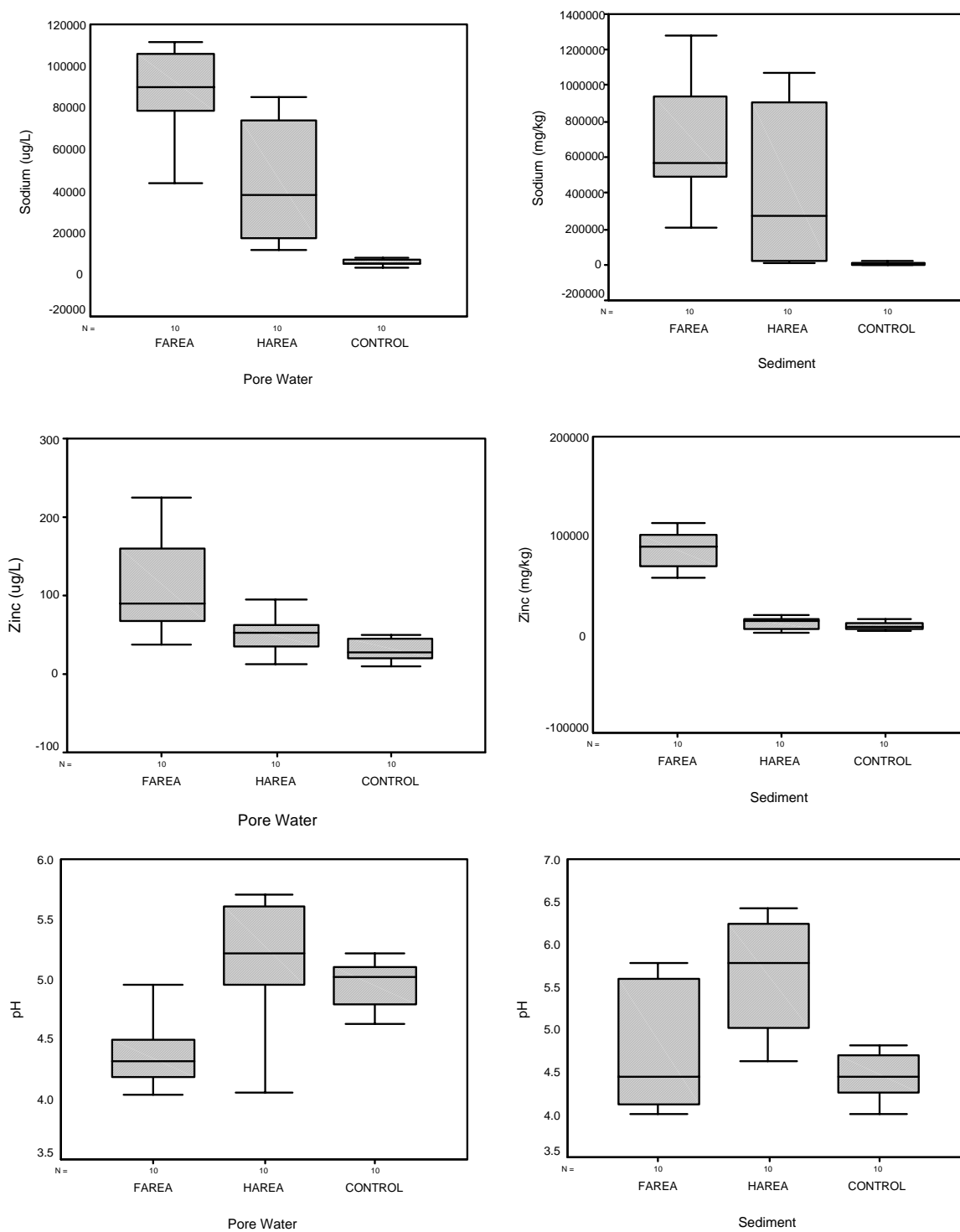


**FIGURE 2. Comparison of pore water and sediment concentrations for selected analytes at three wetland locations, SRS.**



