CHAPTER 20

METALS IN THE SAVANNAH RIVER SITE ENVIRONMENT

ABSTRACT

This chapter summarizes available monitoring data for mercury and chromium in the Savannah River Site (SRS) environment. Based on a thorough evaluation of these data, including measured <u>concentrations</u> in water, sediment, and fish, there is no evidence to suggest that the SRS has contributed to increased levels of mercury or chromium in the Savannah River. It appears that industries upriver from the SRS are the primary contributors to elevated mercury concentrations in onsite streams and the Savannah River.

INTRODUCTION

Operations at the SRS introduced several heavy metals into the environment. Of the metals that have entered the SRS environs, mercury and chromium appear to be the only metals that have been investigated with sufficient regularity to warrant a thorough analysis of reported environmental monitoring data. This chapter discusses the various sources of available data and attempts to identify the SRS's role as a contributor to the levels of mercury and chromium in the environment surrounding the SRS. See Chapters <u>15</u>, <u>17</u>, and <u>18</u> for a detailed discussion regarding atmospheric and <u>effluent</u> releases of metals and other chemicals.

Because of the toxic nature of many metals, it is important to evaluate concentrations measured in various environmental <u>media</u>. Water, sediment or soil, and fish are some of the most common media that have been examined. It is particularly important to evaluate fish, not only because of their popularity as a food item, but also because certain metals (including mercury) have the ability to bioaccumulate. Water concentrations of metals that are well below regulatory guidelines can, therefore, cause relatively high concentrations in edible fish tissue that approach and even exceed recommended intake levels.

MERCURY

Mercury in the environment can result from both natural and anthropogenic sources. Natural sources of mercury include various minerals in soil, such as cinnabar (mercury sulfide or HgS), and degassing processes (e.g., the eruption of Mt. St. Helens and other volcanoes). Anthropogenic sources include the burning of fossil fuels, the chlor-alkali industry, the pulp and paper industry, seed fungicide treatment, and mercury catalysts used in industry (EPA 1992; Phillips and Russo 1978; Kvartek et al. 1994; Watras and Huckabee 1994).

Based on groundwater monitoring, the F-Area and H-Area <u>seepage basins</u> appear to be two of the most significant potential sources of mercury to the aquatic environment from SRS operations. Mercury was used at the SRS as a processing aid in the F and H <u>separation areas</u>. As a catalyst, mercury increases the dissolution rate of <u>uranium</u>-aluminum alloy <u>reactor fuel</u>, <u>plutonium</u>-aluminum targets, and scrub-alloy scrap in nitric acid. As a precipitating agent, mercury removes chloride ions, which can corrode stainless steel in processing equipment. It also entered the separation areas as an impurity in NaOH. Effluents associated with these processes have been discharged to F-Area and H-Area seepage basins since 1959. Between 1959 and 1981, approximately 3600 and 840 lb of mercury were released to F-Area and H-Area seepage basins, respectively (Horton 1974b). Use of the F-Area and H-Area seepage basins was discontinued in November 1988, and the Effluent Treatment Facility became operational to treat wastes that were previously sent to the seepage basins. The SRS continues to burn coal, which can contain 600 ppb mercury (Olotka 1973). Kvartek et al. (1994) provides a detailed summary of the SRS operations that used mercury.

The SRS has historically maintained that the majority of mercury in onsite streams and reservoirs resulted from pumping Savannah River water for use as reactor <u>coolant</u>. Mercury was introduced to the Savannah River by upriver industries, including the Olin Corporation, a mercury-cell-type chlor-alkali plant, near Augusta, Georgia, which began operation in 1965. The plant manufactures chlorine gas and caustic soda through the electrolysis of brine by a mercury electrode. Following notification by the Georgia Water Quality Control Board (GWQCB) in response to a 1970–1971 survey (<u>GWQCB</u> 1971), the Olin Corporation significantly reduced mercury discharges. However, for at least five years it discharged large quantities of mercury directly to the Savannah River.

During September 1970, the release of mercury to the F-Area and H-Area seepage basins came under routine observation, and subsequent attempts were made to determine soil, sediment, and water concentrations to assess the rate of movement into Four Mile Creek. In July 1971, the SRS began monitoring fish collected from onsite ponds and streams and the Savannah River for mercury. This program has consistently monitored both onsite and offsite locations, and large numbers of fish have been analyzed for mercury content. Information regarding water and sediment concentrations, based on the available documents, is more limited. A 1974 document (Horton 1974a) described the mercury environmental monitoring program at that time. Water samples from F and H treblers were composited for weekly analysis; Savannah River water samples from six locations were analyzed monthly; and water samples from four burial ground wells, one 200-H well, and four locations at Four Mile Creek were analyzed semiannually. Sediment samples from two Savannah River locations, four Four Mile Creek locations, and one location each in Upper Three Runs, Steel Creek, Beaver Dam Creek, and Lower Three Runs were analyzed semiannually. Unfortunately, significant gaps appear to exist in actual sampling, but we have attempted to locate all information pertaining to mercury investigations in the Savannah River vicinity by the SRS and other agencies and researchers. Available information is generally restricted to water, soil or surface sediment, and fish concentrations. Consequently, the following discussion focuses on the concentrations measured in these media.

