CHAPTER 18

RELEASES OF CHEMICALS TO SURFACE WATER

ABSTRACT

This chapter provides information about waste disposal practices, processes, effluent, and environmental monitoring data that *Radiological Assessments Corporation (RAC)* used to characterize releases of chemicals to Savannah River Site (SRS) streams. Monitoring for chemicals was generally not conducted until the late 1980s. Fortunately, many of the processes, including the separations processes in F-Area and H-Area and the raw materials manufacturing processes in M-Area, had periods of peak production in the late 1980s when monitoring data are available. Monitoring data suggest that the releases of metals, nitrates, pesticides, and polychlorinated biphenyls (PCBs) were not detectable in the Savannah River. Concentrations measured upstream of the SRS were the same or greater than downstream concentrations or less than detection limits. Although large amounts of some chemicals were released to seepage basins and Site streams, the impacts to surface water extending beyond the Site boundary do not appear to be measurable.

INTRODUCTION

This chapter describes releases of arsenic, cadmium, chromium, coal and coal ash, gasoline, hydrogen sulfide, lead, manganese, mercury, nickel, nitrates, uranium, and zinc to surface water. It also summarizes the accidental spills to surface waters and fish kills that have been reported. Chapter 5, the Phase I Task Four 4 report addendum (Stetar et al. 1994), and several Savannah River Site (SRS) documents (including Reinig et al. 1973) contain descriptions of surface water flow and waste discharges into streams and sewers. Before about 1985, amounts were reported in pounds in historical documents. These amounts were converted to kilograms to make comparisons easier. Chapter 17 addresses releases of chlorinated solvents to surface water; because of their rapid volatility, volatilization of these compounds into the air may be more important than their concentrations in offsite surface water.

Because of the large amount of surface water and rainfall at the SRS, the U.S. Environmental Protection Agency (EPA) and state agencies have required that the SRS file a Spill Prevention Control and Countermeasures Plan. For this study, we photocopied and reviewed the Spill Prevention Control and Countermeasures Plans for 1987 and 1997, which are kept by the Environmental Protection Department. The plans listed all of the fuel, oil and solvent tanks, transformers, and transfer stations, by area. The plans contained information about tank capacity and contents and described containment features such as dikes (Graham et al. 1987; Westinghouse 1997). The total number or total capacity of the tanks has not been compiled but could be derived from these documents if releases were thought to warrant it.

Metals were released to surface streams from coal and ash and processing in M-Area, H-Area, and F-Area. The Spill Prevention Control and Countermeasures Plans characterized metals in waste effluents discharged to seepage basins and Site streams and ponds at the SRS; nitrate releases from M-Area, H-Area, and F-Area; and chlorinated solvent releases from M-Area. The Plans discuss the use of these materials, their discharge into wastewater going to the seepage

basins or to Site streams, and how the material discharged could be transported to the Savannah River.

A report justifying selecting 16 metals to be analyzed in 210 stream sediment samples was written in 1985 for a part of a Comprehensive Cooling Water Study done for the SRS. Sources of metals were thought to be (a) metals in the Savannah River water used to cool reactor and powerhouse operations, (b) 12 point source National Pollution Discharge Elimination System (NPDES) continuous flow outfalls, (c) shallow groundwater outcropping to Four Mile Creek from releases to the F-Area and H-Area seepage basins, (d) leachate from reactor heat exchanger tubes at the C-Reactor, K-Reactor, and P-Reactor, (e) and naturally occurring concentrations in sediments (Gladden et al. 1985).

Measurements of metals in Tim's Branch sediments in 1984, 1985, and 1986 were reported in Specht (1991). Concentrations in sediments at the "creek mouth" were also reported, but the location of the creek mouth is not clear. The report containing these values appeared to be a photocopy of overheads for a presentation. The values were not referenced and details about the sample collection, number of samples, the time of year they were taken, and the analysis were not included. It is likely that the concentrations presented were averages. The same data appear to have been used by Pickett (1990), who reported that in 1985 and 1986, Tim's Branch and Upper Three Runs Creek sediments were sampled monthly at six locations for metals. Eight samples were taken for each location (Pickett 1990). The source of the data for both Pickett (1990) and Specht (1990) was a study attributed to Starkel et al. (1987), with Environmental and Chemical Science, Inc. A report of this original study was not located.

The history of liquid effluent discharges in M-Area is important for characterizing releases. From 1952 through 1958, all effluents were discharged directly to Tim's Branch. It has been difficult to determine when the M-Area settling basin was first put into operation and what percentage of the liquid effluent discharged from M-Area went to the basin or was discharged directly to Tim's Branch. The discharge history of M-Area reported by Specht (1991) indicated that all effluents were discharged to Tim's Branch from 1952 to 1973 and that the settling basin was not completed until 1973. Pickett (1990) said that 313-M was not diverted to the basin until 1973. Other documents suggest that a seepage basin was put into use in 1958 (Christensen and Brendall 1981). Because many of the documents that describe the history of the discharges are concerned with uranium releases and uranium releases first went to the seepage basin from 313-M in 1973, the seepage basin was assumed to be used first in 1973 for these historical analyses. However, based on the history of uranium releases from M-Area and the history provided by Specht (1991) and Pickett (1990), we believe that effluents containing most of the solvents and metals were being discharged to the basin before 1973. In their discussion of the solvents released to the M-Area sewers, Christensen and Brendall (1981) indicate that solvents had been released to sewers leading to the seepage basins since 1958. Except for 7 months in 1982 when all discharges were diverted from Tim's Branch, some effluent was discharged to Tim's Branch until the effluent treatment plant began operating in 1985. Certainly, more effluent was diverted to the seepage basin with time. For reconstructing releases, we can assume that all chemicals in the effluent were released to Tim's Branch from 1952–1958. Some portion, perhaps one-half, went to Tim's Branch from 1958 to 1973, and less than 40% went to Tim's Branch from 1973 to 1982. After 1982, process water with fewer chemicals went to the stream, and after 1985, all effluent was diverted to the treatment facility.

All M-Area liquid effluents were probably released to Tim's Branch from 1952–1958, before the settling basin was used. Measured uranium releases were highest from 1964 to 1970 (Chapter 5), but this was thought to have been the result of process changes, including overflow from a waste holding tank and inadvertent loss of etching solution. We expect that the releases of other metals would not have occurred in the same pattern as uranium.

Upperbound estimates of the amounts of waste discharged to Tim's Branch include 1.35×10^8 gal y^{-1} in 1982 before diversion in May to the settling basin (Gordon 1982; Colven et al. 1985); 2.6×10^8 gal y^{-1} average, ranging from 1.0×10^8 to 3.6×10^8 gal y^{-1} in 1970 (Monier 1970); and 2.6×10^8 gal y^{-1} in 1970 (Hardt 1970).

Effluent monitoring for many of the chemicals of concern was reported in Merz (1982). If we assume that concentrations of metals in effluent were the same in 1982 as in previous years, we can estimate a total release for each metal for which Merz (1982) reported a concentration. Merz (1982) was concerned with process sewer discharges and resulting groundwater contamination, especially from solvents. He estimated that 32,000 lb of heavy metals were contained in the settling basin and only chlorinated organics had penetrated the settling basin to enter the groundwater. The metal concentrations in a 24-hour composite sample of sewer effluent going to Tim's Branch and to the settling basin, dated December 1981, were given in a table in Merz (1982). The source of the data is not referenced and we assume it was collected by Merz. Information about how the samples were collected and the analytical methods used are not included in the memorandum. If we assume average discharges to Tim's Branch were 2.6×10^8 gal y^{-1} or 9.84×10^8 L y^{-1} (Monier 1970; Hardt 1970) the milligram per liter concentration of metal in the effluent reported by Merz can be used to estimate the total kilograms discharged each year or the total kilograms discharged from 1952 to 1982, a 31-year period (assuming 365 d y^{-1} and 3.78 L gal^{-1}). Although effluent metal concentrations in 1982 and discharge volumes in 1970 are not representative of the entire time period of operations, this is the best monitoring data that is available to us. No other effluent monitoring data for metals in M-Area effluent were reported, as far as we know.

ARSENIC

Arsenic is a known human carcinogen. Arsenic was not a process chemical and site inventories reported amounts less than 0.25 lb, suggesting it was used as an analytical standard or in other laboratory applications. Although the ranking ratio for arsenic was very low (see Appendix C3), arsenic leached or carried in runoff from the coal piles to surface water was a concern, and this arsenic would not have been accounted for in the Site-wide inventory. Therefore, we compiled information on arsenic in surface water runoff from the coal and ash piles. We also reviewed Savannah River Ecology Laboratory (SREL) studies on arsenic levels in the swamp from the ash and coal piles and discussed them in the coal and ash section of this chapter. In 1981, Bradley estimated that about 90 kg of arsenic was in sludge and sediment of the M-Area seepage basin. Arsenic was released to Tim's Branch from M-Area in very small amounts (Bradley 1981), especially when compared to the amounts of metals like nickel, lead, and uranium that were released. The Site does not appear to contribute to arsenic levels in the Savannah River (Westinghouse 1996a).

CADMIUM

Cadmium is a carcinogenic metal. Cadmium compounds can cause lung disease, kidney damage, and skeletal and reproductive effects. Cadmium can cause cancer of the prostate and lung in humans. Cadmium may accumulate in meat, fruit, and fish. Shellfish, such as mussels, scallops, and oysters, are a major source of dietary cadmium. Cigarette smoking may be another important source of cadmium exposure. Liquid effluent from M-Area and various coal and ash pile runoff and leachate contained cadmium. In 1985, Lower estimated that although the continuous flow outfalls discharged no cadmium, the daily delivery of cadmium to Site streams totaled about 0.91 kg d^{-1} for the entire Site (Lower 1985). Coal and ash were probably much more important sources of cadmium from the SRS than process releases. The coal and ash section of this chapter contains a discussion of cadmium in coal ash and coal pile runoff basin effluents.

Separations Areas

Elevated levels of cadmium were observed in groundwater samples collected from wells adjacent to the F-Area seepage basin in 1982–1983 (Christensen and Gordon 1983b). Accounts of releases to the F-Area basin do not report cadmium and the source was said to be unknown (Lower 1985). Extensive sampling of the seepline was conducted in 1989 and 1990 and was published by Haselow et al. (1990). Cadmium was the only metal to exceed the maximum background soil value, but it was exceeded for only 1 sample out of 26. All the metals were less than the primary drinking water standard except cadmium from F-Area. Levels of cadmium at the seepline were between the proposed standard of 5 μg L^{-1} and the established standard at the time of 10 μg L^{-1}. The source of the cadmium in the Creek was said to have been the F-Area seepage basin but records did not address why and how much cadmium was discharged to the basin. Cadmium was not used in large quantities in F-Area processes.

M-Area

Cadmium was released in small amounts to M-Area wastewater. Based on effluent monitoring data from a time period when the average production rate for 313-M was 17,500 cores per month, Looney et al. (1987) estimated M-Area cadmium effluent discharges to the M-Area settling basin to have been 1 kg y^{-1}. Using this information, a total disposal mass, based on an average production rate of about 13,000 cores per month, over a 13.5 year period, was estimated to be 10 kg for cadmium, or about 0.74 kg y^{-1} (Looney et al. 1987). The estimate is probably most representative for the years 1971–1985.

In 1985 and 1986, Tim's Branch and Upper Three Runs Creek sediments were sampled monthly at six locations for metals. Eight samples were taken for each location. The most distant sampling point was in Upper Three Runs Creek, just downstream of the confluence with Tim's Branch. Mean concentrations plus or minus the standard error at this point were 0.4 $\pm$ 0.07 mg kg^{-1} for cadmium, compared to 1.5 $\pm$ 0.2 mg kg^{-1} just downstream of where the outfall enters Tim's Branch. The control or background location had levels of 0.1 $\pm$ 0.3 mg kg^{-1} (Pickett 1990). For comparison, a very conservative EPA preliminary remediation goal (corresponding to a 10^{-6} increased cancer risk for soil ingestion, inhalation, and dermal absorption) is 38 mg kg^{-1} for a residential scenario and 850 mg kg^{-1} for an industrial scenario (EPA 1996). The sediment

concentrations at the outfall was about 15 times the background levels Dilution appeared to be about 4 fold from the outfall to Upper Three Runs Creek (Pickett 1990). It seems likely that further dilution in Upper Three Runs Creek and the Savannah River swamp would result in very low concentrations entering the Savannah River. Since January 1984, cadmium has been analyzed in water samples collected from the Savannah River. Cadmium was found to be routinely undetectable. Any cadmium detected in Site stream sediments would not have come from the Savannah River; but would have been due to Site discharges. Site discharges may have been about 1 kg y^{-1} from M-Area to Tim's Branch and an undetermined amount from F-Area to Four Mile Creek. These discharges resulted in concentrations at or near the drinking water standard at the creek (Haselow et al. 1990). Discharges from the Site do not appear to have added detectable levels of cadmium to the Savannah River.

CHROMIUM

Chromium solutions were used at the SRS as corrosion inhibitors. Chromium was a component of waste solutions resulting from dissolving stainless steel and it was also used in cleaning solutions in the separations areas (Du Pont 1988). Chromium leached from coal and ash also contaminated groundwater beneath and surface water adjacent to the D-Area coal pile runoff basin.

In 1985, chromium was detected in water from four outfalls and an amount per day was calculated based on average effluent flow (Table 18-1). The total discharge was reported to be 3316 kg d^{-1} (Lower 1985).

Table 18-1. Chromium Concentration and Transport from Four Outfalls

Outfall	Concentration (mg L^{-1})	Mass transport (g d^{-1})	Receiving stream
A-001	0.16	287	Tim's Branch/Upper Three Runs
D-001	0.01	2,900	Beaver Dam Creek
F-008	0.033	126	Four Mile Creek
H-012	0.002	3	Four Mile Creek

[a] Source: Lower (1985).

D-Area

Chromium and other metals have also been of concern in surface water near D-Area. In 1985, Lower reported that measurements showed that the intake concentration of chromium at pumphouse 5G, the cooling water intake for D-Area operations, was one-fifth of the effluent concentration. The effluent measured included discharges from the D-Area powerhouse, heavy water production facilities, and ash basin (Lower 1985). Chromium release from the coal piles and ash disposal basins is discussed in the coal and ash section of this chapter.

As an Additive to Cooling Water

Chromium corrosion inhibitors, which were added to cooling water, were an important source of chromium released to surface streams. A 1973 report acknowledged that chromates used to inhibit corrosion in circulated chilled water and heating systems created pollution problems when leaks or spills of cooling water occurred. The report stated that an organic, biodegradable substitute was being evaluated for plantwide use (Du Pont 1973a).

Memorandums concerning spills occurring over the last two decades documented many spills and leaks of chromium-treated water (Jewell 1990). Some of the more significant spills are listed in Table 18-2.

Table 18-2. Spills and Leaks of Chromium-treated Process or Cooling Water

Date	Release	Reported amount	Remedial action
November 1977	Chromium released in effluent from retention basin 281-8H to Four Mile Creek in excess of NPDES	Not reported	Diluted to below detection limit
1977	Underground leak found in 241-H chromate cooling water system	Not reported	Leak repaired
May 1981	Cooling water containing chromium	9000 gal	Sent to the 281-8F retention basin
March 1987	Spill of cooling water containing chromium in concentrations up to 526 mg L^{-1}	10,000 to 15,000 gal	Released to an outfall to Four Mile Creek
April 1987	Water containing chromium to A-Area	More than 6950 gal	Contained and drummed

The largest and most well described of these spills occurred on March 28, 1987. From 10,000–15,000 gal of chromate-containing cooling water leaked to the ground from a cooling line that served tanks 29 and 32 in H-Area. The spill flowed into a nearby storm sewer and discharged through an outfall to Four Mile Creek before being contained with sandbags and pumped to H-Area seepage basins. The sodium chromate concentration in the cooling water was 526 mg L^{-1} (Jewell 1990; Durant 1994), suggesting that as much as 30 kg of chromium may have been released to the creek if all 15,000 gallons were not contained. Depending on how quickly the spill was contained, the release may have been smaller. Information needed to estimate releases from other spills is not available.

Site workers have not been able to tell us how much of the water used by the SRS was treated with chromium. It is likely that some water was treated and some was not. We have very little information on chromium use in cooling water and do not have enough information to determine whether a significant quantity of chromium was released to site streams and transported to the Savannah River. However, water quality monitoring data for the Savannah River do not suggest a measurable amount of chromium has been released from the SRS (see Chapter 20).

M-Area

In 1981, Bradley estimated that 113.6 kg of chromium was in sludge and sediment of the M-Area seepage basin. Concentrations of chromium, measured in a 24-hour composite sample of sewer effluent sampled in December 1981 when the plant was operating, were 0.003 mg L^{-1} in sewer effluent going to both the settling basin and to Tim's Branch. From these data, about 114 kg was estimated to have been in the settling basin sludge (Merz 1982). If we assume average discharges to the Tim's Branch were 2.6×10^8 gal y^{-1} or 9.8×10^8 L y^{-1} (Monier 1970; Hardt 1970; Colven et al. 1985). The chromium concentration of 0.003 mg L^{-1} reported by Merz would lead to an estimate of 2.95 kg discharged to the creek each year or 92 kg total from 1952 to 1982, a 31-year period, assuming 365 d y^{-1} and 3.78 L gal^{-1}.

In March through May 1985 the influent to and effluent from the M-Area settling basin was sampled and analyzed weekly for 10 weeks. Based on these sampling data, a removal efficiency was calculated for the basin (the influent concentration minus the effluent concentration divided by the influent concentration). The influent concentration of chromium was 0.037 $\pm$ 0.037 mg L^{-1}, the effluent concentration was 0.006 $\pm$ 0.006 mg L^{-1}, and the removal efficiency was estimated to be about 84% (Colven et al. 1985).

In 1984, a partial failure of the wooden dam at Steed's Pond, which received M-Area effluents, occurred, and samples were taken to determine if radioactive materials were migrating from the pond. The 1985 Annual Environmental Report reported the highest chromium concentration in Steed's Pond sediment was 290 μg g^{-1}, compared to an average background in the southeastern U.S. of 38 μg g^{-1}, ranging from 11–60 μg g^{-1} (Pickett 1990; Zeigler 1986a).

In 1985 and 1986, Tim's Branch and Upper Three Runs Creek sediments were sampled monthly at six locations for metals. Eight samples were taken for each location. The most distant sampling point was in Upper Three Runs Creek, just downstream of the confluence with Tim's Branch. Mean sediment concentrations plus or minus standard error at this point were 11.6 $\pm$ 2.2 mg kg^{-1} for chromium, compared to 80.2 $\pm$ 8.6 mg kg^{-1} just downstream of where the outfall enters Tim's Branch. The control location had levels of 7.2 $\pm$ 0.6 mg kg^{-1} (Pickett 1990).

For comparison, conservative EPA preliminary remediation goals, corresponding to a 10^{-6} increased cancer risk, are 210 mg kg^{-1} for a residential land use scenario and 450 mg kg^{-1} for an industrial land use scenario (EPA 1996).

Separations Areas

Chromium was discharged to the F-Area and H-Area seepage basin. Like mercury, it contaminated the groundwater beneath the basins. Some small amount of chromium outcropped to surface water at Four Mile Creek and may have eventually traveled to the Savannah River.

A 1% sodium dichromate solution was used in the Receiving Basin for Offsite Fuels (RBOF), 224-H, to clean lithium-aluminum alloy targets. The resulting liquid waste, containing about 1.25 mg L^{-1} chromium, was discharged to the H-Area seepage basin. After 1982, the chromate solutions used for lithium-aluminum target cleaning were sent to the 242-H evaporator rather than being directly discharged to the basins. The evaporator overheads were sent to the seepage basin and the bottoms were sent to waste tanks. The evaporator was effective in removing most of the chromium. In 1983, the contents of waste tank 23, which also contained

chromium, was sent to the evaporator, and this further reduced chromium releases to the seepage basin (Holcomb and Emslie 1984).