**FIGURE 2 (Continued).**





**FIGURE 2 (Continued).**

**TABLE 7. Comparison of concentrations in the F-Area tree-kill zone with results from other investigations.**

Constituent	Units	Greenwood <sup>a</sup>	Koch <sup>b</sup>	Fourmile <sup>c</sup>	Seaman <sup>d</sup>	F-Area
Aluminum	µg/L	6,800	2,163	357	27,600	24,700
Cadmium	µg/L	<5	2.3	1.9	5.9	10.2
Cobalt	µg/L	-	7.3	2.2	191	185
Manganese	µg/L	7,200	520	580	3,700	3,683
Magnesium	µg/L	-	1,017	543	3,000	9,049
Nickel	µg/L	86	2.79	3.4	32	36
Nitrate-Nitrite	µg/L	310,000	9,890	144	87	111
Sodium	µg/L	150,000	5,316	5,538	73,500	88,850
Zinc	µg/L	300	24.7	47	110	115
pH	unitless	-	5.0	6.15	4.14	4.47
Conductivity	µS/cm	3,250	339	78	-	789

a. Greenwood et al. (1990).

b. Koch (1999); Koch and Friday (1999).

c. Fourmile Branch, 3rd Quarter 2000 (unpublished data).

d. Seaman (2000).

## CONCLUSIONS

Ecological conditions varied markedly between the F-Area and H-Area study sites. Although the structure and species composition at H-Area differed from conditions prior to impact, a relatively diverse vascular flora existed and plant vigor was robust, especially hydrophytic plants whose roots were exposed to saturated sediments. There were no areas, other than open standing water, that did not support biological life at H-Area. Plant life at F-Area was absent except for those species that could marginally survive on hummocks, debris, or other elevated structures. Although levels of some constituents have declined during the last decade, toxic conditions clearly remain in the pore water and sediment at the F-Area tree-kill zone.

Results of the analyses of variance identified significantly higher concentrations in pore water of Al, Ba, Cd, Ca, Co, Mg, Mn, Na, Ni, Tl, Zn, and nitrate-nitrite at F-Area than was found at H-Area or the control. The F-Area tree-kill zone also had a significantly lower pH, and higher electrical conductivity and water hardness. With the exception of Ba, Ca, Mg, and Tl, concentrations of these constituents in sediment were also significantly elevated in F-Area. Although aluminum has been previously thought to be the primary toxicant, the elevated levels of other constituents suggest that multiple toxicants or synergistic interactions may play a role in inhibiting plant growth. To specifically identify the causal factor or factors would require controlled toxicological studies using swamp tupelo or other species of native wetland flora.

Constituents whose concentrations did not differ significantly between locations included As, Be, Cu, and Cyn in pore water and Ba, Ca, Cr, Hg, Mg, Pb, and V in sediment. These analytes probably do not adversely affect plant growth. Volatile and semivolatile organic compounds were either not detected in pore water and sediment, or concentrations at F-Area were not significantly different from the other locations. Organic compounds do not appear to affect the establishment of native flora.

Based on the concentrations of hydrogen ions and analytes in pore water and sediment from this study, I conclude that the most logical explanation of the tree-mortality at F- and H-Areas is the result of acid leachate migration associated with the disposal of chemicals in the F- and H-Area seepage basins. Trends indicate that concentrations of some constituents have declined and this observation is also supported by laboratory experiments using leachate treatments.

Although there have been numerous monitoring and sampling activities in the vicinity of the F- and H-Area seepage basins, this is the first investigation that has comprehensively examined pore water and sediment chemistry in both tree-kill zones and a control. The data from this investigation should prove useful in evaluating natural or assisted remediation of the site, and the piezometers that were installed as part of this effort can also facilitate continued monitoring activities and regulatory compliance issues associated with the seepelines and Fourmile Branch.

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