Upriver Industrial Sources of Mercury

The Olin Corporation in Augusta, Georgia, discharged significant amounts of mercury directly to the Savannah River, particularly during the late 1960s. From August 1965 through August 1970, the reported discharge rate from the Olin Corporation was 12 lb d⁻¹ (EPASWL 1971, cited in <u>Tilley and Wilhite</u> 1972). Before a study conducted by the GWQCB in 1970, discharge rates of 10 lb d⁻¹ were reported (<u>GWQCB</u> 1971). Following the study and notification by the GWQCB, discharge rates were reportedly reduced to less than 0.25 lb d⁻¹. On May 20, 1970, the Olin Corporation had a recorded discharge of 2.65 lb, and by July 14, 1970, the recorded discharge had been reduced to 0.51 lb (<u>D'Itri</u> 1972, cited in <u>Newman and Messier</u> 1994).

Although the reported discharge rates differ slightly, it is clear that significant quantities of mercury were discharged directly to the Savannah River. Assuming a discharge rate of 10 lb d^{-1} for 5 years, more than 18,000 lb of mercury would have been discharged directly to the Savannah River between 1965 and 1970.

SRS Separations Area Seepage Basins

The chemical separations facilities (F-Area and H-Area) and associated seepage basins are located between Upper Three Runs Creek to the north and Four Mile Creek to the south (Fenimore and Horton 1973). Water movement in the area is complex because underlying sediments are not uniformly permeable; however, in general, water moves slowly away from the groundwater divide, which is offset toward Four Mile Creek. Water then moves at an accelerating rate down the gradient to <u>outcrop</u> at the springs, swamps, and beds of the two streams.

Two separate and distinct <u>water tables</u> exist below the F-Area seepage basins. A perched groundwater table is located 10 to 15 ft below the ground surface, and water either seeps through the less permeable underlying strata or flows laterally a maximum of 150 ft to the edge of the supporting strata. Flow is then vertical to the normal water table located 60 to 65 ft below the ground surface. The nearest outcrop area, a line of springs along the edge of the Four Mile Creek swamp, is 1600 ft from the basins. Based on detection of <u>tritium</u> in Four Mile Creek, travel time from the basins to Four Mile Creek was estimated to be between 8 and 12 years with a flow rate of between 0.37 and 0.55 ft d⁻¹ (Fenimore and Horton 1973).

Geological characteristics of the H-Area basins are quite different from those of the F-Area basins. The water table is located 15 to 25 ft below the ground surface, and the outcrop area along Four Mile Creek is only 400 to 600 ft from the basins. The soil contains a high percentage of clay and has a relatively low permeability except for narrow zones of extremely high permeability. Based on detection of tritium in Four Mile Creek, travel time from basin 1 was estimated at 3.25 years with a flow rate of about 0.5 ft d⁻¹, and travel time from basin 4 was estimated at 3.75 years with a flow rate of about 1.0 ft d⁻¹ (Fenimore and Horton 1973). The flow rate from seepage basins in the H-Area likely is higher than in the F-Area because of the narrow zones of high permeability. See Chapter 5 for a more detailed description of surface water flow, groundwater outcropping, and seepage basin geography.

Between 1959 and 1982, more than 3600 and 840 lb of mercury were released to H-Area and F-Area seepage basins, respectively (Figure 20-1) (Horton 1974b). Use of these basins continued through 1988, after which they were capped and did not receive additional effluent. Information regarding annual releases of mercury from F-Area and H-Area from 1971 through 1982 was provided in a 1985 memorandum (Lower 1985). No information was available regarding annual releases between 1959 and 1970, but cumulative (1959 through 1981) releases of 3600 and 840 lb from the H-Area and F-Area, respectively, have been reported. Figure 20-1 shows the reported releases from 1971 through 1982 and average annual releases from 1959 through 1970 based on cumulative releases between 1959 and 1981.

During 1972, several studies were conducted to identify mercury concentrations in the environs of H-Area seepage basins (<u>Horton</u> 1974b). Soil samples were collected from seepage basins 1, 2, and 4. Basins 1, 2, and 3 were full of water, and basin 4 was dry at the time. Seepage basin 3 was not sampled because it had not been used since 1964.

Two locations each in basins 1 and 2 were sampled above the water level. Basin 1 had concentrations of 135 and 6500 ppm, and basin 2 had concentrations of 970 and 5040 ppm. Four soil samples each in basins 1 and 2 were collected from the top 6 in. of soil in the bottom of the basins. Basin 1 had concentrations of 87, 1640, 1730, and 780 ppm, and basin 2 had concentrations of 150, 850, 830, and 410 ppm. The higher concentrations in soil in one location above the water level in both basins (6500 and 5040 ppm) were attributed to splashing and evaporation. The total volume of soil containing these higher concentrations was estimated to be very small. Based on these concentrations, it was estimated that 99% of the mercury releases to these basins could be accounted for in the soil. However, the large variation between samples and the limited number of samples makes this estimate questionable.