Chromium concentrations in wastewater going to the H-Area basins have been recorded since October 1980. Chromium releases before that time were not measured (Holcomb and Emslie 1984). The H-Area seepage basin received about 546 kg of sodium dichromate (about 217 kg of chromium) each year before 1982. A 1987 safety analysis report said that releases from January 1981 through July 1983 were 737 kg, which averages to about 24 kg mo^{-1} over 31 months or 285 kg y^{-1} (Hurrell et al. 1987). Based on an average flow rate of 1,261,000 gal wk^{-1} to H-Area and 311,700 gal wk^{-1} in F-Area, Holcomb and Emslie (1984) reported that in 1975, an estimated 123 kg of chromium had been released to F-Area seepage basin and 2318 kg to the H-Area seepage basin (Christensen and Gordon 1983b; Holcomb and Emslie 1984).

In 1980 and 1981, H-Area seepage basins were analyzed for chromium. Chromium releases from H-Area effluents to the seepage basins were said to have ranged from 2 to 5 mg L^{-1}. A chromium level greater than 1.5 mg L^{-1} was reported during a time when no material was being cleaned using the chromium solution at RBOF. H-Area personnel postulated that chromium could have been leaching along the lines to the seepage basins or that it could have been coming from corrosion inhibitors from waste tank cooling, although the cooling water was not supposed to be discharged to the seepage basins (Morris 1982). At times, the chromium concentration in the effluent discharged to the seepage basin was 10–30 mg L^{-1} (Clontz 1981). In 1981, a Request for Technical Assistance was completed for a chromium-free cleaning solution that was said to have been needed to comply with EPA release regulations. Methods to treat and reduce the amount of chromium waste solutions were also examined (Monson 1981).

In 1981, an analysis of effluents released to the seepage basin showed a maximum chromium concentration of 10.6 mg L^{-1} and an average concentration of 1.55 mg L^{-1}. Monitoring wells downgradient of basins showed chromium contamination exceeding the drinking water standards (Lower 1985). Looney et al. (1987) calculated inventories for the H-Area seepage basins from influent data, which included 590 kg of chromium through 1985. Based on measurements taken in 1960–1970, 1975, and 1983, the total disposal mass to the F-Area seepage basins from 1954 to 1983 was estimated to have been 47 kg of chromium, (Killian et al. 1987a) averaging to 1.5 kg y^{-1}. Killian et al. (1987b) predicted that before mid-1982, when the cleaning solutions were first sent to waste tanks, 554 kg of sodium dichromate (about 220 kg) of chromium was sent to the H-Area basins annually. Chromium concentrations in wastewater going to the basins have been measured routinely since October 1983. Eleven samples of H-Area effluent/H-Area seepage basin influent were taken from September to December 1983. The concentration of chromium averaged 0.072 mg L^{-1}. A maximum value of 0.36 mg L^{-1} was reported (Killian et al. 1987b). Table 18-3 summarizes the various estimates reported.

Table 18-3. Estimates of Chromium Discharged to the Separations Area Seepage Basins during Various Time Periods

Time period	Annual average to H-Area seepage basin (kg y^{-1})	Annual average to F-Area seepage basin (kg y^{-1})	Reference
1952–1981	217		Hurrell et al. (1987)
1982–1983	285		Hurrell et al. (1987)
1952–1975	2318	123	Holcomb and Emslie (1984)
1960–1983	220	1.5	Killian et al. (1987a)
1971–1985	590		Looney et al. (1987)
1954–1982	554		Killian et al. (1987b)

Because of the chromium releases to the separations area seepage basins and subsequent contamination of groundwater that outcrops into Four Mile Creek, chromium concentrations in Four Mile Creek were of interest. The chromium that traveled from the basins to the groundwater, subsequently outcropped into Four Mile Creek, and eventually traveled to the Savannah River seems to have been a very small amount. In 1987, the Site collected sediment samples to analyze for chromium from the Savannah River at river mile 120 and 187. Four Mile Creek enters the Savannah River at about river mile 150. The respective concentrations were 0.0193 and 0.0158 mg L^{-1}. These concentrations were more than 2 orders of magnitude less than concentrations measured in Four Mile Creek in 1987 (Mikol et al. 1988). Chapter 20 summarizes the results of additional chromium monitoring of Site stream and Savannah River sediments and water. Results of sediment, water, and fish sampling show no significant differences between chromium concentrations in onsite streams and other Savannah River locations, suggesting chromium contamination of the Savannah River is not detectable. Chromium concentrations measured in onsite streams and Savannah River water and reported in the Annual Environmental Reports from 1984 through 1991 have been well below the drinking water standards and near or below detection limits.

COAL AND COAL ASH

Steam and electricity were produced by as many as seven coal-fired power plants in the A-Area, C-Area, D-Area, F-Area, H-Area, K-Area, and P-Area. Liquid effluent from the F-Area and H-Area coal-fired power plants were diverted to coal-pile runoff or ash basins. Coal-fired steam plants in the reactor areas had floor drains that discharged to the ash and coal-pile runoff basins (DOE 1987). The largest power plant was in D-Area. The D-Area power plant released fly ash and coal pile runoff into the Beaver Dam Creek stream and swamp system. Most of the information in historical records is concerned with the D-Area power plants. Beaver Dam Creek received most of the coal and ash basin liquid effluents generated onsite. After 1982, D-Area had a coal pile runoff basin and ash basin that received powerhouse ash sluice. In addition, a filled ash disposal basin was used as a sanitary spray field for sanitary treatment plant effluent (Peralta and Lewis 1982).

Coal Storage

Coal was stored at all of the seven power plants. Surface runoff from the coal storage piles was discharged to surface streams until 1977, when the National Pollution Discharge Elimination System (NPDES) was initiated. To meet NPDES discharge requirements and also in response to SCDHEC requests, seven unlined earthen containment basins were constructed at each coal storage location to intercept, stabilize, and treat surface runoff from the coal piles (DOE 1987; Christensen and Gordon 1983a). To comply with the NPDES permit issued in 1977, coal pile runoff containment basins were constructed in D-Area and A-Area in 1978 and basins in C-Area, F-Area, K-Area, H-Area, and P-Area were completed by March 1981 (Cummins et al. 1990). Rainwater runoff from the coal piles flowed into the containment basins through ditches and sewers. The basins were designed to diminish the entry of large amounts of low pH runoff into surface streams. Releases of sulfur compounds, magnesium, chromium, cadmium, manganese, and arsenic in the runoff from the coal piles are of concern. The basins would have retained these compounds, but releases before the basins were constructed went into Site streams. Acid from oxidation of sulfur materials in the coal was washed by rain into the runoff basins. Monitoring of groundwater at the seven basins showed concentrations of some heavy metals above background levels (Christensen and Gordon 1983a). Because the groundwater beneath the piles does not flow offsite, it was not evaluated as a part of this dose reconstruction study. Runoff to surface water does flow into site streams which eventually flow into the Savannah River, so surface water contamination by coal and ash pile runoff were considered. Coal pile runoff basins in C-Area, K-Area, H-Area, F-Area, and P-Area were all active in 1982; L-Area and R-Area basins were not active (Peralta and Lewis 1982). The C-Area and F-Area basins have been inactive since 1985 when the coal piles were removed (Westinghouse 1992a).

Coal Reject Piles

One of the few studies done on metals in coal pile leachate was reported by Carlson (1990). He reported that acidic leachate from a reject coal pile in D-Area and inactive ash basin was contaminated with metals and sulfate and was stressing vegetation, presumably because of the low pH. The leachate from the coal pile had contaminated the water table with sulfate (up to 22,200 mg L^{-1}) and metals, especially iron and aluminum. The reject coal pile was located adjacent to one of the old ash basins. The volume of reject coal placed along the berm surrounding the basin and the time period over which it was deposited was unknown. The pile was about 380 m long, up to 30 m wide, and 2.5 m thick. By 1981, the pile was covered with soil. An area of stressed vegetation was noted north of the pile. Numerous seeps at the base of this coal pile were observed. These seeps combined to enter outfall D-003 and eventually flow into the Savannah River. The seeps had elevated levels of iron, aluminum, lead, nickel, arsenic, cadmium, and sulfate. Three of the seeps had levels of lead, nickel, chromium, and cadmium that exceeded hazardous concentration levels of inorganic pollutants from coal storage areas referenced by the author (Carlson 1990) as having been developed by Wachter and Blackwood in 1978. Two seep samples exceeded the EPA's hazardous waste levels for arsenic.

Ash Disposal

A large quantity of coal ash has been produced by the SRS. Coal ash typically contains the toxic metals arsenic, cadmium, chromium, lead, mercury, and selenium. Ash is of concern as an air pollutant, contributing to particulate emissions, and a surface water contaminant because of contamination of precipitation runoff from ash disposal piles and leaching of toxic compounds from piles and disposal basins (Evans et al. 1980). Chapter 17 describes the releases of ash to air. The solubility of trace elements in coal ash depends on the coal source, combustion, and chemical properties of rainfall and runoff (especially the pH because many of the metals are more soluble at low pH). Metals can leach into groundwater and contaminate surface water from coal and ash pile runoff or overflow from a basin (Evans et al. 1980). Significant quantities of inorganic salts may leach from the ash into the ground. Sluicing the fly ash to the basin and the small particle size of the fly ash makes it possible for the ash to pass through the basin entirely in suspension. Smaller particle size also increases the tendency of the metals to become dissolved in the water and be transported more readily through the drainage system (Guthrie and Cherry 1976; Monier and Bebbington 1970).

Many ecological studies have been conducted on the swamp areas influenced by ash basin effluent. Many studies, conducted primarily by the SREL, have determined levels of metals, the pH and other characteristics of effluent from the coal ash basins, and the effects of effluent on biota in the receiving swamp. The findings of many of these studies have been published in the open literature (Cherry and Guthrie 1979; Cherry et al. 1979; Guthrie and Cherry 1976; Skinner et al. 1978; Rodgurs et al. 1978; Lagnese and Dzombak 1993; Evans and Giesey 1978; Evans et al. 1980).

There were five dry ash piles onsite at the SRS: three in C-Area and two in A-Area. After they became inactive, ash piles were seeded with grass to help prevent erosion and runoff. In 1987, the two active piles were said to have been surrounded by a containment dike. The Radiological Sciences Group Monthly Report for November 1970 mentions ash having been hauled by truck and dumped on the ground at 100-C and 3/700, which is consistent with the 1987 assessment of dry ash piles (Du Pont 1970a). Ash at the 700-Area powerhouse was handled dry and placed in a 2-acre pile. At the other areas, ash was disposed of by sluicing ash and water slurries to ash basins. The ash settled out and water was discharged from the basins through permitted outfalls (Arnett et al. 1992).

In 1987, there were 6 active and 4 inactive ash basins. The ash basins, located near the coal-pile run off basins, received ash sluicewater from the powerhouses. Groundwater contaminants associated with these basins include metals and sulfates. Leachate from the ash basin in D-Area was suspected of being the cause of dead vegetation in an area immediately north of the ash basin. This was also said to be a result of surface drainage from the D-Area sanitary wastewater plant discharge. The toxic component of the leachate or surface runoff that was the cause of the dead vegetation had not been specifically identified in 1987 (DOE 1987).

Washwater from the 700-A Area powerhouse may have also been contaminating sediments and adversely affecting a wetland area below the outfall A008 (DOE 1987).

Since start-up the bottom ash and fly ash from the D-Area plant were combined and sluiced into one of two settling basins. This plant burned 451,940 metric tons of coal annually, producing 32,650 metric tons of ash that was sluiced into a settling basin by approximately 4.5 billion liters of water (Rodgurs et al. 1978). The two basins were filled with ash in about 1975, and a larger

basin to the east of the two was constructed. Overflow water from the basins drained into a 2.5-km^2 swamp that connects with Beaver Dam Creek. The creek flows through a small lake and a second swamp before reaching the Savannah River. Periodic flooding of the Savannah River caused backwater up to the junction of Beaver Dam Creek and the first swamp (Evans and Glesy 1978).

The ash and sluice water eventually emptied in the Savannah River after passing through the swamp. The basin effluent was diluted from water from Beaver Dam Creek and then from the flow of Four Mile Creek before it entered the river. The "influence from the ash" was said to "no longer be apparent" after the Four Mile Creek entrance (Rodgurs et al. 1978), suggesting ash components were not detected in Beaver Dam Creek once it merged with Four Mile Creek.

After 1975, sluiced coal ash from the D-Area power plant was pumped into a 14.6-ha settling basin, with a calculated retention time of about 39 days. The waters of this basin then emptied into a 6.1-ha basin with a calculated retention time of 22 days. The effluent of the second basin passed through a flume and into a swampy area. This water then flowed down a channel into Beaver Dam Creek. The effluent from the basin was said to have been diluted approximately 20 fold by the creek water depending on the time of year. This water then entered the Savannah River swamp and eventually the Savannah River (Newman et al. 1985).

The DOE 1987 survey reported coal ash generation by the power plants in cubic yards per year (DOE 1987). Table 18-4 summaries the annual ash generated by each area.

Table 18-4. Annual Ash Generated by Area[a]

Area	Location	Ash generated in $yd^3\ y^{-1}$ and discharged to the ash basins
700-A	788-A	5,000
400-D	488-1D and 2D	65,000
200-H	288-H	13,000
100-K	188-K	18,000
100-P	188-P	18,000
Total		119,000

[a] Source: DOE (1987).

The annual ash disposal rate was approximately 50,000 $yd^3\ y^{-1}$ from 1952 until 1983 and has been approximately 65,000 $yd^3\ y^{-1}$ in 1983 and the years after. This amounts to 1.94×10^6 yd^3 of ash from 1952 to 1983. The DOE (1987) survey did not include the 200-F Area powerhouse. In 1992, the 200-F powerhouse had been permanently shutdown. The powerhouse was said to have generated approximately 15,000 $yd^3\ y^{-1}$ when it operated, presumably resulting in a total of about 4.65×10^5 yd^3 of ash (Arnett et al. 1993).

The amount of coal ash discharged to the basins can be estimated using several different reports. The amount of metals discharged might be calculated using values of metals in typical coal ash. However, we lack the data necessary to determine the transport of metals from the basins to the streams, swamp, and the Savannah River.

Many researchers have examined the solubility and transport of metals in ash effluent, which is usually discharged to ponds, streams, or lakes. The effluent from sedimentation ponds that was

widely used to settle ash particles from fly ash and bottom ash transport streams was of particular concern. The effluent sluicing water contains a variety of inorganic chemicals from leachate of bottom ash and fly ash: metal cations such as Al^{+3}, Cd^{+2} and Ni^{+2}, and metal oxyanions, such as AsO_4^{2-}, SeO_4^{3}, and MnO_4^{2-}. A number of studies have examined the environmental fate and transport and ecological effects on plants and animals in and around ash ponds. Most of these studies have attempted to find ways to remove contaminants of concern for regulatory agencies. Sluice pond or basin water often contains metals from the ash particles and sometimes at concentrations that can exceed discharge limits. Promoting metal absorption and precipitation (pH dependent reactions) can reduce the concentration of metals in water leaving the ponds (Lagnese and Dzombak 1993).

The 1970 Radiological Sciences Division November monthly report stated that leaching of chemical elements from power plant department ash basins did not contribute hazardous concentrations of toxic chemicals to the river. Leachate samples were collected on three different dates in the fall of 1970 from ash basin effluents in P-Area and D-Area and were analyzed for metals by a spark source mass spectrometer and for mercury by an emission spectrographic technique. Concentrations of arsenic, barium, selenium, cadmium, and iron in ash basin effluent were found to be slightly higher than drinking water standards, but the authors concluded that "on-site plant streams provide a more than adequate dilution" (Du Pont 1970a). Metal concentrations were not determined in the Savannah River or Site streams as a part of this analysis.

In 1979, Guthrie and Cherry (1979) studied the accumulation of heavy metals in biota in the D-Area coal ash drainage system. They determined concentrations of metals in water and sediments of the basin and in Upper Three Runs Creek, which they considered an uncontaminated stream (Table 18-5).

Table 18-5. Concentrations of Selected Metals in Water and Sediments of the D-Area Ash Basin and Upper Three Runs[a]

Metal	Mean water concentration in mg L^{-1} in the ash basin	Mean water concentration in mg L^{-1} in Upper Three Runs	Mean sediment concentration in mg L^{-1} in the ash basin	Mean sediment concentration in mg L^{-1} in Upper Three Runs
Manganese	0.75	0.31	96.0	53.0
Zinc	0.37	2.6	6.5	2.1
Chromium	0.16	0.08	38.0	6.50
Cadmium	0.12	0.14	1.7	0.71
Mercury	0.04	0.006	0.80	0.70

[a] Source: Guthrie and Cherry (1979).

The sediments of the ash basin contained 2 to 10 times higher concentrations of metals, except for mercury. This study was not very helpful for determining the reduction of metals by sedimentation and dilution of the effluent in the creek. Zinc and cadmium were higher in the water from Upper Three Runs Creek than in water from the basin (Guthrie and Cherry 1979). No explanation for this was given, and it was not clear whether the samples contained sediment or were filtered. M-Area effluents could have been the source of the metals in Upper Three Runs Creek, depending on the sample location.

In 1978, metal removal by the seepage basin in D-Area was studied. The removal was determined to be effective because the concentration of iron in the basin effluent was reduced by 90% from the concentration in waste entering the basin. Concentrations of arsenic, chromium, and manganese were reduced by 86, 87, and 83%, respectively. Mercury concentrations were not measured (Peralta and Lewis 1982).

Skinner et al. (1978) studied cadmium in the food chain in the coal ash basin. They studied what this and what many similar journal articles call "an island composed completely of coal ash." The island was described as a 140 × 380-m island located in an ash basin, approximately 600 m southwest of the D-Area coal-fired plant, composed of coal ash that had accumulated since 1952. The ash island had received more than 3 kg m^{-2} of fly ash between 1952 and 1975. A good description of the plants that grow on the island and the ecosystem can be found in Skinner et al (1978). The coal ash basin was sampled for cadmium between October 20 and November 25, 1975. Coal ash generally has higher levels of cadmium than coal, often in the 12–35 ppm range. This has been a concern for using fly ash as a soil amendment or fertilizer. Cadmium inputs to the island were from coal ash via sluice water from boiler grating, stack precipitators, and aerial deposition. Samples of plants, snails, insects, spiders, and soil were taken from the island. Cadmium in soil was bound to organic matter and was held to the soil surface. Approximately 42% of the cadmium was extracted by distilled water in 1 hour. Cadmium concentrations averaged 0.12 $\pm$ 0.002 μg g^{-1} dry weight, with 0.05 $\pm$ 0.01 (standard error) μg g^{-1} of the cadmium water extractable (Skinner et al. 1978). The study documented in Skinner et al. (1978) was designed to examine concentrations in insects and other biota living on the ash, not cadmium leaving the Site.

Rodgurs et al. (1978) studied the removal of contaminants in the swamp and found approximately 1200 m^2 of swamp area was necessary to remove most of the ash influence. Selenium, cadmium, arsenic, and mercury levels varied from 0.12 to 0.04 mg L^{-1} in the swamp water southwest of the 400-D powerhouse. Sediment concentrations were about 1 order of magnitude higher.

Water, sediment, and duckweed samples were collected at six sampling stations and were analyzed using a neutron activation analysis procedure. The results of the analysis in the best available copy of this document are in very small type and are illegible. The text stated that dissipation by settling was most apparent for metals that were at the highest concentrations in the basin water and in the sediments at the stream-swamp confluence. The mean concentrations at the station furthest from the ash basin and closest to the river would be the most representative of effluent closest to where offsite exposure could occur. Levels of metals at the furthest sampling stations were reported not to have been influenced by the ash (Rodgurs et al. 1978).

Newman et al. (1985) sampled for metals dissolved in water from six different locations associated with the 400-D power plant ash basins and compared them to samples taken from Par Pond. Site A was located in the ash settling basin. Sites D and E were in the swamp about 300 m and 1 km below the confluence of the effluent stream and Beaver Dam Creek. Beaver Dam Creek goes on to empty into the Savannah River swamp and then eventually into the Savannah River, but samples below Site E were not reported. Table 18-6 summarizes the results.

These data indicate that the concentrations were decreased because of settling and dilution. A general decrease was seen in the concentrations of arsenic, cadmium, and chromium with distance away from ash basins. However, copper, zinc, and manganese concentrations seem to have been higher 1 km down the creek than at the first basin discharge point, and no explanation

was given for this. Turbulence stirring up sediments in the creek was mentioned and may have accounted for the increases (Newman et al. 1985).

Table 18-6. Concentrations of Dissolved Elements in Ash Basin Effluent and Swamp Waters into Which It Discharges at Various Locations (in mg L^{-1})[a]

Element	Effluent from the first ash retention basin		Effluent from the second retention basin		After a swampy area 250 m below the outfall from the second basin		Beaver Dam Creek, 300 m below where the effluent enters		Beaver Dam Creek, 1 km below where the effluent enters		Par Pond, control site	
	Mean	SD[b]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Manganese	27	±22	25	±21	30	±17	86	±45	82	±44	3	±5
Arsenic	49	±32	46	±30	43.9	±30.7	2.5	±2.0	2.2	±1.7	1.3	±1.6
Cadmium	0.38	±0.17	0.39	±0.30	0.38	±0.37	0.21	±0.07	0.23	±0.27	0.07	±0.07
Chromium	0.50	±0.55	0.45	±0.47	0.31	±0.35	0.35	±0.31	0.38	±0.38	0.05	
Copper	2.6	±0.6	2.6	±0.67	2.6	±0.9	3.0	±0.9	3.0	±1.0	0.8	±0.9
Zinc	9	±6	8	±4	8	±7	12	±17	10	±16	2	±4
Magnesium	1733	±228	1723	±228	1726	±241	1333	±180	1332	±188	1070	±111

[a] Source: Newman et al. (1985).
[b] SD = standard deviation.

In a similar study conducted in 1978, Beaver Dam Creek was compared to Steel Creek, which was described as an adjacent creek not receiving any ash effluent. Steel Creek did receive production reactor cooling water and purge water from reactor fuel and target assembly basins until 1967. They sampled and subjected samples of precipitator ash from the power plant to leaching to predict how readily metals in the ash might be dissolved and enter Beaver Dam Creek in solution. Cadmium, nickel, and zinc were elevated by about a factor of 2 to 4; however, the authors concluded that determining statistically significant differences was difficult and that the trace metal contamination was minor (Evans and Giesey 1978).

Studies have suggested that many metals concentrate in biota. Chromium and arsenic can concentrate in some plants. Guthrie and Cherry (1979) studied plant uptake and found that plants contained 15% of the total heavy metal concentration found in the benthos. Their report stated that "The objective of this work was to examine mechanisms which operated to remove pollutants from the ash basin effluent received by a swamp drainage system". However, a removal rate for biological components of the system could not be determined from these studies. The major mechanism of removal was determined to be settling of particulates in the basin. As flow rates decreased father from the basin, the settling increased (Guthrie and Cherry 1976). Taken together, these studies suggest that much of the contaminants of concern in ash are removed by the basins and by the swamp area between the ash basin discharge points and the Savannah River. Most of the removal was attributed to settling (Rodgurs et al. 1978), but removal by biota also occurred (Guthrie and Cherry 1979; Skinner at al. 1978). There is a potential for migratory waterfowl and other wildlife onsite to ingest and perhaps concentrate some of these metals, and this may be a pathway of exposure to evaluate in later phases of the dose reconstruction study. River quality monitoring for these metals does not suggest that Site streams are a source of metals to the Savannah River (Westinghouse 1996a).

GASOLINE

Many gasoline tanks and several pumping stations and associated tank trailers have operated at the SRS over the years. Spills to surface water seem to have been less of a concern than leaks to groundwater. The Spill Prevention Control and Countermeasures Plan submitted by the SRS to the states and the EPA includes a list of all of the gasoline tanks in each area and a description of the tanks, their capacities, and containment features (Westinghouse 1997). The best description found for many of the tanks is in the Part 70 Operating Permit Application, which includes estimates of air emissions of gasoline and components like benzene (Westinghouse 1996b). The CIIS Database from 1994 indicated that 49 locations reported total gasoline stores of about 1.99×10^5 kg (Meyer et al. 1995).

In 1987, the SRS had about 75 underground storage tanks used to store petroleum products; they were located in D-Area, TNX, C-Area, F-Area, H-Area, CS, K-Area, L-Area, P-Area, R-Area, A-Area, and M-Area. Many of the tanks have been leak tested and those that failed were excavated and repaired in the late 1980s. The potential for these tanks leaking, the inadequacy of leak detection systems, and other problems perceived with tank and drum storage of chemicals were discussed in the Site Environmental Survey (DOE 1987). In response to a Tiger Team Assessment Information request, a list of SRS underground storage tanks and their contents and capacities were compiled in 1990. A memo (Morris 1990) listed the tanks and their location, capacity, and status (in use or abandoned). The memo stated that all of the petroleum tanks installed before 1965 or of unknown age were tightness tested and abandoned or temporarily closed in 1989. The leaking tanks were buried at the Diesel Fuel Storage Facility in N-Area. Benzene and lead have been found in groundwater in levels exceeding the drinking water standard near some of storage areas (Arnett et al. 1993). This contaminated groundwater has not moved offsite or outcropped into surface streams.

The records needed to estimate the amount of gasoline and other fuel that was released to surface waters over the years are not available. A summary of the fuel and oil spills that have been reported since 1980 is provided later in this chapter.

HYDROGEN SULFIDE

Hydrogen sulfide was used in D-Area to make heavy water as described in the Phase I Task 3 report (Meyer et al. 1995). An undated Teletype, likely from the late 1950s, reported a release of about 2 tons of hydrogen sulfide to Beaver Dam Creek on December 29. A stripper level control system malfunctioned and process waste containing hydrogen sulfide was released. The technical standard of 10 mg L^{-1} hydrogen sulfide in wastewater was thought to have probably been exceeded (French 195?). Evans and Giesey (1978) reported that 900 kg y^{-1} of hydrogen sulfide was discharged to Beaver Dam Creek in the mid-1970s. Three spills of hydrogen sulfide to surface water from D-Area were reported for the 1980s: (1) 364 kg released to Beaver Dam Creek in February of 1981, (2) 182 kg released to the process sewer in May 1982, and (3) 364 kg released to the same process sewer in December 1981 (Jewell 1990).

Hydrogen sulfide is a gas at atmospheric pressure and readily evaporates from surface water. It is also soluble in water, so it could be transported some distance. Some microorganisms oxidize hydrogen sulfide to elemental sulfur. Hydrogen sulfide oxidation occurs readily in oxygenated

surface water, like creeks. The half-life of hydrogen sulfide in soil and aquatic environments generally ranges from one to several hours (ATSDR 1997). It seems likely that the rapid oxidation of hydrogen sulfide might have limited the amounts that could have traveled to the Savannah River.

Total sulfides have been measured in the Savannah River for many years. It is not known how much of the sulfides are hydrogen sulfide, but sulfide loading from the Site have not been considered a water quality issue (Zeigler et al. 1986b, 1987).

LEAD

Groundwater analysis suggests that lead has migrated from waste disposal sites. Lead in groundwater has been found to be elevated near the Chemical Metal and Pesticides (CMP) pits, the Savannah River Laboratory (SRL) seepage basins (galvanized well casings contributing to elevated lead concentrations were noted) and the Silverton Road waste site. Lead in groundwater under the D-Area coal pile runoff basins has exceeded the drinking water standard. Groundwater contaminated by these sources does not appear to flow offsite.

Lead was also discharged to the separations area seepage basins. Lower (1985) stated that 623 kg was discharged to the F-Area and H-Area seepage basins in calendar year 1975 alone, an estimate much larger than other estimates. Looney et al. (1987) calculated an inventory for the H-Area seepage basins from influent data of 1475 kg for lead, presumably for 1971–1985, or about 109 kg y^{-1}. Based on monitoring done in 1960–1970, 1975, and 1983, the total disposal mass to the F-Area seepage basins from 1954 to 1983 was estimated to have been 436 kg of lead (Killian et al. 1987a), or an average of 15.4 kg y^{-1}. Eleven samples of H-Area effluent/H-Area seepage basin influent were taken from September to December 1983. The concentration of lead averaged 0.18 mg L^{-1}. A maximum value of 0.54 mg L^{-1} was reported (Killian et al. 1987b). No mention of measurable amounts of lead outcropping to Four Mile Creek has been noted.

M-Area

M-Area used lead powder mixed with oil as a lubricant in the process (Gary 1996) as described in the section on releases of lead to the air from M-Area (see Chapter 17). A Waste Characterization and Reduction Study estimated the annual use of lead powder, which was 99% lead, to be 1126 kg for all M-Area facilities (Lockwood Greene 1983).

In 1981, Bradley estimated that 273 kg of lead was in sludge and sediment of the M-Area seepage basin, resulting from a discharge of 0.23 kg d^{-1} (Bradley 1981). An M-Area settling basin characterization study published in 1985 estimated that the basin then contained 155 kg of lead (Colven et al. 1985); 95 kg in the sludge, 55 kg in the soil to a depth of 6 ft, and 5 kg in the liquid. In March through May 1985, the influent to and effluent from the M-Area settling basin was sampled and analyzed weekly for 10 weeks. Based on these sampling data, removal efficiency was calculated for the basin (the influent concentration minus the effluent concentration divided by the influent concentration). The influent concentration of lead was 0.407 $\pm$0.50 mg L^{-1}, the effluent concentration was 0.110 $\pm$0.31 mg L^{-1}, and the removal efficiency was estimated to be about 71% (Colven et al. 1985). Based on effluent monitoring data from a time period when the average production rate for 313-M was 17,500 cores per month, Looney et al.

(1987) estimated M-Area effluent discharges to the M-Area settling basin to have been 60 kg y^{-1} for lead.

As with many of the other metals, estimates of the amount of lead discharged to the settling basin can be determined. However, releases to the Savannah River cannot be estimated because not enough is known about dilution, adsorption, and other reactions and transport and fate parameters that influence the amount to reach the river.

In 1984, the wooden dam at Steed's Pond, which received M-Area effluents, partially failed, and samples were taken to determine if radioactive materials were migrating from the pond. The 1985 annual environmental report reported the highest lead concentration in Steed's Pond sediment was 65 μg g^{-1}, compared to an average background of 13 μg g^{-1}, ranging from 3-26 μg g^{-1} in the southeastern U.S. (Pickett 1990). Measurements of lead in Tim's Branch sediments in 1984, 1985, and 1986 were reported to be 2.0 μg g^{-1} in sediments above M-Area and 33.7 μg g^{-1} in sediments below M-Area. A concentration of 1.7 μg g^{-1} in sediments at the creek mouth were reported (Specht 1991). The furthest sampling point was in Upper Three Runs Creek, just downstream of the confluence with Tim's Branch. Mean concentrations $\pm$ standard error at this location were 8.9 $\pm$ 3.8 μg g^{-1} for lead, compared to 33.7 $\pm$ 5.7μg g^{-1} just downstream of where the outfall enters Tim's Branch. The control location had levels of 2.0 $\pm$ 0.2 μg g^{-1} (Pickett 1990).

It is unclear how much liquid waste containing lead would have been discharged to Tim's Branch rather than the seepage basin during this time. Estimates of the amounts of waste solvents discharged to the seepage basins and Tim's Branch made by Christensen and Brendall (1981) suggest that the volumes discharged were variable but about 15–60% of the total went to the creek in the late 1970s. From this estimate, we might expect that 0.03–0.14 kg d^{-1} of lead may have gone to Tim's Branch, corresponding to 11–50 kg y^{-1}. Concentrations of lead, measured in a 24-hour composite sample of M-Area sewer effluent sampled in December 1981 when the plant was operating, were 0.003 mg L^{-1} in sewer effluent going to the settling basin and 0.008 mg L^{-1} in sewer effluent going to Tim's Branch. From these data, about 273 kg of lead was estimated to have accumulated in the settling basin sludge (Merz 1982). If we assume average discharges to the Tim's Branch were 2.6×10^8 gal y^{-1} or 9.84×10^8 L y^{-1} (Monier 1970; Hardt 1970; Colven et al. 1985) then the concentration of 0.008 mg L^{-1} reported by Merz would lead to an estimate of 7.8 kg discharged each year or 244 kg total from 1952 to 1982, a 31-year period, assuming 365 d y^{-1} and 3.78 L gal^{-1}.

Lead concentrations in the Savannah River and in Site streams have been less than 0.5 mg L^{-1}, the limit of detection reported for water quality monitoring of the Savannah River. After the first year, monitoring for lead was not continued for the Savannah River because all of the samples were less than the detection limit (Du Pont 1964). SREL data showed that lead levels in the river were less than 0.02 mg L^{-1}, using a more sensitive analytical technique. Concentrations from outfalls ranged up to 0.024 mg L^{-1}, corresponding to a lead transport of about 0.5 kg d^{-1} according to Lower (1985).

MANGANESE

Manganese dioxide was used in the separations area head end process. Much of the manganese in the wastewater was sent to the waste tanks (Du Pont 1974c), but some was discharged to the seepage basins as manganous nitrate. A 1985 memorandum stated that moderate

levels were generally not a health concern, and discharge limits were for corrosion of pipes caused by manganese oxides (Lower 1985). Eleven samples of H-Area effluent/H-Area seepage basin influent were taken from September to December 1983. The concentration of manganese averaged 0.56 mg L^{-1}. A maximum value of 3.2 mg L^{-1} was reported (Killian et al. 1987b). Extensive sampling of the seepline was conducted in 1989 and 1990 and was published by Haselow et al. (1990). Levels of manganese were greater than the secondary drinking water standard at the seepline. The highest concentration found was 0.72 mg L^{-1}, recorded at Road A-7 in 1984. Manganese was not identified in effluents at outfalls F-008, H-008, H-012, which discharge into Four Mile Creek.

Manganese was reported for four outfalls in 1981: (1) C-004, which discharges to Four Mile Creek with a concentration of 0.05 mg L^{-1} and an estimated transport of 46 kg d^{-1}, (2) D-001, which discharges to Beaver Dam Creek with a concentration of 0.14 mg L^{-1} and an estimated transport of 40 kg d^{-1}, (3) F-007, which empties into Upper Three Runs with a concentration of 0.052 mg L^{-1} and an estimated transport of 32 g d^{-1}, and (4) P-019, which runs into Par Pond/Lower Three Runs at levels of 0.05 mg L^{-1} and an estimated transport of 44 kg d^{-1}. Lower (1985) reported that in 1984, the average concentration measured in the Savannah River upstream of the SRS was 0.22 mg L^{-1}, said to correspond to an annual transport of 1.38×10^6 kg for that year or 3788 kg d^{-1}. This implies that 1.38×10^6 kg of manganese was being brought onto the Site in cooling water taken from the river.

Manganese discharges to the separations area seepage basins were not routinely measured. Wells downgradient of the 200-Area seepage basins contained elevated manganese. Drinking water standards for manganese were exceeded in 1981 at wells located at the CMP pits. Manganese was identified as a potential contaminant in the groundwater near the Silverton Road Waste and in groundwater and runoff released from ash and coal. (Lower 1985). Evans and Giesey (1978) reported that 675 kg y^{-1} of potassium permanganate and other manganese compounds were discharged to Beaver Dam Creek in the mid-1970s. An electrolytic process was conducted in D-Area for several years that involved pound per batch quantities of potassium permanganate (personal communication with Robert Garvin, retired 1996). The SRL seepage basins were estimated to have received 433 kg of manganese during 28 years of operation (Lower 1985).

During March through May 1985, the influent to and effluent from the M-Area settling basin was sampled and analyzed weekly for 10 weeks. Based on these sampling data, a removal efficiency was calculated for the basin (the influent concentration minus the effluent concentration divided by the influent concentration). The influent concentration of manganese was 0.034 $\pm$ 0.20 mg L^{-1}, the effluent concentration was 0.008 $\pm$ 0.009 mg L^{-1}, and the removal efficiency was reported to be about 83% (Colven et al. 1985). Any release estimate determined from this limited information would be extremely uncertain. Discharges of process wastewater to site streams may have been about 800 kg y^{-1} in the mid-1970s and early 1980s. The uncertainty associated with this estimate probably spans at least an order of magnitude.

Concentrations of manganese in water and sediments were not significantly different between sampling locations above the SRS and locations along and below the SRS boundary, which indicates the SRS did not contribute detectable amounts of manganese to the river (Westinghouse 1996a).

MERCURY

Chapter 17 provides a description of the use of mercury at SRS facilities and a brief summary of the toxicity and environmental fate of mercury released into the environment.

The SRS and the SREL have done a considerable amount of research on mercury in the environment. In their 1994 document, *Assessment of Mercury in the SRS Environment*, Kvartek et al. (1994) concluded that no significant releases of mercury to the Savannah River were likely to have occurred. They believe that any releases would have been well below the SCDHEC standard, based on process knowledge (Kvartek et al. 1994).

Several dozen SREL reports pertinent to mercury have been generated. Most of these report the findings of studies of bioaccumulation and the effects of mercury on the ecosystem of Par Pond, Upper Three Runs, Four Mile Creek, and areas adjacent to the Savannah River swamp (Kvartek et al. 1994; Gladden 1997).

Sources of Mercury

Bebbington (1990) acknowledged that mercury had been accumulating in the sediments of the 25-million gallon cooling water basins in the reactor areas, in Par Pond, and L-Lake. The mercury was presumed to come from Savannah River water, with the source said to be operations upstream of the Site (Bebbington 1990). Savannah River water, presumably contaminated upriver of the Site, was used onsite for cooling water and was subsequently pumped into Site streams and ponds.

In the 1970s, commercial fishing rights were suspended because of mercury contamination in the Savannah River. In June 1973, a monitoring program for mercury in water, sediment, and fish in onsite streams and Par Pond was started in order to show that SRS operations were not contributing to mercury in the Savannah River. The annual reports attribute mercury found in fish and sediments onsite to offsite sources upriver (Lower 1985; Arnett et al. 1993). Mercury can be found in Savannah River sediment and water upstream of the SRS because of discharges from a mercury-cell-type chlor-alkali plant, called the Olin Corporation plant, near Augusta, Georgia (GWQCB 1971; Lower 1985). The chlor-alkali plant was discharging large amounts of mercury into the Savannah River. From 1965 to 1970, a discharge rate of 5.5 kg d^{-1} was reported (Tilly and Wilhite 1972).

Page 15 of the 1990 Summary Pamphlet to the Environmental Report stated, “Since 1989, concentrations of mercury in fish collected at all onsite locations have been higher than those in fish collected from the Savannah River, indicating a possible onsite source of mercury. The SRS streams are not open for public fishing” (Cummins et al. 1991). None of the other annual report summaries or reports, before or after 1990, suggest that any of the mercury came from SRS operations. SREL personnel interviewed in 1996 maintained that the mercury contaminating onsite fish originated offsite and was brought onsite in the river water used for cooling.

Mercury Use in the Separations Areas

Mercury was used as a catalyst to dissolve aluminum fuel at a rate of 7.95 kg d^{-1} in H-Area where it was used routinely and at 0.18 kg d^{-1} in F-Area where it was used occasionally (Horton 1974a).

The 221-H large and small dissolvers used about 7 kg and 5 kg, respectively, for each run in the 1980s (Kvartek et al. 1994). In 1970, it was discovered that mercury was an impurity in sodium hydroxide (1.5 ppm in 50% NaOH) amounting to a total contribution of about 0.0045 kg d^{-1} in F-Area and 0.0091 kg d^{-1} in H-Area (Du Pont 1971a). Horton (1974a) estimated that through the early 1970s (presumably from 1959–1973), 1600 kg of mercury was released to the H-Area seepage basins and 380 kg to the F-Area seepage basins from this source.

About 80 tons of mercury was said to have been used in separations processes from 1954 to 1972 (Du Pont 1972a). The 80-ton amount is mentioned in several monthly reports and documents evaluating the underground waste tanks (Du Pont 1972a, 1971a). Use in 221-H and 221-F from 1974 to 1992 totaled about 3.5×10^4 kg or about 40 tons, and 11.3 tons (1.02×10^4 kg) was used in the tritium facilities from 1960 through 1987 (Kvartek et al. 1994). Horton (1973) used essential materials transaction reports to estimate consumption for the Separations Department to be 8.2 tons from 1960–1972. Routine use of mercury as a catalyst in H-Area in 1982 was about 3640 kg, which included recycled and new mercury (Holcomb and Emslie 1984). If we use the estimates for the years 1954-1972 and 1974-1992 of 80 tons and 40 tons, respectively, for the separations areas, then add 3.3 tons for these areas for 1973 and 11.3 tons for the tritium facilities from 1960-1987, a total of 135 tons results. We estimate that about 135 tons of mercury may have been used at the Site from 1954 to 1992.

Mercury Released to the Seepage Basins

Most of the mercury was discharged with the waste to underground tanks, but some of the liquid waste containing mercury went to the seepage basins. Neutralized low-activity waste sent to the separations area seepage basins was said to be 0.3% mercuric oxide (Christensen and Gordon 1983b). The February 1972 Monthly Progress Report for the separations areas said that more than 99% was sent to separations waste tanks and the rest went to the seepage basins (Du Pont 1972a). All of the evaporator overheads that contained mercury from separations processes were sent to the seepage basins. There were two evaporators in both the F-Area and H-Area (DOE 1987). In 1972, a heat exchanger was installed in H-Area to remove and recycle mercury from the 242-H evaporator overheads (Hurrell et al. 1987). This exchanger removed mercury by condensation and impingement, producing mercury that could be recycled into the dissolution process and decreased mercury releases to the seepage basin. Operational changes in F-Area in the 1970s also reduced mercury releases (Holcomb and Emslie 1984).

In 1977, the F-Area seepage basin was said to have received 150,000 gal of evaporator overheads each day when all facilities were running normally (Starks 1977). In recent years, mercury was recovered from the evaporator condensers and put into 1000-g bottles and returned to the process (Du Pont 1980). Kvartek et al. (1994) reports that technical personnel associated with waste management operations indicated that during normal operations, one bottle of mercury (about 32 kg) was recovered each month in H-Area and one bottle was recovered each year in F-Area. The SRP history for the separations area reported that mercury recovery averaged about

268 kg each year from the 241-1H and 242H evaporators (Du Pont 1988). Mercury was not recovered from the F-Area evaporators. About 25 kg of mercury was discharged annually to the seepage basins via evaporator overheads from buildings 242-F and 242-H. An additional 37 kg was collected annually at 242-H and returned to 221-H for reuse (Du Pont 1988). In 1988, evaporator overheads and other liquid effluent from the 200-Areas were sent to the Effluent Treatment Facility, which removed mercury.

Starting in September 1970, mercury discharges to the seepage basin were routinely monitored using trebler monitors (Du Pont 1971a). These samples were used to estimate releases to the seepage basins. The start-up or year that discharges began is assumed to be 1959 for H-Area, when HM processing began, and 1954 for F-Area.

About 12 different reports contained estimates of mercury releases to the seepage basins for different time periods. Different release estimates, many based on the same sampling data, are compiled in Table 18-7. Quarterly, monthly, daily, or annual estimates reported in pounds or tons were converted to kilograms per day or kilograms per year.

Table 18-7. Estimates of Mercury Discharged to the F-Area and H-Area Seepage Basins

Time period	Seepage Basin	Minimum (kg d^{-1})	Average (kg d^{-1})	Maximum (kg d^{-1})	Average (kg y^{-1})	Reference
F-Area Seepage Basin						
1959–1973	F				27	Horton (1974)
1959–1973	F				25	Kvartek, et al. (1994)
1955– 1970					24	Hurrell et al. (1987)
1955 – 1982	F				15.8	Christensen and Gordon (1983b)
Sept 1970–May 1972	F				20.5	Du Pont (1972b
Sept.–Dec. 1970	F	0.032	0.064	0.168	22.1	Du Pont (1972b); Du Pont (1973b)
Jan.–June 1971	F	0.0018	0.036	0.186	13.1	Du Pont (1972b)
July–Dec. 1971	F	0.0045	0.091	1.04	33.2	Du Pont (1972b)
Jan.–May 1972	F	0.027	0.032	0.772	11.7	Du Pont (1972b)
Jan.–June 1971	F		0.032		8.5	Bebbington (1971)
1971	F				24[a]	Horton (1974)
1971	F				23.6	Lower (1985)
1971	F				24	Hurrell et al. (1987)
1971	F	0.0018	0.063	0.92	23.3	Du Pont (1973b)
1972	F				7.2	Hurrell et al. (1987)
1972	F	<0.003	0.018	0.11	7.41	Du Pont (1973b)
1972	F				7.27	Lower (1985)
Jan.–March 1973	F	<0.009	0.0136	0.072	5.63	Du Pont (1973b)
1973	F				7.3	Horton (1974)
1973	F				5.6	Hurrell et al. (1987)
1973	F				5.68	Lower (1985)
1974	F				2.6	Hurrell et al. (1987)
1974	F				2.48	Du Pont (1974a)
1974	F				2.63	Lower (1985)

Table 18-7. Estimates of Mercury Discharged to the F-Area and H-Area Seepage Basins

Time period	Seepage Basin	Minimum (kg d^{-1})	Average (kg d^{-1})	Maximum (kg d^{-1})	Average (kg y^{-1})	Reference
1975	F				0.77	Hurrell et al. (1987)
1975	F				0.772	Lower (1985)
1976	F				2.9	Hurrell et al. (1987)
1976	F				2.91	Lower (1985)
1976—1977	F				1.7	Du Pont (1988)
1977	F		0.00136		0.25	Du Pont (1979)
1977	F				2.9	Hurrell et al. (1987)
1977	F				2.91	Lower (1985)
1987	F				0.82	Hurrell et al. (1987)
1978	F				0.818	Lower (1985)
1978	F				0.895	DuPont (1977a)
1979	F				1.36	Hurrell et al. (1987)
1979	F				1.36	Lower (1985)
1980	F				3.22	Hurrell et al. (1987)
1980	F				3.23	Lower (1985)
1981	F				0.682	Lower (1985)
1981	F				0.68	Hurrell et al. (1987)
1982	F				0.32	Hurrell et al. (1987)
1982	F				0.318	Lower (1985)
1983	F				1.32	Hurrell et al. (1987)
1984	F				7.41	Hurrell et al. (1987)
H-Area Seepage Basin						
1955—1970					96–136[c]	Killian et al. (1987b)a
1955—1970	H				102.2	Hurrell et al. (1987)
1955—1982	H				64.6	Christensen and Gordon 1983b
1959—1973	H				109	Kvartek et al. (1994)
Sept. 1970–May 1972	H				46.5	Du Pont (1972b)

Table 18-7. Estimates of Mercury Discharged to the F-Area and H-Area Seepage Basins

Time period	Seepage Basin	Minimum (kg d^{-1})	Average (kg d^{-1})	Maximum (kg d^{-1})	Average (kg y^{-1})	Reference
Sept. –Dec. 1970	H	0.018	0.38	1.19	29.7	Du Pont (1972b); Du Pont 1973b
Jan.–June 1971	H	0.009	0.091	0.382	33.2	Du Pont (1972b)
July–Dec. 1971	H	0.009	0.059	0.204	21.5	Du Pont (1972b)
Jan.–May 1972	H	0.022	0.068	1.13	24.8	Du Pont (1972b)
Jan.–June 1971	H	0.364	0.109	1.14	29	Bebbington (1971)
1971	H				28	Horton (1974)
1971	H				28.2	Hurrell et al. (1987)
1971	H				28.2	Lower (1985)
1971	H	0.009	0.077	0.38	28.1	Du Pont (1973b)
1971	H				28	Killian et al. (1987b)[a]
1972	H				21.8	Hurrell et al. (1987)
1972	H	0.0045	0.059	0.25	21.9	Du Pont 1973b
1972	H				22	Killian et al. (1987b)[a]
1972	H				21.82	Lower (1985)
Jan.–March 1973	H	0.014	0.054	0.177	19.6	Du Pont (1973b)
1973	H				15.4	Killian et al. (1987b)[a]
1973	H				15.4	Hurrell et al. (1987)
1973	H				21.8	Horton (1974)
1973	H				15.4	Lower (1985)
1974	H				7.7	Killian et al. (1987b)[a]
1974	H				7.7	Hurrell et al. (1987)
1974	H				7.73	Lower (1985)
1974	H				7.64	Du Pont (1974a)
1975	H				6.9	Killian et al. (1987b)[a]

Table 18-7. Estimates of Mercury Discharged to the F-Area and H-Area Seepage Basins

Time period	Seepage Basin	Minimum (kg d^{-1})	Average (kg d^{-1})	Maximum (kg d^{-1})	Average (kg y^{-1})	Reference
1975	H				6.9	Hurrell et al. (1987)
1975	H				6.91	Lower (1985)
1976	H				7.41	Lower (1985)
1976	H				7.4	Hurrell et al. (1987)
1976	H				7.4	Killian et al. (1987b)[a]
1976–1977	H				4.5	Du Pont (1988)
1977					8.3	Killian et al. (1987b)[a]
1977	H				8.2	Ross (1979); Fleming (1981); Smith (1981); Wilhite (1980)
1977	H				8.27	Hurrell et al. (1987)
1977	H				8.27	Lower (1985)
1978	H				6.954	Lower (1985)
1978	H				6.95	Hurrell et al. (1987)
1978	H				6.9	Killian et al. (1987b)[a]
1978	H				6.95	Du Pont (1977a)
1978	H				7	Ross (1979); Fleming (1981); Smith (1981); Wilhite (1980)
1979	H				4.4	Ross (1979); Fleming (1981); Smith (1981) (1980)
1979	H				4.36	Hurrell et al. (1987)
1979	H				4.4	Killian et al. (1987)a
1979	H				4.4	Lower (1985)
1980	H				2.36	Lower (1985)
1980	H				2.36	Hurrell et al. (1987)
1980	H				2.4	Killian et al. (1987b)[a]
1980	H				2.38	Ross (1979); Fleming (1981); Smith (1981) (1980)
1981	H				2.64	Ross (1979); Fleming (1981);

Table 18-7. Estimates of Mercury Discharged to the F-Area and H-Area Seepage Basins

Time period	Seepage Basin	Minimum (kg d^{-1})	Average (kg d^{-1})	Maximum (kg d^{-1})	Average (kg y^{-1})	Reference
						Smith (1981); Wilhite (1980)
1981	H				2.63	Hurrell et al. (1987)
1981	H				2.6	Killian et al. (1987b)[a]
1981	H				2.64	Lower (1985)
1982	H				8.95	Lower (1985)
1982	H				8.96	Ross (1979); Fleming (1981); Smith (1981); Wilhite (1980)
1982	H				8.9	Killian et al. (1987b)[a]
1983	H				24.5	Killian et al. (1987b)[a]
1983	H				24.5	Hurrell et al. (1987)
1984	H				27.6	Hurrell et al. (1987)
1984	H				27.6	Killian et al. (1987b)[a]

Table 18-7. Estimates of Mercury Discharged to the F-Area and H-Area Seepage Basins

Time period	Seepage Basin	Minimum (kg d^{-1})	Average (kg d^{-1})	Maximum (kg d^{-1})	Average (kg y^{-1})	Reference

[a] The data in Killian et al. (1987) were said to have been derived from Christensen and Gordon (1983b) and were estimated by the Health Protection Department of the SRS.

[b] The 1971 discharge to F-Area Seepage Basin was atypical and included an inadvertent loss of mercuric nitrate from 221-F in June and July (Horton 1974). Discharges were less in 1972 than the loss in 1971 because the Site began recovery of mercury in 242-H evaporator overheads.

[c] Killian's estimate was for 1630 kg from 1955 to 1972, a period of 17 years averaging out to 96 kg y^{-1}. The seepage basin probably received little mercury from 1955–1959, before the H-Area processes were running. Averaging the total of 1630 kg by the 12 years when the H-Area was contributing discharges results in an estimate of 136 kg y^{-1}.

Horton (1974a) made several estimates of mercury releases to the seepage basins; the highest estimate was 1636 kg in H-Area and 382 kg in F-Area from 1959-1974. The amount of mercury added after 1973 before the seepage basins were closed in 1988 was said to have been much less than the amount discharged from 1959–1973 (Horton 1974a, 1974b).

A Works Technical report for June 1972 reported mercury releases to F-Area and H-Area seepage basins for four, 6-month periods between September 1970 and May 1972 (Du Pont 1972b). This report summarized the results of the routine monitoring program started in September 1970. During that time (21 months), a total of 36 kg of mercury had been discharged to the F-Area seepage basins and 81 kg to the H-Area seepage basins. The weeks with the highest discharges for F-Area (the week ending July 16, 1971) and H-Area (the week ending October 9, 1970) were noted, but activities that occurred during the week that might have accounted for the higher releases were not mentioned. Table 18-7 summarizes average annual and daily average maximum and minimum concentrations based on the weekly composite samples provided in the report, Du Pont (1972b).

A monthly report from the Health Physics Section for April 1973 summarized the mercury discharges for the same time period based on the same weekly composite samples (Du Pont 1973b). The above normal 1971 F-Area discharge of 24 kg was said to have been due to the inadvertent loss of mercuric nitrate from 221-F in June and July. The H-Area discharges were also less in 1972 than in 1971 because recovery of mercury in 242-H evaporator overheads was initiated (Du Pont 1973c). The maximum, minimum, and average daily discharges and the annual averages from values in this report are summarized in Table 18-7.

A monthly report from December 1974 summarized releases through November to the F-Area seepage basin as 0.10 kg d^{-1}, for a total of 0.35 kg that month and a total of 2.28 kg for the year-to-date (Du Pont 1974a). We extrapolated Du Pont's values of 2.28 kg for 11 months to 2.48 kg for 12 months for Table 18-7. Releases to the H-Area were 0.021 kg d^{-1}, for a total of 0.741 kg for November 1974 and 7.15 kg year-to-date, correlating to a release of 7.7 kg for 1974 (Du Pont 1974a).

F-Area Seepage Basins

The first seepage basin constructed was in F-Area in 1954. Three more basins were built just south of F-Area and received effluent from 1954–1988.

Except for occasional peaks, one as high as 0.173 kg d^{-1}, the weekly composite samples for F-Area show a fairly constant discharge of about 0.045 kg d^{-1} in late 1970 and early 1971. Samples of the 242-F evaporator effluent suggest almost all of the mercury was from this source (Bebbington 1971).

Monitoring was also conducted from January through November 1985, while reprocessing of the Rocky Flats scrub alloy fuel was being done in F-Area. Mercury concentrations at the trebler leading to the F-Area seepage basin ranged between 20 and 191 µg L^{-1} (Kvartek et al. 1994).

Based on monitoring done in 1960–1970, 1975, and 1983, the total disposal mass to the F-Area seepage basins from 1954 to 1983 was estimated to have been 450 kg of mercury (Killian et al. 1987a), or an average of about 15 kg y^{-1} over the entire 30-year period.

H-Area Seepage Basins

The four seepage basins in H-Area, which were situated in series, were used from 1955 to 1988. The basins were closed in 1988 and have been capped. The water table is at a depth of about 6 m below the basins, and the basins are closer to the groundwater discharge zone along Four Mile Creek than the F-Area basins (Kvartek et al. 1994). In 1972, sediment analysis in H-Area indicated that about one-half of the estimated inventory for mercury could be accounted for in the top 6 in. of soil in the bottom of Basins 1 and 2, and most of the remaining mercury was said to have been accounted for in 14.5 ft of soil below Basin 4 (Holcomb and Emslie 1984). H-Area discharges of mercury were much greater than those from F-Area. Eleven samples of H-Area effluent/H-Area seepage basin influent were taken from September to December 1983. The concentration of mercury averaged 0.043 mg L^{-1}. A maximum value of 0.28 mg L^{-1} was reported (Killian et al. 1987b). Looney et al. (1988) calculated inventories for the H-Area seepage basins from influent data. Looney et al. estimated that 1805 kg of mercury had been discharged to the H-Area seepage basin through 1985. In 1971, a special sampling study was done to assess the mercury releases from the 242-H evaporator from the mercuric nitrate catalyst used for dissolving. Since October 1971, a trap was used to remove the mercury that settles from the overheads. The SRS experimented with other methods to remove more mercury from the overheads. During January through June 1971, 20.5 kg was removed at 242-H and 14.5 kg went from 242-H and 211-H to the H-Area seepage basin. The average mercury discharge rate to the basin was 0.109 kg d^{-1}. Before the program for mercury removal, the average amount discharged to H-Area seepage basins ranged from 0.36–1.14 kg d^{-1} (Bebbington 1971). Samples of the 211-H discharges and evaporator overheads did not account for the discharges going to the seepage basins. It was discovered that a manhole directly downstream of the evaporator (called the P-58 manhole) had pooled mercury in a low spot. The mercury was overflowing from the low spot into the sewer line that discharged into the seepage basin. The elemental mercury removed from the manhole weighed approximately 3.4 kg. A dam was then built to increase the trapping capacity and prevent continuous overflowing (Bebbington 1971). It is not clear if mercury was removed regularly after this. H-Area discharges ranged from 0.09 to 1.27 kg d^{-1}, decreasing to less than 0.16 kg after the mercury trapped in the manhole was removed (Bebbington 1971).

Horton (1974a) estimated that the mercury released to the seepage basins since startup totaled 1636 kg in H-Area (from 1959 through January 1974). In 1972, the H-Area discharges were reduced by passing evaporator overheads through a heat exchanger to remove mercury by condensation and impingement. The water discharged was also further purified with a hydroclone (Horton 1974a).

A series of memos (Ross 1979; Fleming 1981; Smith 1981; Wilhite 1980) about analysis of the seepage basins in F-Area and H-Areas for pH and mercury included a handwritten memo with ‘Bob Scaggs’ written across the top and a handwritten table that appears to tabulate the pounds of mercury that went through the trebler in H-Area for 1977–1982. These values are summarized in Table 18-7. The memo does not describe how the values were calculated from the trebler sample concentrations received from the laboratory analysis.

Analysis of the concentration and measurements of the average discharge per day led researchers in 1970 to conclude that perhaps the 242-H waste evaporators were not the principal source, as previously thought. “It also appears that some or all of the sources may be very

erratic," they said. For several days of the sampling, the 242-H evaporator was down and the source of mercury seemed to be Receiving Basin for Offsite Fuels (RBOF) waste. In September 1970, sampling was done over four, 3-day periods between September 8–25 (Bebbington 1971). Bebbington (1971) reported that from January to June 1970, 14.5 kg of mercury was discharged to the H-Area Seepage Basin at an average rate of 0.11 kg d^{-1}. During the same time period, 4.2 kg was discharged to the F-Area seepage basin at an average rate of 0.03 kg d^{-1}. (Bebbington 1971).

Clearly, the results of various studies done to characterize mercury releases to the basins are variable. Although data from longer time periods of monitoring might be considered more reliable, it is difficult to judge the quality of the estimates and rank or weight them accordingly. We might assume that about 26 kg y^{-1} was released to the F-Area seepage basins from 1955–1970 for a total of 416 kg for the 16-year period. From 22–24 kg may have been released in 1970 and 1971, decreasing to 7.3 in 1972 and 6.2 in 1974 for a total of 60 kg in those 4 years. From 1975 to 1980, releases were reported to be from 0.6 to 3 kg y^{-1}, totaling about 12 kg for the 6 years. From 1981–1984, about 10 kg may have been released. From 1985 to 1989, releases were lower, averaging less than 0.8 kg y^{-1} or less than 4 kg, and may have been close to zero because of the effluent treatment plant. The amount released to the F-Area basins from 1959–1989 totaled from these values is 501 kg. Because of the variability among the estimates (which may be 50%) and the sampling variability (approximately 15%), the true value is probably between 175 and 825 kg.

For H-Area, a similar tabulation suggests less than 1818 kg may have been released from 1959–1970. From 1970 to 1974, about 106 kg may have been released; from 1975–1980 about 37 kg; and from 1981–1985 about 95 kg. It is interesting that according to Killian et al. (1987b) (using data from Christensen and Gordon 1983a), releases from 1974 to 1979 averaged about 7.5 kg y^{-1} decreasing to 4.5 kg in 1979, less than 3 kg in 1980 and 1981, then increasing to 25 and 28 kg in 1983 and 1984. Discharges in 1971 and 1984 may have been the peak discharges. After 1985, releases were probably less than 8 kg y^{-1} but may have been close to zero because of the Effluent Treatment Facility. The true value for the amount discharged between 1959–1989 is probably between 1000 and 3000 kg. In comparison, the Olin Chlor-alkali plant may have discharged more than 9000 kg directly into the Savannah River between 1965 and 1970, an amount 3 to 4 times greater than the total amount that may have been discharged to all of the seepage basins during their operation.

Table 18-8. Estimates of Mercury Releases to the Seepage Basins for 1955–1989

F-Area		H-Area	
Date	Releases (kg)	Date	Releases (kg)
1955–1970	416	1959–1970	1820
1970–1974	60	1970–1974	106
1975–1980	12	1975–1980	37
1981–1984	10	1981–1984	95
1985–1989	3	1985–1989	45
1959–1989	501	1959–1989	2103

Kvartek et al. (1994) said that according to Horton (1974a), the chemical separations areas released 2000 kg of mercury into the seepage basins through the early 1970s.

It should be noted that mercury discharge to the seepage basin may not necessarily correlate with production. Discharge to the seepage basin is more likely related to mercury recycling and recovery efforts.

The transcript of a presentation given in 1992 by E.L. Albenesius included answers given in response to questions from the audience about mercury (Albenesius 1992). Someone, it is not clear who, estimated that the seepage basins (presumably F-Area and H-Area seepage basins) contained about 16 tons of mercury (Albenesius 1992). This estimate is much larger, nearly 10 fold higher, than any others we have found. It may be that the value may have been confused with estimates for the burial ground, which range around 10 tons.

The estimates of mercury released to the seepage basins are very uncertain. The mercury discharge estimates are based on measurements of mercury in liquid effluent entering the seepage basins. Analytical precision for the photometric method for mercury analysis in water was reported to be 10–15% for 1 to 5 μg L^{-1} (ppb) mercury in water (Du Pont 1971b). The uncertainty in the source terms involves a 10–15% uncertainty in the analytical method. The sample error associated with the trebler proportional samplers was thought to be less than 3% (Wright 1955). The annual release estimates were based on limited data for short time periods of 1 week or several months; therefore, variability is high.

The Seepline and Four Mile Creek

Upper Three Runs Creek runs to the north of the seepage basins and Four Mile Creek runs to the south. Basin constituents seep to the underlying water table and then flow horizontally to the south toward Four Mile Creek. A small fraction may flow toward Upper Three Runs Creek (Haselow et al. 1990). Four Mile Creek is bordered by wetland areas and some portion of the groundwater moving to Four Mile Creek reaches the surface before entering the creek. The transition of upland to wetland vegetation defines what is called the seepline (Haselow et al. 1990). A small percentage of the water filtering through the seepage basin soil migrates into deeper groundwater but most of the groundwater reaches the surface at the seepline adjacent to Four Mile Creek. The flow of the groundwater to Four Mile Creek is estimated to be moving at a rate of about 15 cm d^{-1} (Looney et al. 1988). Simulations of flow in the system indicate that travel time for unretarded constituents from the basins to Four Mile Creek is about 10 years. Travel time from the basins to Upper Three Runs Creek is estimated to be about 70 years. A steady-state profile of the unretarded contaminant, tritium (tritated water), has developed between the basins and Four Mile Creek. Dixon and Rogers (1994) collected samples from five locations along the seepline in F-Area, five locations along the H-Area seepline, and three stream locations on Four Mile Creek. This sampling was the first in a series of three semiannual sampling events conducted to characterize the shallow groundwater outcropping to Four Mile Creek and associated wetlands. The results showed that groundwater at the seeplines was influenced by contaminates migrating from the seepage basins. Mercury levels were less than drinking water standards, but they had increased in Four Mile Creek from 1989 to 1992 along both seeplines (Dixon and Rogers 1994).

Dixon and Rogers (1994) said that studies in 1988 of the shallow groundwater outcropping at the Four Mile Creek and its associated seeplines and wetlands (published in Looney et al.

1988) were prompted by the observation that vegetation in wetland areas on the north side of Four Mile Creek seemed stressed. Both cadmium in F-Area and nitrate in both F-Area and H-Area seeplines were elevated above the drinking water standards. Haselow et al. (1990) collected soil, stream water, and seepline water samples from Four Mile Creek and its seeplines in 1988 and 1989 as a followup to the recommendations in Looney et al. (1988) and came to the same conclusions. The cadmium, nitrate, and manganese concentrations and the fact that the seepwater generally had a low pH confirmed that contaminants from the seepage basins were impacting the water chemistry along the seeplines. Discharges to the seepage basins were stopped in 1988, and the basins were capped and sealed in 1990. A quarterly tritium survey and a semiannual sampling program for metals, inorganics, and selected radionuclides have been conducted since 1992 (Dixon and Rogers 1994).

Well samples indicate that mercury has traveled through the soil below the seepage basins into groundwater in both the H-Area and F-Area. Mercury was also identified as a contaminant of soil adjacent to buried pipelines that transported liquids to the seepage basins (Kvartek et al. 1994). Groundwater monitoring wells show the groundwater contained mercury at an average concentration of 0.0035 mg L^{-1} and a maximum concentration of 0.0079 mg L^{-1} in 1993. Monitoring well data from 1994 demonstrate that the mercury plume from the H-Area seepage basins intersected the seepline along Four Mile Creek (Kvartek et al. 1994).

Three studies have analyzed the groundwater below F-Area intersecting the surface at the seepline along Four Mile Creek for mercury. Looney et al. (1988) found that dissolved mercury concentrations at the seepline downgradient from F-Area were below the detection limit. Subsequently, Haselow et al. (1990) found one sample above the detection limit, and Dixon and Rogers (1994) found a maximum mercury concentration of 0.005 mg L^{-1} at the seepline, which is within the range of background concentrations reported. The researchers concluded that mercury in the groundwater downgradient from F-Area had not yet reached the seepline at Four Mile Creek as of 1993 (Kvartek et al. 1994).

Bebbington (1971) stated that a study to determine quantities of mercury released to the environment concluded, based on analysis by the SRS and the Federal Water Administration the plant operations were not increasing the concentration of mercury in the Savannah River and that Four Mile Creek had mercury levels below the limit of detection, which at that time was 0.1 ppb. However, “significant quantities of mercury were being discharged to both the H-Area and F-Area seepage basins”. The Separations Department was asked to try to identify the source of mercury and reduce the discharge because the potential for mercury to move from the seepage basin to the creek existed (Bebbington 1971).

Studies have been done to determine how materials migrate from the seepage basins. Although most of the mercury is probably accounted for in the basin soils (Christensen and Gordon 1983b), data on mercury in soils, sediments, and suspended solids from Four Mile Creek indicate that mercury has migrated into the creek. A 1971 measurement indicated that about 0.36 g d^{-1} of mercury from 200-Area seepage basins was migrating into the creek (Lower 1985). In 1973, another analysis was said to confirm this (Du Pont 1973c). In a 1974 memo, Horton asserts that nearly all of the 3600 lb of mercury released to the H-Area seepage basins can be accounted for in the soil. However, later in the report he says, “Considering the concentrations measured and the quantities of soil they represent one can account for 99% of the mercury released to these basins but the large variation between samples make such accounting questionable” (Horton 1974a). The mercury in Basins 1, 2, and 3 was thought to be nonleachable. A laboratory leaching

study referred to by Horton (1974a) described mercury in the seepage basins as virtually immobile. The retention of mercury by the F-Area seepage basins had not been studied. Horton (1974a) recommended that the soil, vegetation, solubility, leachability, and volatility of mercury from the basins be studied further. Volatilization of mercury from the basins was not addressed.

Creek sediment sample concentrations also demonstrated an influence from the seepage basins. A high concentration (0.59 μg g^{-1}) in sediments of Four Mile Creek at Road C was thought to be due to either the addition of mercury to the creek by F-Area Cooling water, which enters just upstream of Road C, or to precipitation of mercury in the creek water with chemicals in F-Area discharges (Horton 1974a). The first explanation seemed most likely.

Mercury migration from the F-Area and H-Area seepage basins to Four Mile Creek is also addressed in the analysis of mercury monitoring data in Chapter 20. Mercury migration from the basins to the creek has occurred, but the rate of migration has not been quantified because the mercury concentrations in the downstream water samples and in the river have been below the limit of detection. A conservative rate of 22 g d^{-1} of mercury migration to the creek was calculated based on the seepline concentrations and the rate of flow of creek water above and below the seepline. Using this rate, we calculated that about 240 kg of mercury may have been transported to the creek between 1959 and 1989. We recognize that mercury from the 200-Area seepage basins may not have reached Four Mile Creek until about 10 years after the seepage basins received liquid effluents containing mercury. Horton (1974b) calculated a migration rate of about 0.36 g d^{-1}, which would provide a release of 4 kg from 1959 to 1989. Based on flows of 15,900 L min^{-1} above the basins and 30,850 L min^{-1} below and concentrations of 0.023 and 0.020 μg L^{-1} above and below, a transport of 0.53 g d^{-1} above the basins and 0.89 g d^{-1} below the basins was calculated. The difference, 0.36 g d^{-1}, was estimated to be the contribution from the basins (Horton 1974a). This calculation of the contribution of mercury to Four Mile Creek was based on the results of only two samples of suspended sediments.

It is unknown what fraction of the amount of mercury discharged to the seepage basins was transported to Four Mile Creek and eventually to the Savannah River. Several studies suggest that mercury in the seepage basins is not very mobile. The amount of mercury transported offsite from this source was said to be negligible, and concentrations in the River were below detection limits. Discharges to the creek in groundwater were estimated to be as much as 8 kg y^{-1}, based on monitoring data (Horton1974a; Lower1985; Kvarteketal1994). It seems unlikely that cumulative releases of mercury to the Savannah River would have exceeded 28 kg, assuming 0.27 of the 2604 kg discharged to the seepage basin reached the creek. The amount of mercury in the creek would have been reduced by sedimentation, absorption to sediments, retention by organic matter and biota in the swamp uptake by plants and animals in the creek, and other removal mechanisms that may have reduced the amount to reach the river to a very small fraction. The quantity that was transported from the seepage basins to Four Mile Creek and eventually the Savannah River seems to have never been measurable.

Chapter 5 describes calculations of cesium movement from the seepage basins to Four Mile Creek and through the swamp to the river. This research suggests that an average of 10% (ranging from 2 to 50%) of the cesium measured at Road C reached Road A, a distance of about 5 mi down Four Mile Creek. Four Mile Creek meanders about another 5 mi to the Savannah River. We might predict a similar reduction occurs for mercury so about 1% of the original activity in the seepage basins reaches the River. Horton (1974a) reported a concentration in Four Mile Creek below the H-Area seepage basins to be 0.20 mg L^{-1}. The maximum concentrations reported at the

seepline were 0.0015 mg L^{-1} reported by Looney et al. (1988). If we assume that the movement of cesium and mercury from the basins to the creek are similar, then the reduction may be similar. Ten percent of the maximum concentrations of mercury reported in Four Mile Creek for 1988 is 0.00015 mg L^{-1} or 0.15 µg L^{-1}. One percent of the maximum concentration at the seepline is 0.015 µg L^{-1}. These concentrations are below typical detection limits and less than the drinking water standard which is 0.002 mg L^{-1} or 2 µg L^{-1}.

Mercury in Waste Tanks

Most of the mercury in the canyon liquid wastes went into the high level waste tanks. Mercury in the waste tanks is discussed in the section on releases of mercury to air in Chapter 17. In 1992, a monitoring well with mercury levels exceeding the drinking water standard was reported, suggesting mercury may be leaking from underground waste tanks in the separations areas (Kvartek et al. 1994). However, the groundwater beneath the area has not traveled offsite. There is no evidence that these tanks have contributed to releases to surface water.

Other Surface Water Discharges

Mercury was identified as a contaminant present in three NPDES effluents discharged to streams in 1981, which are identified in Table 18-9 (Lower 1985).

Table 18-9. Mercury Discharged to Streams[a]

Outfall	Mercury concentration (µg L^{-1})	Transport (g d^{-1})	Receiving stream
A-001	0.3	0.34	Tim's Branch to Upper Three Runs Creek
F-008	0.2	0.77	Four Mile Creek
H-012	0.7	1.2	Four Mile Creek

[a] Source: Lower (1985).

Lower (1985) found that mercury concentrations were below the detection limit in stream waters at some undefined point below these three point sources. Sediments below these points were not analyzed for mercury.

M-Area releases of mercury have not been of concern. Measurements of mercury in Tim's Branch sediments in 1984, 1985, and 1986 were reported to be 0.02 mg kg^{-1} in sediments above M-Area and 0.4 mg kg^{-1} in sediments below M-Area. A concentration of 0.001 mg kg^{-1} in sediments at the "creek mouth" was also reported, but it is not clear whether this location was where Tim's Branch joins Upper Three Runs or where Upper Three Runs joins the river. These data were part of a set of presentation overhead transparencies and their source was not referenced. Details about the sample collection, number of samples, the time of year they were taken, and the analysis were not included. It is likely that the concentrations presented were averages (Specht 1991). An explanation for the higher concentration in Tim's Branch below M-Area than above was not given. As far as we know, mercury was not used in M-Area processes and was not discharged to Tim's Branch via the M-Area process sewers. Looney et al. (1987)

estimated that 0.05 kg y^{-1} of mercury was discharged to the settling basin based on effluent monitoring data from the1970s and 1980s.

The 1993 Federal Facility Agreement Progress Report identified mercury as a contaminant for the D-Area oil seepage basin (1952–1975); old TNX seepage basin (1954–1980); Gunsite 218 rubble pit (mid 1950s–mid-1960s); Central Shops sludge lagoon (1950s–1986); TNX groundwater, which does not appear to be migrating offsite; and Par Pond. The document identified seven other units with a potential for mercury contamination but for which no confirmation of contamination had yet been made. These sites were described by Kvartek et al. (1994). From 1974 to 1984, mercury in equipment, lights, etc. was probably buried at the sanitary landfill 740-G. Well samples indicate that mercury was released into groundwater from the sanitary landfill, but this groundwater does not outcrop to surface water and does not flow offsite (Kvartek et al. 1994).

The use and potential release of mercury from the tritium facilities in H-Area are described in the section on air releases of mercury in Chapter 17. Waste mercury from the facilities was buried in the burial grounds. Mercury in liquid effluents from the tritium facilities did not appear to be a concern.

Mercury in the Burial Grounds

Until the end of 1968, all of the mercury drained during pump maintenance and replacement was buried as waste, usually in 1-L polyethylene bottles that were placed in metal cans. The cans were buried in the old burial ground (643-E) of the Solid Waste Disposal Facility (SWDF), formerly called 643-G and also referred to as the burial ground (Orebaugh and Hale 1976). The SWDF is located between F-Area and H-Area. The original burial site was operated from 1953 until 1972 and was called the old burial ground. Another area, called the new burial ground (643-7E), was opened in 1972. The groundwater beneath the old burial ground SWDF flows toward Four Mile Creek. Mercury has been detected in groundwater beneath the SWDF. The maximum concentration detected in 1993 was 0.0046 mg L^{-1}. Soil studies suggest that mercury disposed of at the old burial ground SWDF was adsorbed onto soils as mercury vapor (Kvartek et al. 1994).

Beginning in 1968, metallic impurities and oxidized mercury in the mercury were removed through decanting and the mercury was reused. As a result of this recycling, the amount of mercury buried was reduced and no new mercury was added to the tritium facilities inventory after 1987 (Kvartek et al. 1994). Several reports estimate that between 1956 and 1968, before the Site began recycling mercury drained from the pumps in 1968, the tritium facility disposed of about 10,000 kg of mercury in the old burial ground (643-E) SWDF (Westinghouse 1992b). After 1968, mercury trapped in the gold traps, collected from leaks or spills, and mercury that could not be drained from equipment was buried. The old burial ground was filled in 1972 (Kvartek et al. 1994). In 1973, Horton estimated that 10 tons (20,000 lb or 9126 kg) of mercury had been buried. He considered that of the 1455 kg used from 1968–1972, about 454 kg were recovered from spills and was in storage. The remaining 1000 kg might have existed as unmeasured increased inventory in the process facilities or may have been buried in discarded process equipment (Horton 1973). Horton (1974b) reported that mercury burial was stopped in 1974. Hale (1973) reported that burial began in 1956 and that the records he reviewed did not show any burial of mercury after 1968. After 1968, and certainly after 1974, waste mercury was presumably stored in 234-H or recycled. In early 1968, the mercury drained from the pumps was returned back to

the pumps. Before 1968, mercury was obtained at low cost in a used form from Oak Ridge and purified, and efforts to recycle and conserve mercury were not made (Horton 1973). An example of the kind of disposal occurring after 1968 was found in Murphy (1986). Murphy suggested that two Sprengel pumps were drained and sent to the burial ground; and at least one Sprengel pump, which was replaced in 1985, could not be drained without a significant tritium release, so it was sent to the burial ground undrained and in a welded container. At that time there were 57 mercury pumps operating in the tritium facilities (Murphy 1986).

Most of the estimated 20,000 lb (10 tons) of waste mercury in the burial ground was thought to have been buried in 200–300 5-gal steel cans that contain 2–3 L (about 27–40 kg) of mercury each (Kvartek et al. 1994). Liquid mercury was placed in a 1-L polyethylene bottle, surrounded by two polyethylene bags. Two or three bottles in bags were then placed in a 5-gal steel can. These cans were buried throughout 44 acres of the low-level beta/gamma waste trenches in the 643-G burial ground (Oblath 1985). Burial depth and location were not specified in records or in instructions for burial. The trenches were 20 ft deep with a minimum burial depth specification of 4 ft. The polyethylene packaging was expected to have a lifetime greater than 100 years. A potential source of release to the soil would be rupture of the cans, polyethylene bags, and bottles because of physical contact with earth moving machinery, an activity that has not been reported (Kvartek et al. 1994; Orebaugh and Hale 1976). Reports from the mod-1970s state that the burial containers were expected to remain intact for several decades and routine monitoring to detect transport of mercury from the burial ground was not recommended at the time (Hale 1973; Horton 1973).

Mercury in the groundwater beneath the burial ground (both at 643-G and 643-7G) was monitored annually from 1977 to 1984, except for 1980. The groundwater monitoring data were said to indicate that mercury was not migrating from the burial ground and they suggested that no observable amounts of mercury were being released from the burial ground to Four Mile Creek in the 1980s (Oblath 1985). Because measurements in control wells (adjacent to the burial ground but under an area where no waste was buried) were similar to concentrations from samples taken from wells monitoring the burial ground, the mercury in the burial ground monitoring wells was thought to perhaps be due to sources other than the buried waste (Oblath 1985). This may have been true for the new burial ground, which contained little mercury wastes, but the consistent presence of mercury in some of the wells in the mid to late 1980s may be due to migration from mercury-containing waste in the old burial ground. This groundwater has not migrated offsite. Well samples and soil samples around the SWDF taken in 1992 suggest that mercury has leaked from storage containers into groundwater (Kvartek et al. 1994), but the groundwater has not traveled offsite.

Orebaugh and Hale (1976) mathematically modeled transport using 9000 kg of mercury as the source term, corresponding to the 10 tons of mercury buried in trenches reported in Horton (1973). They examined the soil redox potential, pH characteristics, and inorganic chloride and sulfate concentrations and concluded that mercury in the soil was in a stable complex. The modeling took into account the soil moisture, mercury solubility, soil composition, burial depth, soil porosity, and permeability to water and gases of the trench fill soil and surrounding and underlying soil. This soil had been studied extensively over the years because of a concern about the leaching of buried radioactive materials. Experiments were conducted to measure mercury vaporization from soil and determine the diffusivity of mercury vapor through soil with varying moisture contents and the solubility of mercury was also experimentally determined. In the course

of these experiments, the researchers determined that mercury on colloids could be an important transport mechanism in soil. They found that transport could occur through vaporization into the air or in water. Transport in water could occur by dissolved mercury in water percolating through the soil and soil water containing mercury on oxide colloids of iron and silicon. They concluded that colloidal suspension was the dominant mode of transportation of mercury from the burial grounds. An estimate of the amount of mercury that could travel from the 9000-kg of buried mercury to the water table and travel horizontally to surface water was 219 mg h^{-1}, 206 mg h^{-1} on colloidal suspension of iron and silicon oxides, and 13 mg h^{-1} of dissolved mercury. As a worst case (which assumed that all of the mercury in bottles, bags, and steel cans was released to the soil), they estimated that this flux could contribute 0.2 μg L^{-1} to Four Mile Creek using a flow of 10^6 L h^{-1}. The drinking water standard reported by Orebaugh and Hale for that time was 5.0 μg L^{-1}. The authors concluded that the contribution from the burial ground would not contribute to an environmental impact (Orebaugh and Hale 1976; Kvartek et al. 1994). Kvartek et al. (1994) calculated that the exposure an adult worker would receive by consuming maximally contaminated water directly from Four Mile Creek, daily for 30 years, corresponded to a risk of 1.9×10^{-6} mg kg-d^{-1}. The risk estimated for an offsite individual consuming the water for 70 years was 5×10^{-6} mg kg-d^{-1}. Neither estimate exceeded the EPA's reference dose for mercury.

We have characterized the burial of mercury to the extent possible. At this time, development of a source term for releases to surface water from the burial grounds is not warranted because groundwater under the burial ground area has not migrated offsite and no problems with surface water runoff or related discharged have been documented.

Mercury Spills

We did not find documentation of mercury spills to surface water. No large spills of mercury were reported in the fault tree databanks or documents reporting spills to the states or EPA. A document about a spill at TNX of an unknown amount of water containing 14 μg L^{-1} mercury reported that concentrations in soil below the spill were measured and ranged from 46 to 545 mg g^{-1}. The researchers estimated that a soil volume of 20 ft^3 might contain mercury in excess of 20 mg g^{-1} (Looney 1994). Monitoring studies have not provided any evidence of large spills of mercury to surface waters onsite.

Summary

Based on available data, it is not apparent that Site activities have contributed to elevated mercury concentration in any offsite environmental media. Chapter 20 provides a detailed discussion of mercury concentrations in environmental media.

NICKEL

M-Area

Nickel salts were released to M-Area liquid effluent from the plating rinse tanks. This was recognized as a problem, and methods to reduce the amounts were being studied in 1970 (Hardt 1970). The *Process Waste Characterization Flow Reduction Study* for M-Area, published in

1983, estimated that the annual use of nickel chloride for Building 313-M, used in a form that was 24.5% nickel, was about 2273 kg (Lockwood Greene 1983).

M-Area effluent discharges to the M-Area settling basin, based on effluent monitoring data from a time period when the average production rate for 313-M was 17,500 cores per month, were estimated by Looney et al. (1987) to have been 1500 kg y^{-1} for nickel. An M-Area settling basin characterization study published in 1985 estimated that the basin then contained 3585 kg of nickel in the sludge, 53 kg in the soil (to a depth of 6 ft), and 3.5 kg in the liquid for a total of 3640 kg. Accumulation of metals was also assessed for sediments of the overflow ditch and Lost Lake. This information was not compiled here because these contaminants did not reach surface water leaving the Site (Colven et al. 1985). In 1984, a partial failure of the wooden dam at Steed's Pond, which received M-Area effluents, occurred and samples were taken to determine if radioactive materials were migrating from the pond. The 1985 Annual Environmental Report reported that the maximum nickel concentration in Steed's Pond sediment was 5300 μg g^{-1}, about 500 times higher than an average background of 10 μg g^{-1}, (ranging from 3-18 μg g^{-1}) in the southeastern U.S. (Pickett 1990). From March through May 1985, the influent to and effluent from the M-Area settling basin was sampled and analyzed weekly for 10 weeks. Based on these sampling data, a removal efficiency was calculated for the basin (the influent concentration minus the effluent concentration divided by the influent concentration). The influent concentration of nickel was 5.95 $\pm$ 5.0 mg L^{-1}, the effluent concentration was 0.573 $\pm$ 0.98 mg L^{-1}, and the removal efficiency was estimated to be about 90% (Colven et al. 1985).

A 1970 memo described releases to Tim's Branch from M-Area processes and estimated that 3544 kg of nickel sulfate and 486 kg of nickel chloride were released each year to the process sewers that went into Tim's Branch (Hardt 1970). A 24-hour composite sample of sewer effluent taken in December 1981 when the plant was operating showed nickel concentrations of 0.89 mg L^{-1} in sewer effluent going to the settling basin and 0.118 mg L^{-1} in sewer effluent going to Tim's Branch. From this data, 13,635 kg were estimated to have accumulated in the M-Area settling basin sludge and sediment, corresponding to an average discharge rate of 1.4 kg d^{-1} (Merz 1982; Bradley 1981). If we assume average discharges to the Tim's Branch were 2.6×10^8 gal y^{-1} or 9.84×10^8 L y^{-1} (Monier 1970; Hardt 1970), then the concentration of 0.118 mg L^{-1} reported by Merz would lead to an estimate of 116 kg discharged each year or 3600 kg of nickel total from 1952 to 1982, a 31-year period, assuming 365 d y^{-1} and 3.78 L gal^{-1}. Measurements of nickel in Tim's Branch sediments in 1984, 1985, and 1986 were reported to be 2.4 mg kg^{-1} in sediments above M-Area and 783 mg kg^{-1} in sediments below M-Area (Specht 1991). Monthly sampling of Tim's Branch and Upper Three Runs Creek sediments in 1985 and 1986 showed that nickel concentrations clearly decreased with distance from M-Area. The furthest sampling point was in Upper Three Runs Creek, just downstream of the confluence with Tim's Branch. Mean concentrations $\pm$ standard error at this point were 13.1 $\pm$ 1.2 mg kg^{-1} for nickel, compared to 783.0 $\pm$ 228.9 mg kg^{-1} just downstream of where the outfall enters Tim's Branch (Pickett 1990).

Releases of nickel to Tim's Branch may have ranged from 116 kg to more than 2000 kg y^{-1}, based on the amount of nickel compounds said to have been used and discharged in the 1970s.

Concentrations of nickel in water and sediments of the Savannah River have been similar upstream and downstream of the SRS, and nickel levels in fish have been less than levels of concern (Westinghouse 1996a).

NITRATES AND NITRIC ACID

The primary human health concern associated with nitric acid discharges is the formation of nitrates that, if they contaminate drinking water, can cause adverse health effects, especially in babies and infants. Nitrates were used and produced by several processes onsite. The H-Area, F-Area, and M-Area seepage basins received process wastewater consisting primarily of nitric acid and sodium nitrate (Peralta and Lewis 1982), and nitrates were released to Tim's Branch and Four Mile Creek.

To allow comparison, amounts in gallons, pounds, and kilograms were converted to tons. In the 1950s, 1960s and much of the 1970s, nitrate measurements for drinking water samples were reported as total nitrate (NO_3). Sometime around 1977, the total nitrogen or NO_3-N was reported. Many of the site documents report 'nitrates', 'as NO_3' or 'NO_3-N, or 'nitrogen' so that it is possible to tell which reporting method was used. In many of the reports the drinking water standard was given as a comparison value. We have assumed that documents reporting a drinking water standard of 45 mg L^{-1} reported concentrations in mg L^{-1} as nitrate, rather than NO_3-N which corresponds to a drinking water standard of 10 mg L^{-1}. The amount of NO_3 is related to the amount of NO_3-N measured by the molecular weight ratio of NO_3/N which is 62 ÷ 14 or 4.43. To facilitate comparisons, and ease in reproducing tables, the old reporting preference was used. Any data reported as NO_3-N was converted to NO_3 by multiplying by 4.43. If the new reporting preference is more familiar to the reader, the NO_3 values could be converted to NO_3-N by dividing these values by 4.43.

Separations Areas

Nitrates were primarily a concern for the releases to surface water or to the seepage basins and underlying groundwater that outcrops to surface streams. Nitrate in Four Mile Creek comes from groundwater beneath the F-Area and H-Area seepage basins outcropping into the creek and from surface water runoff. Information about nitrate concentrations in the seepage basins, groundwater, seepline or outcrop areas, and Four Mile Creek was reviewed and is summarized below.

Seepage Basins

The separations areas have routinely released large volumes of liquids containing nitrates to seepage basins since their startup in 1954. Nitric acid was the primary source of nitrates. Sodium nitrate was produced from neutralization of nitric acid solutions with sodium hydroxide in the uranium recovery process (Monier 1970). For example, plutonium was separated from uranium by adjusting the oxidation state of plutonium to +3 by using ferrous sulfamate and hydroxyamine nitrate as a reductant in the Purex process (Bebbington 1990).

A 1974 memo characterizing nitrate releases to the separations area seepage basins estimated the average annual release based on measurements taken from 1961 through 1970. About 295 tons y^{-1} was discharged to the F-Area seepage basin and 267 tons y^{-1} to the H-Area seepage basin for a total of 562 tons y^{-1}. The total for this 10-year time period was 6182 tons. The releases of nitrate to the seepage basin was determined by considering the total cation content of

the seepage basin wastewater and assuming all of the anions to be nitrate. A study done in 1972 suggested that more than 90% of the anions were nitrate (Horton and Carothers 1974).

Table 18-10 shows an example of the release estimates corresponding to weekly nitrate analysis of liquid released to the seepage basin from 5/25/73 to 7/6/73. These release estimates to the seepage basins were based on nitrate analyses and volume measurements taken by the trebler samplers.

Table 18-10. Estimates of Nitrate Releases to the Seepage Basin Based on Anion Analysis in 1972[a]

	Nitrate release estimates (tons y^{-1})	
Week ending	F-Area	H-Area
5/25/73	177	91
6/01/73	390	57
6/08/73	211	343
6/15	–	211
6/22	257	200
6/29	650	148
7/6	333	268
Average	336	198

[a] Source: Horton and Carothers (1974).

Holcomb and Emslie (1984) reported that in 1975, an estimated 50.5 tons of nitrate was released to F-Area seepage basin and 113.5 tons to the H-Area seepage basin, for a total of 164 tons that year. Hazardous constituent inventories from 1983 reported 3090 tons of nitrate in the F-Area seepage basin and 2900 tons of nitrate in the H-Area Seepage basins (Christensen and Gordon 1983b; DOE 1987). Eleven samples of F-Area and H-Area effluent/ seepage basin influent were taken from September to December 1983. In the F-Area seepage basin the concentration of nitrate averaged 538 mg L^{-1}. A maximum value of 1950 mg L^{-1} and a minimum value of 67 mg L^{-1} was reported (Killian et al. 1987a). In the H-Area seepage basin the concentration of nitrate averaged 1220 mg L^{-1}. A maximum value of 6740 mg L^{-1} and a minimum value of 90 mg L^{-1} was reported (Killian et al. 1987b). Looney et al. (1987) calculated inventories for the H-Area seepage basins from influent data, which included 1 million kilograms, or 1100 tons, of nitrates. The nitrate inventory was based on assuming 115.5 tons y^{-1} was released for the years 1971–1985 (Looney et al. 1987). In the Environmental Information Documents for the H-Area seepage basins and the F-Area seepage basins, Killian et al. (1987a and 1987b) said nitrate releases varied but averaged about 242 tons y^{-1} in H-Area and 257.7 tons y^{-1} in F-Area, based on measurements from 1961–1970, 1975, and 1983. Killian et al. (1987a and 1987b) compiled tables of nitrate releases, based on data from Christensen and Gordon (1983a) and 1983 and 1984 quarterly monitoring data. Their estimates for 1961–1970 agree well with those of Horton and Carothers (1974) on which all of the subsequent estimates were probably based.

We made release estimates for the years in the shaded areas of Table 18-11 by relating the 1961–1970, 1975, and 1983 estimates (Horton and Carothers 1974; Holcomb and Emslie 1984; Killian et al. 1987a and 1987b) to production during these years and attempting to correlate production to release amounts during the years that releases were not reported. The estimates for each year are shown in Table 18-11.

Table 18-11. Estimates of the Amount of Nitrates Released to the F-Area and H-Area Seepage Basins Made by Horton and Carothers (1974) and Later Killian et al. (1987a and 1987b)[a]

Year	Tons to F-Area seepage basin	Tons to H-Area seepage basin	Total tons to both seepage basins	Predicted amount eventually released to Four Mile Creek tons to seepage basins × 0.27
1954	70	76	146	39[b]
1955	245	168	413	111
1956	271	419	690	186
1957	46	431	477	129
1958	0	202	202	54
1959	234	42	276	74
1960	294	110	404	109
1961	91	99	190	51
1962	309	186	496	134
1963	433	310	744	201
1964	820	562	1383	373
1965	175	372	547	148
1966	153	175	328	88
1967	194	204	398	107
1968	244	157	402	108
1969	255	402	658	177
1970	270	204	474	128
Average 1961–1970	295	267	562	152
1971	165	644	809	218
1972	234	250	484	131
1973	247	248	495	134
1974	229	95	324	87
1975	50	113	162	44
1976	262	115	377	102
1977	125	67	192	52
1978	182	84	266	72
1979	172	48	220	59
1980	242	79	321	87
1981	278	126	404	109
1982	193	101	294	79
1983	95	118	212	58
Average 1961–1970, 1975, 1983	258	242	499	135
1984	235	120	355	96
1985	217	147	364	98
1986	194	120	314	85
1987	219	78	297	80
1988	192	33	225	60
1989	59	0	59	16

[a] The shaded values were estimated from reported values based on correlations to F-Canyon and H-Canyon production (mass of U or number of U-235 tubes charged to the dissolvers) for each year or time period.
[b] These amounts are theoretical. Realistically, it may have taken 4 to 9 years for contaminants in the seepage basins to travel to Four Mile Creek.

Groundwater

Studies of nitrate in groundwater in 1968 and 1969 showed nitrate concentrations in the main flow of groundwater from the basins to the creek ranging from 100–300 mg L^{-1} in H-Area and from 100–200 mg L^{-1} in F-Area. The springs along the edge of the swamp bordering the creek contained maximum concentrations of 220 mg L^{-1} in F-Area and 240 mg L^{-1} in H-Area (Horton and Carothers 1974), compared to 3 mg L^{-1} measured in background groundwater (Holcomb and Emslie 1984).

The nitrate concentrations in groundwater were determined in 1973 and 1974 by sampling 65 wells in F-Area and 50 wells in H-Area. The concentration in the main flow path from the basins to Four Mile Creek ranged from 100 to 300 mg L^{-1} in F-Area and from 100–200 mg L^{-1} in H-Area (Horton and Carothers 1974). For comparison, the drinking water standard at that time was 45 mg L^{-1}. The report's authors estimated that it would take more than a decade after seepage basin operation stops for the nitrate in the groundwater to be reduced to acceptable levels based on what was known about biological removal and reduction of nitrate to nitrogen (Horton and Carothers 1974).

Seepline and Four Mile Creek

Nitrates from the seepage basins outcropped to Four Mile Creek. Extensive sampling of the seepline was conducted in 1989 and 1990 and was reported by Haselow et al. (1990). Levels of nitrate were greater than the drinking water standard at both the F-Area and H-Area seepline, but levels in the creek were less than one-half the standard. In 1974, the springs or outcrop areas along the edge of the swamp bordering Four Mile Creek had maximum concentrations of 975 mg L^{-1} in F-Area and 1063 mg L^{-1} in H-Area (Horton and Carothers 1974). In 1982, the average concentration of nitrate discharged to the F-Area and H-Area basins was estimated from measurements to be 5316 mg L^{-1} in F-Area and 2658 mg L^{-1} in H-Area. The nitrate concentration at the 'outcrop location' at Four Mile Creek was reported to be 961 mg L^{-1} for F-Area and 1072 mg L^{-1} (as NO_3-N) for H-Area, suggesting a reduction in the concentrations between the basins and the seepline of 6 fold for F-Area and 2.4 fold for H-Area (Peralta and Lewis 1982).

Dixon and Rogers (1994) collected samples from five locations along the seepline in F-Area, five along the H-Area seepline, and three stream locations on Four Mile Creek. This sampling was the first in a series of three semiannual sampling events aimed at characterizing the shallow groundwater outcropping to Four Mile Creek and associated wetlands. The results showed that groundwater at the seeplines was influenced by contaminates migrating from the seepage basins. Nitrates were found to be greater than the drinking water standard at the H-Area seepline (Dixon and Rogers 1994).

In a short-term study, the flow of the creek and nitrate concentrations were determined using a continuous paddlewheel sampler and U.S. Geological Survey flow gauge at six locations from August 13 to September 24, 1974. From these data, estimates of the amount of nitrate in the creek and flowing past each location were made (see Table 8-12).

Table 18-12. Nitrate Concentrations in Four Mile Creek in 1974

Location	Average nitrate concentration (mg L^{-1})	Maximum nitrate concentration (mg L^{-1})	Quantity of nitrate calculated to flow past each location (tons y^{-1})
H-Area cooling water	0.28	0.58	0.34
H-Area cooling tower effluent	2.3	3.6	2.1
Below H-Area Seepage Basins 1, 2, and 3	2.9	12.8	19
Below H-Area Seepage Basin 4	9.9	18.0	88
F-Area effluents	0.03	0.08	0.08
Below F-Area Seepage Basins 1, 2, and 3	9.6	17.1	153

[a] Source: Horton and Carothers (1974). Reported as NO_3

The authors concluded that the large increases at locations below each of the basins demonstrated that the seepage basins were the major contributor of nitrate. The text explains that based on these measurements, predictions were made about releases to the creek each year. Releases were estimated to be 88 tons y^{-1} for the H-Area basins and 65 tons y^{-1} for the F-Area basins or a total of 153 tons (Horton and Carothers 1974). These studies summarized in this document suggest that 27% (153 tons found in the creek ÷ by 562 tons released to the basins) of the nitrate released to the seepage basins emerges into the creek. They acknowledge that the estimates are based on a limited number of creek measurements taken over a short time and suggest monthly analysis be conducted over several years to determine more accurate values. The results were said to agree with previous findings that the input of nitrate to Seepage Basin 1 of F-Area averaged 1200 mg L^{-1} and the maximum groundwater concentration in the main flow toward Four Mile Creek was reported to be about 300 mg L^{-1}. These values suggest a reduction factor of 0.25 (Horton and Carothers 1974).

Determining the amount of nitrate reaching Four Mile Creek was of interest for understanding dilution of other contaminants as they move from the seepage basin to groundwater and then into Four Mile Creek. As groundwater flowed into Four Mile Creek, the nitrate in it was diluted to about one-fifth of the drinking water standard or about 8.7 mg L^{-1}. Horton and Carothers (1974) said that the concentrations in the creek below the H-Area seepage basins, which averaged about 9.9 mg L^{-1}, were diluted at least 25 times by the C-Area cooling water. Therefore, the concentrations flowing to the river would have averaged less than 0.4 mg L^{-1}. This dilution seems to be based on predicted flow levels rather than concentration measurements. The authors predicted that if all 560 tons y^{-1} of the nitrate discharged to the basins were to enter the creek, the concentration would be 80% of the drinking water standard (presumably about 36 mg L^{-1}). The authors recommended that a monthly nitrate analysis of Four Mile Creek water below the seepage basins be continued to determine the fraction of released nitrate that emerges into the creek and that the rate of chemical reduction of nitrate to nitrogen be determined in the laboratory (Horton and Carothers 1974). Interestingly, the 1974 concentration estimates based on 1973 trebler sample data suggest a reduction factor of 0.32 for H-Area (88 tons/267 tons), 0.22 for F-Area (65 tons/295 tons), and 0.27 for both basins combined (156 tons/540 tons). Based on releases to the seepage basins and calculated dilution and retardation values derived from measurements, we might conclude that as much as 3888 tons (14,402 tons in

the 36 years from 1954 to 1989 × 0.27 y^{-1} = 3888 tons) of nitrates may have reached Four Mile Creek. The estimates are compiled by year in Table 18-11. The creek water was diluted again by at least a factor of 25 as it mixed with C-Area cooling water before entering the river.

In summary, a 6-fold reduction for F-Area and a 2.4-fold reduction for H-Area in the concentrations of nitrates from the basin to the seepline were predicted, based on 1982 monitoring data. About 27% of what was released to the seepage basins was predicted to reach Four Mile Creek based on 1973 monitoring data. Further dilution in Four Mile creek was predicted to be about 25 fold from adding C-Area cooling water to Four Mile Creek. It is likely that further reduction and dilution occurred in the swamp before Four Mile Creek water entered the Savannah River. River water quality monitoring data do not indicate that Four Mile Creek has a significant impact on nitrate concentrations in the river.

M-Area

Large amounts of nitric acid were used in the M-Area processes. Nitric acid was routinely drained from cleaning tanks and discharged to the sewers. It leaked from process equipment and sewer drains. Not surprisingly, there is a nitrate groundwater plume underneath M-Area that has been well characterized in recent years (Gordon 1982; Merz 1982). In a study of waste reduction methods, Hardt (1970) estimated that 135.75 tons of salts (probably primarily nitrates and phosphates), including 83.2 tons of sodium nitrate and 2.35 tons of aluminum nitrate, were being released to Tim's Branch annually (Hardt 1970).

In a file of memos dated from 1968 to 1970, a one-page memo from J.A. Monier estimated volumes and concentrations of chemical wastes discharged to Tim's Branch in 300-Area effluent each year based on production data for 4 months from November 1968 through February 1969 (Monier 1970). References for the estimates, the data from which they were determined, and how they were determined were not included in the report. Monier (1970) estimated that 25,000 gal of 50% nitric acid and 35,500 gal of sodium nitrate solution had been discharged to Tim's Branch in 1 year.

In 1981, Bradley estimated that 0.39 tons of nitrates were discharged each day to the M-Area settling basin. Based on effluent monitoring data from a 13-year time period when the average production rate for 313-M was 17,500 cores per month, M-Area effluent discharges to the M-Area settling basin were estimated by Looney et al. (1987) to have been about 55 tons y^{-1} for nitrate.

Concentrations of nitrates measured in a 24-hour composite sample of sewer effluent sampled in December 1981 when the plant was operating, were 14.6 mg L^{-1} (64.7 mg L^{-1} as NO_3) in effluent going to the settling basin and 10.2 mg L^{-1} (45 mg L^{-1} as NO_3) in effluent going to Tim's Branch. The ratio of inflow and outflow concentrations of nitrate for the M-Area settling basin was calculated to be 13, suggesting a reduction of more than 90% (Merz 1982).

From March through May 1985, the influent to and effluent from the M-Area settling basin was sampled and analyzed weekly for 10 weeks. Based on these sampling data, a removal efficiency was calculated for the basin (the influent concentration minus the effluent concentration divided by the influent concentration). The influent concentration of nitrate was 361 $\pm$ 180 mg L^{-1}, the effluent concentration was 156 $\pm$ 70 mg L^{-1} as NO_3-N, and the removal efficiency was estimated to be about 57% (Colven et al. 1985A *Process Waste Characterization Flow Reduction Study* from 1983 (Lockwood Greene 1983) described process solutions, volumes,

concentrations, and typical flowthroughs for M-Area processes. Consumption data from plant records for 1982 and 1983 were compiled and the content of solvents, nitrates, and metals in effluent from various processes were estimated as a part of the characterization. Based on the concentration of major anions and cations in bulk chemicals, a calculation was made to project the annual use in pounds per year. The study estimated the annual use of 50% nitric acid to be 164.3 tons by 320-M, 260.5 tons by 313-M, and 39.1 tons of 100% nitric acid by 320-M, for a total of 251.6 tons of 100% nitric acid used each year in M-Area (Lockwood Greene 1983). In a study of waste reduction methods, Hardt (1970) estimated that each year about 36 tons of acids, which included about 33.5 tons of nitric acid, were being released to Tim's Branch. These amounts represented 100% nitric acid solutions, calculated from larger amounts of more dilute solutions actually discharged (Hardt 1970).

Nitric acid discharged to the sewer and neutralizer from the 313-M core plating line process in 1983 ranged from 37.35 to 135 tons y^{-1} according to flow process charts compiled by Martin in 1983 and reproduced in a report by Colven et al. (1985). Colven et al. (1985) examined production and throughput data and estimated the amount of chemicals released into effluent in 1982:

- The Cap cleaning process in Building 313-M was said to have released 3.5 tons of sodium nitrate and 16.0 tons of nitric acid to the sewer
- 33.4 tons of nitric acid were discharged to the sewer from the final slug cleaning process
- Building 313-M uranium recovery process discharged an estimated maximum of 53 tons and a minimum of 19.1 tons of sodium nitrate (based on production)
- Core recovery process in Building 313-M released 27.6 tons of sodium nitrate and 0.3 ton of nitric acid
- 321-M component cleaning process discharged 1.5 ton of sodium nitrate and 1.5 ton of nitric acid
- 321-M tube cleaning process discharged 7.85 tons of sodium nitrate and 10.25 tons of nitric acid
- 320-M cleaning room processes discharged 5.52 tons of sodium nitrate and 2.8 tons of nitric acid (Colven et al. 1985). The discharges for all of the processes examined totaled 64.3 tons of nitric acid and 237.3 tons of sodium nitrate.

In 1982, the amount of nitric acid released in 1982 for all of M-Area totaled 302 tons (Colven et al. 1985). If the plant had released 302 tons each year for the entire time period M-Area facilities operated before the effluent treatment plant started up in 1985, a total, very conservative estimate of about 9664 tons results. A more reasonable estimate can be made using estimates of the production during various time periods. The production in 1982 was probably about 90% of the production in 1985, leading us to predict that about 335 tons of nitrates may have been released in 1985. If we presume that production from 1954–1959 was 20–40% of the production in 1985, production from 1960–1981 was 30–80% of that in 1985 and that production in 1983 and 1984 was equal to that in 1982, that production in 1986 equaled 1985 and that production in 1987–1989 was about 40% of that in 1985, then we can estimate the following:

67–135 tons y^{-1} were discharged from 1954–1959
100–268 tons y^{-1} were discharged from 1960–1981
about 302 tons y^{-1} were discharged from 1982–1984
about 335 tons y^{-1} were discharged from 1985–1986

about 135 tons y^{-1} were discharged from 1987–1989.

It is difficult to estimate how much of the nitrate in effluents went to the seepage basins compared to how much went to Tim's Branch. Estimates of the amounts of waste solvents discharged to the seepage basins and Tim's Branch made by Christensen and Brendall (1981) suggest that the volumes discharged were variable but about 15–60% of the total went to the creek in the late 1970s. If we assume 100% of the discharges went to the creek before 1959, 60% between 1959 and 1985, and 20% after 1985 when the treatment plant was operating, the following conservative estimates for the amount of nitrates that may have been discharged to Tim's Branch are the result:

67–135 tons y^{-1} from 1954–1959, or a total of 402–810 tons for those 6 years
60–160 tons y^{-1} from 1960–1981, or a total of 1320–3520 tons for those 22 years
about 181 tons y^{-1} from 1982–1984 or a total of 543 tons for those 3 years
about 200 ton y^{-1} in 1985 and 67 tons in 1986 after the treatment plant was operating
about 27 tons y^{-1} from 1987–1989 or a total of 81 tons for those three years.

These estimates total a range of about 2613–5220 tons for the 36-year time period of M-Area operation, or about 72 to 145 tons y^{-1}. This is a very rough estimate of the discharges to Tim's Branch based on very little information. Estimates for the portion of M-Area effluent discharged to the Tim's Branch from 1981 and production information for 1982–1989 was used to estimate values for the entire 36-year period. Release estimates for 1954–1981 are especially uncertain.

Our estimates compare surprisingly well with the Hardt (1970) estimate of 85.5 tons and the 142 tons estimated by Monier (1970). The 1981 daily discharge estimate of 0.39 tons d^{-1} by Bradley (1981) totals 142 tons at an operating rate of 365 d y^{-1}.

Information on dilution and reduction of nitrate from Tim's Branch to the Savannah River is not sufficient to determine the release of nitrate to the river from the discharge of about 145 tons y^{-1} from M-Area to Tim's Branch. The river water quality monitoring data suggest that the discharge did not cause nitrate levels downstream of the SRS to be significantly different from levels upstream. Sampling data from 1973 found an average of 0.45 mg L^{-1} in Tim's Branch near Upper Three Runs and the same concentration in Tim's Branch at Highway 278. Average nitrate levels in the Savannah River were similar, averaging about 0.30 mg L^{-1} (Du Pont 1967).

Water Quality Monitoring for Nitrates

Nitrate analysis was a part of the Savannah River water quality monitoring program initiated in 1959. In general, nitrate concentrations downstream of the SRS were not different from concentrations upstream. Nitrates in Site streams were less than 9 mg L^{-1} (as NO_3) except for Four Mile Creek at Road A-7, which averaged about 35 mg L^{-1} in the mid-1970s and reached maximum concentrations of about 80 mg L^{-1} in later years. Average nitrate concentrations reported in the health physics section of the June 1973 monthly report for Site streams are shown in Table 18-13.

Table 18-13. Average Nitrate Concentrations Reported in June 1973[a]

Sampling location	mg L^{-1} (NO_3-N)	mg L^{-1} (NO_3)
Upper Three Runs at Highway 278	0.45	1.99
Upper Three Runs at Road C	0.22	0.97
Upper Three Runs at Road A	0.20	0.89
Tim's Branch Near Upper Three Runs	0.45	1.99
Four Mile Creek at Road A-7	7.9	34.99
Steel Creek at Road A	0.27	1.19
Beaver Dam Creek near swamp	1.2	5.32
Savannah River at 681-3G	1.3	5.76
Lower Three Runs at Patterson's Mill	0.16	0.71
Lower Three Runs below Par Pond	0.22	0.97

[a] Source: Du Pont (1973d).

The highest nitrate concentrations were in Four Mile Creek at Road A-7 (Du Pont 1973d) Quarterly monitoring of nonradioactive components of wastewater effluents, including nitrates, began in 1982 in compliance with Resource Conservation and Recovery Act and South Carolina Hazardous Waste Regulations (Holcomb and Emslie 1984).

In 1979, a monthly Works Technical Report gave estimates of the concentration of water quality parameters in the Savannah River, for the month and year-to-date for 1978. The tables were dated December 1978. The average, maximum, and minimum nitrate concentrations for several constituents are summarized in Table 18-14.

Table 18-14. 1978 Nitrate Concentrations in (NO_3-N), Reported in a 1979 Technical Works Monthly Report of Sampling Data[a]

Location	Average concentration (mg L^{-1})	Maximum concentration (mg L^{-1})	Minimum concentration (mg L^{-1})
Savannah River No. 2 upstream	0.85	3.8	<0.02
Savannah River No. 10 downstream	0.63	2.3	<0.02
Upper Three Runs at Highway 278	0.232	0.620	0.12
Upper Three Runs Thermal Effects Lab	0.13	0.18	0.07
Upper Three Runs at Road A	0.13	0.19	0.07
Tim's Branch, Road C	0.11	0.41	<0.02
Four Mile Creek, Road A-7	3.8	6.5	2.0
Steel Creek. Road A	0.49	4.45	0.05
Beaver Dam at Swamp	0.66	3.0	0.23
Savannah River, 3-G	0.28	0.48	<0.02
Par Pond	0.03	0.09	<0.02

Nitrates were also monitored in the swamp receiving effluent from the D-Area ash and coal pile runoff basins. The nitrate concentrations measured in the swamp water averaged about 5.2 mg L^{-1} and ranged from 1 mg L^{-1} to 9.1 mg L^{-1}, below the drinking water standard of 10 mg L^{-1}

(Guthrie and Cherry 1976). These concentrations correspond to 4.43 mg L^{-1} and 40 mg L^{-1} reported as NO_3. Routine releases of nitrates likely overwhelm any accidental spills. In March of 1997, a vendor trailer line broke and spilled 863 kg of 57% nitric acid in F-Area. It was neutralized and washed into the Old F-Area basin. About 38 L reached Three Runs Creek (Durant 1994).

Although elevated nitrate concentrations were measured in site streams, impact beyond the Site boundary is not supported by concentrations measured in Savannah River water. Upriver concentrations were apparently greater than downriver concentrations much of the time.

PESTICIDES

Pesticides were used at the Site for rodent, insect, and vegetation control. Most were applied by outside contractors, and since at least the 1980s, contractors were required to be certified pesticide applicators (DOE 1987). In recent years, the choice and application rate of pesticides are controlled by a guidance committee (Du Pont 1973a). The U.S. Forest Service also uses some herbicides and insecticides in their SRS timber management program (Du Pont 1977b).

There is little documentation of pesticide use before the 1970s. We do not know if DDT and other commonly used insecticides were used to control mosquitoes and other insects during this time period. Concentrations of insecticides and herbicides measured in water, sediments, and soils have been very low or undetectable (Gladden et al. 1985). Very low or trace quantities that were detected were attributed to offsite farm and industrial sources. Pesticides detected in onsite stream sediments were said to have come from upriver sources in river water that was pumped to the SRS facilities and released to streams. None of the pesticides in river water samples have exceeded the drinking water standards.

In the monthly reports from 1970, the Radiological Sciences Division reported using herbicides to destroy contaminated vegetation along seepage basins, creeks near effluent and on top of burial areas. Herbicides were also said to have been used to control *Potamogeton*, a weed in Par Pond. The reports did not specify which compounds were used (Du Pont 1970b).

Beginning in 1967, water and sediment samples were analyzed for pesticides. From 1967 to 1970, the analyses were performed by the Federal Water Pollution Control Administration (known as the Environmental Protection Agency after 1972) under contract with the SRS. Seven stream and two river water samples were analyzed semiannually for pesticides from 1967 to 1971 by the Department of the Interior Laboratory in Athens, Georgia (Arnett et al. 1993), part of the Federal Water Pollution Control Administration. All analysis results showed less than the minimum measurable concentrations except for dieldrin, which was detected in the river water both upstream and downstream of the SRS at a range of 0.03 to 0.04 μg L^{-1} (ppb) (Du Pont 1971c).

From 1971 to 1975, the work was performed by the U.S. Geological Survey. After 1975, the U.S. Department of Interior's Water Quality Laboratory performed the analyses (Du Pont 1978). According to the 1979 Annual Environmental Report, DDD, DDE, DDT, dieldrin, and chlordane were the pesticides most often identified in stream and river sediment samples. These pesticides, with the exception of chlordane, were reportedly not used at the SRS. The annual report states that the "concentrations of pesticides and polychlorinated biphenyls (PCBs) detected in sediment continue to indicate offsite sources" (Du Pont 1980).

In 1971, the river water analysis detected only dieldrin, both above and below the SRS, at concentrations of 0.04 μg L^{-1}. Dieldrin was said to be an agricultural chemical not used at the SRS. Other pesticides, including: aldrin, DDD, DDE, DDT, diazinon, endrin, ethion, heptachlor, lindane, malathione, parathion, methyl-trithion, silvex, trithion, 2,4-D, and 2,4,5-T were not above detection limits (Du Pont 1972c).

In 1972, water samples contained 0.01 to 0.02 μg L^{-1} dieldrin. "Trace" quantities of aldrin, DDT, DDD, DDE, and chlordane, all attributed to agricultural sources, were found in sediments (Du Pont 1973e).

In a Works Technical Monthly Report for 1971, dieldrin in river water up and downstream was reported to be 0.04 μg L^{-1}. Dieldrin in Four Mile Creek and Pen Branch was measured at a concentration of 0.02-0.03 μg L^{-1} and was attributed to the river water taken in for use at the site, then discharged. The herbicide 2,4-D was detected at Four Mile Creek at Road A at very low levels (0.03 μg L^{-1}). This was said to be "the first indication of SRP contribution in our pesticides monitoring program" (Du Pont 1971c).

In 1973, dieldrin was measured in stream and river water at concentrations of 0.01 μgL^{-1}. Trace quantities of aldrin, DDD, DDE, DDT, PCBs, and chlordane were detected in sediments. Of these, only chlordane was said to have been used at the SRS. Although it was not specifically discussed, the data show that chlordane was not detected above the plant but was found below the plant in sediments at a concentration of 1 μg L^{-1}, which is at the limit of detection (Du Pont 1974b).

In 1974, trace quantities of deildrin in river water were again attributed to offsite sources. Chlordane, said to have been used in very small amounts at the SRS, was not above the detection limit in 1974 (Du Pont 1975).

Analyses done in 1975, 1976, and 1977 were similar. The 1977 annual report says that dieldrin, DDT, DDD, and DDE were found in sediments in trace amounts and that "some pesticides and herbicides are used moderately in areas where insect and vegetation control is necessary for security and safety". Information on which pesticides were used in what quantities was not provided (Du Pont 1980).

In 1981, endrin; lindane; methoxychlor; toxaphene; 2,4-D; 2,4,5-TP; and Silvex were added to the list of analytes (Du Pont 1981). Why these chemicals were chosen was not explained and whether these were used or disposed of by the Site is not known. Addition of the chemicals may have been related to the EPA's interest in environmental levels of these chemicals.

In 1980, diazinon was detected in an Upper Three Runs Creek sample, but it was attributed to offsite sources (Du Pont 1981).

Average analytical results and the detection limits for 32 pesticides and 7 PCBs measured in sediment samples were reported in the 1981 annual report (Du Pont 1982). The report presented concentrations of nine compounds in river sediments at sampling location 2 (upstream of the SRS) and location 10 (downstream of the SRS). Most of the values were at the limit of detection.

In 1982, pesticide levels were less than the limit of detection except for heptachlor. Heptachlor concentrations up and downstream of the plant were the same (Du Pont 1983).

Trace quantities of pesticides found from 1983 to 1988 were attributed to forestry and agricultural applications (Zeigler et al. 1985).

Benzene hexachloride, said to be used by farms offsite, was detected in Savannah River sediment in 1985 and in sediments of Upper Three Runs Creek in 1986.

None of the pesticides analyzed for from 1987 to 1990 was above the limit of detection (Cummins et al. 1991).

The Comprehensive Cooling Water study, conducted in 1983 to evaluate environmental effects of intake and discharge of cooling water at the SRS, reviewed the routine annual monitoring program said to have begun in 1976. The program's goal was to determine levels of pesticides, herbicides, and PCBs in stream and river sediments. During 1976 to 1983, water and sediment from seven locations on plant streams and two locations on the Savannah River were analyzed. The number of materials analyzed and the detection limits changed from year to year depending on the offsite vendor who performed the analysis. All of the sediment samples were at or near the limit of detection. Diazinon had been detected in Upper Three Runs since 1981. DDE was detected in Upper Three Runs, but concentrations had decreased since 1979. The highest chlordane concentrations were found in Upper Three Runs at Road F in 1976. This was a control location, upstream of plant effluent, and the contamination was attributed to offsite sources. In 1982, this location again showed the greatest levels of pesticides, attributed again to offsite agricultural uses. In 1982, concentrations for analytes in river sediments were less than the limit of detection except heptachlor. There was no significant difference in heptachlor concentrations above and below the plant, and heptachlor concentrations upstream were greater, leading the authors to suggest that the source was offsite (Gladden et al. 1985).

None of the records we reviewed suggested that any significant spills or leaks of pesticides occurred onsite in the past. No visible evidence of spills or leaks was observed during the inspection of the operations and storage areas conducted in 1987 as a part of the Site Environmental Survey (DOE 1987).

Records do not indicate that pesticide contamination from waste storage areas has been a problem. Documents indicate that the CMP pits previously received pesticides for disposal, but there are no records of the types of materials or quantities received (DOE 1987).

In conclusion, monitoring data indicate that large amounts of pesticides were not released from the Site, and data on the quantities and types of pesticides used before the mid-1970s are lacking. Therefore, source terms for specific pesticides were not determined.

POLYCHLORINATED BIPHENYLS

PCBs, also called arochlors, were used in electrical equipment, such as electrical transformers and capacitors. In the 1970s, it was recognized that PCBs were very persistent in the environment and could bioaccumulate up the food chain. PCBs have also been shown to cause reproductive effects and contribute to cancer in animal studies.

River and stream sediment analyses conducted from 1976 to 1980 showed low concentrations of PCBs at similar concentrations both upstream and downstream of the plant (Du Pont 1977a; Du Pont 1980; Du Pont 1981). The highest level appears to have been 15 μg/kg sediment in 1979 at river sampling location 2, upstream of the SRS.

In most cases of PCB contamination, exposure to fish is one of the pathways of greatest concern. In 1977, fish collected from the River and Site streams had concentrations less than the lower limit of detection, which was 0.5 μg/g (Du Pont 1978).

In 1976 and 1977, it was estimated that the SRS had about 700 PCB-containing transformers, 7 to 12 extrusion presses, 1,500 capacitors, and other hydraulic oils containing PCBs onsite. In 1979, a program was started to identify PCB equipment and PCB-contaminated

items and label them as such. Since early 1985, PCBs have been disposed of at a commercial facility offsite. The SRS has not had any PCB transformers or capacitors in operation onsite since about 1986. The U.S. Environmental Protection Agency (EPA) conducted a multimedia audit at the SRS in July 1986. The Toxic Substances Control Act (TSCA) portion of the audit concentrated on the handling of PCBs. The EPA found one administrative violation involving the lack of an inspection record for one transformer. Other aspects of the PCB program were found to be satisfactory. By 1985, all PCB transformers had been removed from service, and, by 1984, all capacitors containing PCBs had been removed. PCB-contaminated items were stored at one of two places: 740-1A in the salvage yard and in 643-29G at the Radioactive Waste Burial Grounds. Radioactive PCBs that were not accepted by commercial disposal facilities were stored at the Radioactive Waste Burial Grounds. The storage areas were diked and inspected regularly and detailed inventory records were kept (DOE 1987). A letter written in 1986, referencing a request by the EPA for information on hazardous waste treatment at the Site, says about 15 gal of capacitor fluid containing PCBs, weighing about 140 lb was stored inside capacitors packed in 55-gal galvanized drums, stored in a special concrete culvert. This PCB storage began in 1978 (Porter 1986).

Several spills of PCBs have been documented. In 1981, about 100 gal of transformer fluid leaked in the salvage yard. The soil was excavated and disposed of as PCB-contaminated waste. In 1982, 1 L of liquid from a transformer retrofit was spilled inside a truck. In 1985, the extrusion press in 320-M was found to containing about 7000 gal of liquid with about 10,000 ppm PCBs, which apparently spilled and required 103 drums of materials to complete soil and concrete cleanup (DOE 1987).

Nancy J. Lowry (1996) responded to a letter *Radiological Assessments Corporation* sent out to solicit information on inventory amounts from individuals who might have knowledge of chemical usage, purchase, storage, disposal, or other relevant operations onsite. Ms. Lowry said that inventories of PCBs were probably not compiled until the late 1970s when regulations issued under TSCA required PCB users and water generators to develop and maintain records of the PCBs in use and disposed of, beginning July 2, 1978. An annual document log for PCB use and disposal was prepared by July 1979 and each year after that. She believed these records would have been sent to central records storage. She knew of no release of PCBs to the environment.

The information obtained from the records and presented here indicates that large amounts of PCBs were not released from the SRS. Therefore, a source term was not estimated for PCBs.

URANIUM

M-Area

Much of the M-Area process sewer effluent went directly into Tim’s Branch until a seepage basin was put into use in 1973. The seepage basin was apparently built to address concerns about uranium discharges to the creek. The releases were not considered to be of environmental health consequence, but the seepage basin was put into use and sampling of the stream for uranium oxide was initiated in the mid-1950s. Releases after 1985 were predicted to have been negligible because of the Liquid Effluent Treatment Facility (Pickett 1990). Estimates of the total uranium discharged to the Tim’s Branch were said to have been unavailable until 1974 when flow

instruments were installed. Uranium releases to Tim's Branch and the Savannah River have been characterized and are summarized in Chapter 5.

ZINC

Relatively small amounts of zinc were released from a large number of sources. Lower (1985) estimated that about 1.36 kg d^{-1} of zinc was discharged to onsite streams from numerous outfalls.

Although not used in processes in large amounts, zinc compounds were identified as one of the substances released from the coal and ash piles and basins. Zinc has contaminated groundwater under the coal pile runoff basins in D-Area and A-Area as well as groundwater beneath the Silverton Road Waste Site.

Separations Areas

Zinc was released, in relatively small amounts, to the separations area seepage basins and the SRL basin. About 309 kg of zinc was released to the F-Area seepage basin in 1975 (Lower 1985). About 216 kg of zinc was discharged to the SRL seepage basin during its 28-year operating history (Lower 1985). Eleven samples of H-Area effluent/H-Area seepage basin influent were taken from September to December 1983. The concentration of zinc averaged 3.1 mg L^{-1}. A maximum value of 26.5 mg L^{-1} was reported by Killian et al. (1987b). Zinc concentrations at the seepline and in Four Mile Creek were never large enough to be of concern.

M-Area

In 1981, Bradley estimated that 91 kg of zinc was in sludge and sediment of the M-Area seepage basin, resulting from a discharge of about 0.136 kg d^{-1}. The source of zinc was thought to be galvanized pipe and gratings (Specht et al. 1987). According to the Annual Environmental Reports, zinc concentrations in M-Area effluents in the late 1980s were less than the NPDES permit limit. In March through May 1985, the influent to and effluent from the M-Area settling basin was sampled and analyzed weekly for 10 weeks. Based on these sampling data, a removal efficiency was calculated for the basin (the influent concentration minus the effluent concentration divided by the influent concentration). The influent concentration of zinc was 0.141 $\pm$ 0.065 mg L^{-1}, the effluent concentration was 0.024 $\pm$ 0.03 mg L^{-1}, and the removal efficiency was estimated to be about 83% (Colven et al. 1985). Based on effluent monitoring data from a time period when the average production rate for 313-M was 17,500 cores per month, M-Area effluent discharges to the M-Area settling basin were estimated by Looney et al. (1987) to have been 25 kg y^{-1} for zinc.

In 1985 and 1986, Tim's Branch and Upper Three Runs Creek sediments were sampled monthly at six locations for metals. Eight samples were taken for each location. The most distant sampling point was in Upper Three Runs Creek, just downstream of the confluence with Tim's Branch. Mean concentrations $\pm$ standard error at this location were 8.90 $\pm$ 3.8 mg kg^{-1} for zinc, compared to 128.2 $\pm$ 11.4 mg kg^{-1} just downstream of where the outfall enters Tim's Branch. The control location had levels of 13.9 $\pm$ 2.3 mg kg^{-1} (Pickett 1990). A concentration of 5.2 mg kg^{-1}

in sediments at the creek mouth was also reported (Specht 1991). A typical medium value for zinc in soil samples from the United States is 36 mg/kg amounts (ATSDR 1997).

The drinking water standard for zinc is currently 5 mg L^{-1} for taste. The influent to the seepage basins seems to have been less than this. It averaged 0.14 mg L^{-1} in the M-Area settling basin (Colven et al. 1985) and 0.31 mg L^{-1} in the H-Area seepage basin (Killian et al. 1987b). Sediment concentrations were also below levels of health concern. Zinc is not a carcinogen, but it can cause adverse health effects to the blood, kidneys, and other organs if ingested in relatively large amounts (ATSDR 1997). Zinc is also an essential element and lack of zinc in the diet can cause adverse health effects. Zinc lozenges have recently become a popular cold remedy. Because zinc is relatively nontoxic, very large amounts would have had to be released to Site streams to reach concentrations of concern in the Savannah River. River monitoring does not indicate significant concentrations of zinc in the water, sediments, or fish (Westinghouse 1996a).

SPILLS TO SURFACE WATER

Most of the spills and leaks were routed to seepage, settling, or retention basins but some went into outfalls and Site streams. The following paragraphs summarize some of the more significant spills reported over the years.

Releases to Beaver Dam Creek

Releases of acid, caustic, and other chemicals to Beaver Dam Creek are worthy of special mention. Beaver Dam creek conveyed thermal effluents from the D-Area power plant and, before 1982, effluents from the Heavy Water Facility. It also received process water discharges from the Water Treatment Facility, which has been a source of sulfuric acid spills to the creek. The creek also received coal and ash basin effluent discharges. The swamp area at the mouth of the creek appears to have had stressed vegetation in 1985. The 400-D Area power plant seemed to have caused stressed vegetation in two locations: (1) north of the Ash Basin (488-D) where the vegetation was dead and the surface water (thought to be coal runoff or seepage from the ash basin) was reported to be yellow and (2) a delta affected by coal fly ash basin effluent discharges (DOE 1987). According to a paper published on swamp ecology in 1978, additional compounds routinely added to Beaver Dam Creek from the power plant and the Heavy Water Plant were reported to be 3800 L of 30% silica solution, 1800 kg of various detergents, 134,000 kg of sodium phosphates and phosphoric acid, about 450 kg of concrete cleaner, 675 kg of potassium permanganate and other manganese compounds, and 9000 kg of hydrogen sulfide each year in the mid-1970s. Periodic regeneration of ion exchanger in the power plant every 1 or 2 days involved 25 kg or larger additions of sulfuric acid and sodium hydroxide, which were discharged in alternate pulses to Beaver Dam Creek (Evans and Giesey 1978).

Three relatively large spills of sulfuric acid from the D-Area to Beaver Dam Creek were reported to have occurred in November 1977, December 1981, and May 1982. Additional spills may have occurred in the 1950s and 1960s, but they were not thought worthy of reporting by the SRS. These spills would have caused pH changes in the stream and perhaps contributed to total sulfates but would not have been expected to have caused a health hazard offsite. In May 1982, about 22,000 lb of sulfuric acid were released to Beaver Dam Creek because of a valve failure at the Heavy Water Facilities. The pH in the stream dropped to between 2 and 3 for about 8 hours.

Plant personnel calculated that the Savannah River water pH was lowered about 0.2 pH units or from about 6.6 to 6.4 at the mouth of Beaver Dam Creek. A survey of the river by boat after the spill indicated no dead fish in the river (Du Pont 1983). Sulfate concentrations in river water were recorded as a part of the water quality program started in the 1950s. A source term was not estimated for sulfuric acid releases because of its rapid degradation once released to the environment.

In June 1983, about 1100 gal of concentrated sodium hydroxide were released to Beaver Dam Creek because of a spill at the D-Area water treatment plant. The pH in the creek increased from about 6.5 to a maximum of 10.7 because of this caustic spill. The pH remained above 9 for about 9 hours. A survey team was said to have found "no measurable effect on the environs of the creek or the pH Savannah River on the day after the incident" (Zeigler et al. 1985).

Accidental Spills in Other Areas

On April 27, 1983, a caustic spill occurred in K-Area. About 350 gal of 50% sodium hydroxide overflowed a holding tank and dike because of a faulty automatic shutoff valve. Most of the caustic was contained in the drainage ditch using sandbags; however, the spill occurred during a heavy rain, and it is estimated that about 10 gal were carried to a storm sewer outfall. The contained NAOH was neutralized with sulfuric acid then discharged to the stream. Soil beneath the contained sodium hydroxide was removed to the sanitary landfill (Zeigler et al. 1985).

From 300 to 400 gal of 50% sodium hydroxide was found to have leaked from 211-H caustic storage tanks October 14, 1984. The leaked caustic was contained in a ditch and removed, along with 30 tons of soil, to the sanitary landfill (Zeigler et al. 1986a).

Two hundred gallons of uranyl nitrate were inadvertently released from the uranium recycle lab in 773-A to the process sewer on May 21, 1985. The solution had a pH of 1.5 and contained about 670 mg L^{-1} depleted uranium. The release did not exceed the Comprehensive Environmental Response, Compensation, and Liability Act reporting limit of 5000 lb, but it was of concern because of the low pH (Zeigler et al. 1986a).

Fuel and Oil Spills

Numerous fuel and oil spills have occurred on or near the Site. Investigations and reporting of these spills were required by the EPA in the 1980s and Incident Logs are available after 1980. The spills were generally all contained using booms or other containment, and contaminated soil was removed and put into a landfill. In the case of spills that went into an outfall toward the river, such as the 600-gal spill of fuel oil at TNX in 1984, the outfall was barricaded with booms and absorbent pads were placed into the outfall discharge stream to help keep oil out of the river. A "small amount" of oil did reach the river, and this was reported in the local newspapers and to the EPA. Fish were said not to have been affected.

About 160 gal of diesel fuel were spilled in the separations area December 12, 1983, from an overfilled tank. An estimated 10 gal reached a storm sewer that flowed into Upper Three Runs Creek. Water samples collected from the sewer outfall and creek on December 12, 13, and 14 were analyzed for oil. Maximum oil concentrations were 71,000 mg L^{-1} at the outfall and 11 mg L^{-1} in the Creek at Road A. No oil was detected in the Savannah River. Concentrations in the

creek returned to levels considered normal (less than 5 mg L^{-1}) by December 14. Oil-contaminated dirt and gravel at the spill site was excavated and the oil on the surface was absorbed (Zeigler et al. 1985).

On November 15, 1984, an airplane developed a hydraulic line failure and ejected about 1200 gal of fuel over a 25-mi stretch of the Savannah River between Four Mile Creek and Johnson's landing from an altitude of about 5000 ft. Sampling did not find oil concentrations to be greater than normal (Zeigler et al. 1985).

Approximately 600 gal of number two fuel oil spilled at TNX were reported in the 1984 annual report. Boom equipment was installed and most of the oil was removed with skimmers or with contaminated soil (Zeigler et al. 1985). The spill occurred from a fuel oil truck transferring oil into a tank. According to maps, the spill occurred about 500 yd from the Savannah River. Oil reached two storm drains, about 20 and 40 ft from the spill, that drain into the X- outfall. The X-8 outfall to the river was barricaded with booms to decrease the flow of oil into the river, and absorbent pads were placed into the outfall discharge stream to absorb the oil. According to the Investigation Committee Report, "some amount of oil reached the river." A newspaper article in the file, date and author unknown, states that "A thin sheen of oil was visible on the river early this morning moving downstream to a point where [it] is was breaking up near Plant Vogle." The incident review report says that an oil contaminant boom was acquired when oil was discovered in the river. The SRP-Operations Low Potential Unusual Incident form, filled out by M.L. Todd (1984) (Du Pont 1985) says that Health Protection estimated that about 8 to 10 gal of oil reached the X-8 outfall through the two storm drains. A report filed by R.K. Cauthen, Lower Savannah District Environmental Quality Control, December 5, 1984, states,

> Statements made by personnel in charge of the site indicated that they believed that only 6-8 gallons escaped, based on the flow (120 gpm) at the X-8 outfall [and] no trace of the oil remained in the creek on [or] the river. Their belief was based solely on engineering judgment and not on any physical evidence or investigation. …an inspection of the outfall to the creek was made [by us]. The outfall and creek had a heavy sheen of oil for the first 100 yards that was visible. Officials immediately ordered that absorbent rolls be brought to the site… we decided to take our boat out on the Savannah River to see if any oil remained or was entering from the creek. .. oil was continuing to escape from the creek into the River… indicated a sheen, width approximately one-half of the river, meandering downstream. The sheen was followed downstream approximately 21/2 miles to the intake structure for Georgia's Plant Vogtle Nuclear Station, where the amount of oil became extremely heavy. Further downstream, no evidence of oil was noted (Du Pont 1985).

The annual report for that year described the spill and said that the maximum concentrations of oil detected in the river were 15 mg L^{-1} about 20 yd downriver of the outfall tributary and 1.4 mg L^{-1} at Highway 301. Oil concentrations had decreased to less than 1 mg L^{-1} by November 30 (Zeigler et al. 1985). On March 15, 1984, about 2850 gal of diesel fuel leaked from a corroded underground line to the ground in Central Shops. The soil was removed and was not subjected to runoff (Zeigler et al. 1985).

On record in an administrative consent order were numerous other spills documented by the SCDHEC, including:

- February 12, 1981, spill of approximately 800 lb of hydrogen sulfide from 400-D Area to Beaver Dam Creek
- December 5, 1981, spill of approximately 400 lb of hydrogen sulfide from 400-D Area to Beaver Dam Creek
- May 5, 1982, spill of 9000–10,000 lb of concentrated sulfuric acid from 400-D Area to Beaver Dam Creek
- June 7, 1983, spill of 1000 gal of 50% sodium hydroxide from 400-D Area to Beaver Dam Creek
- October 9, 1983, underground leak of oxalic acid at an unnamed location onsite
- November 8, 1977, spill of 2000 gal of sulfuric acid from 400-D area, presumably to the ground
- November 28, 1984, spill of 600 gal of number two fuel oil to soil that drained to an NPDES outfall in the TNX area.

The consent order concluded that the SRS had violated the South Carolina Hazardous Waste Management Regulations by failing to immediately report these spills and take measures to ensure that releases do not occur or recur at a facility.

The number of spills reported in the 1980s raises concerns about the number of unreported spills that may have taken place in the 1950s, 1960s, and 1970s, when reporting to the State and EPA was not required. Certainly many spills, perhaps all spills, were reported in monthly reports, but we really do not know whether all of the significant spills were reported.

Fish Kills

Several fish kills have been reported. A 1955 Monthly Report notes that from May 26 to June 3, newspapers in the region reprinted a release from the Allendale County Game Warden reporting dead fish in the Savannah River up as far as Steel Creek. SRS personnel conducted a survey of Steel Creek and the river on June 2 and no residual evidence of a fish kill was found (Du Pont 1955).

A one-page memo dated February 15, 1966, reported that a fish kill in the Steel Creek Swamp was noted by biological monitoring technicians who estimated several hundred fish had been killed. Their deaths were attributed to thermal shock from unusually cold weather conditions. A temperature of 3^{O}F had resulted in thick ice the week before the kill was noticed, and the kill occurred when warm temperatures returned. A few dead fish were also observed in the Savannah River during this time (Johnson 1966).

A fish kill at Pond C, involving thousands of small bream, happened 1 week after startup of P-Reactor on April 8, 1979. The reactor had been down for 10 days following a scram and the kill was thought to have been because of rapid water temperature changes that occurred when hot water was put back into the cooled pond. A similar kill occurred in June 1975 (Du Pont 1979).

CONCLUSIONS

In summary, historical releases of chemicals to the Savannah River are difficult to determine and quantify. Release estimates are summarized in Table 18-15. In addition, an undetermined amount of chromium used to treat high level waste tank cooling coil water was released. Coal and

ash pile runoff contributed to elevated arsenic, cadmium, chromium, manganese, mercury, lead, nickel and zinc concentrations in on-site surface streams and the surrounding swamp. Releases of uranium to surface water are described in Chapter 5.

Table 18-15. Summary of the Estimated Releases of Chemicals to Surface Water

Release estimate (maximum or estimated range)	Released to
1 kg y^{-1} of cadmium	To Tim's branch
900 kg y^{-1} of hydrogen sulfide	To Beaver Dam Creek
8–50 kg y^{-1} of lead	To Tim's Branch
15–623 kg y^{-1} of lead	To the Separations Area Seepage Basins
1500–3500 kg y^{-1} of mercury	To the Separations Area Seepage Basins
0.1–8 kg y^{-1} of mercury	Entering Four Mile Creek in Groundwater
116–2000 kg y^{-1} of nickel	To Tim's Branch
0–1383 tons y^{-1} of nitrate	To the Separations Area Seepage Basins
Up to 3890 tons y^{-1} of nitrate	To Four Mile Creek in Groundwater
27–200 tons y^{-1} of nitrate	To Tim's Branch

Considerable amounts of hydrogen sulfide were released to Beaver Dam Creek, but hydrogen sulfide would have been chemically transformed and degraded into less toxic or nontoxic forms within hours. Large amounts of chlorinated solvents were released to the M-Area settling basin and Tim's Branch. These releases are discussed in Chapter 17 because most of the solvent released probably evaporated.

Monitoring data were generally very limited for chemicals, particularly during early years. River water quality monitoring data suggest that the amounts of chemicals (including metals, pesticides, PCBs, nitrates, and solvents) introduced in the Savannah River from SRS streams were not detectable. Chemical concentrations upstream were the same or greater than levels downstream of the Site, or the concentrations were at or below detection limits.

Risk Assessment Corporation researchers have reviewed a large amount of effluent and environmental monitoring data related to measured chemical concentrations. Based on these data, it would be very difficult to conclude that Site activities have resulted in measurable offsite impacts for any of the chemicals discussed in this chapter. Localized areas (such as seepage basin water and sediments; coal and ash pile runoff areas; several seepline areas; and, to some extent, onsite surface water) have been affected by various routine and accidental Site activities. However, the data suggest that impacts to surface water extending beyond the Site boundary are not measurable.

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