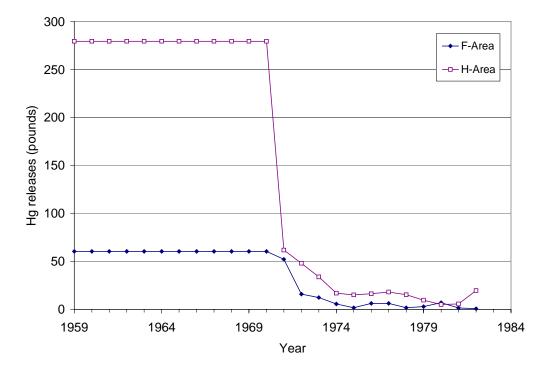


Figure 20-1. Annual releases to F-Area and H-Area seepage basins from 1959 through 1982. Link to <u>tabulated data</u>.

The higher concentrations in the bottom of basins 1 and 2 compared to those in basin 4 indicated that much of the mercury was precipitated in basins 1 and 2. Leaching studies were conducted on soil from basins 1 and 2 to assess the mobility of the mercury in these basins. The first test involved leaching a soil sample with a mercury concentration of 5000 ppm with groundwater collected above the H basins. Only 0.08% was removed after 350 pore volumes. The second test involved leaching a soil sample with a mercury concentration of 630 ppm with 1360 pore volumes of distilled water to remove soluble mercury and 199 pore volumes of 1N NH₄C₂H₃O₂ (ammonium carbonate) to remove exchangeable mercury. These leaching processes removed 0.15% of the mercury. These experiments showed that nearly all the mercury in basins 1 and 2 was both insoluble in water and nonexchangeable with a salt solution, and that the mercury in these basins was virtually immobile.

Since basin 4 was dry, soil samples were collected in two locations from the basin bottom to the water table, 14 ft below the basin bottom. Seven depth increments were analyzed, and elevated mercury concentrations were evident at all depths (Figure 20-2). For reference, typical background mercury concentrations in soil and sediment range from 0.02 to 0.05 ppm (Horton 1974b), and concentrations at all depths were at least an order of magnitude greater than 0.03 ppm.

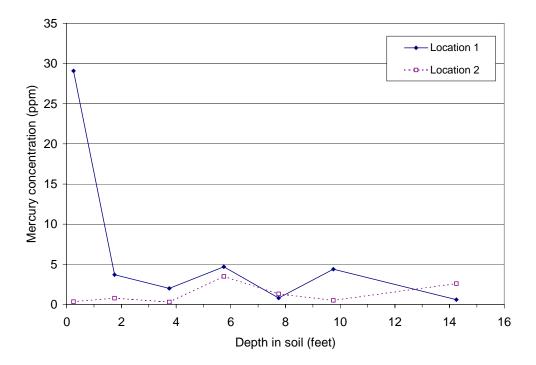


Figure 20-2. Mercury concentrations as a function of soil depth in H-Area seepage basin 4. Link to <u>tabulated data</u>.

An attempt was made to calculate the H-Area seepage basin contribution of mercury to Four Mile Creek based on analysis of suspended sediments in Four Mile Creek water above and below the H-Area seepage basins. However, the estimate of mercury transport, 0.36 g d⁻¹, was based on only two samples. In addition, the concentration above the seepage basins (0.023 ppb) was higher than the concentration below the seepage basins (0.020 ppb). A positive mercury transport rate was calculated only because the water flow rate above the basins (15,900 L min⁻¹) was significantly lower than the water flow rate below the basins (30,850 L min⁻¹). A lower concentration below the seepage basins seems contrary to a measurable mercury transport rate from the H-Area seepage basins.

Based on the difference in flow rate above and below the H-Area seepage basins, an alternative method for calculating mercury transport is possible. Assuming a uniform mercury concentration in <u>seepline</u> water of 1 ppb (which is a conservative assumption) based on reported seepline water concentrations, an estimated mercury transport rate can be calculated from the H-Area seepage basins. If the increase in water flow rate below the basins were attributed only to seepline water contributions, the mercury transport rate would be about 22 g d⁻¹. This is a conservative estimate because seepline vicinity measurements indicate that water concentrations

are generally less than 1 ppb, and the highest concentrations in both sediment and water appear to be in localized areas, likely along a few channels of high permeability. It also assumes no background contribution, and background mercury concentrations of 0.5 ppb have been measured in Four Mile Creek water. It does not seem likely that mercury transport rates would have exceeded this value, and actual transport rates were likely much lower. At any rate, the transport rate of mercury to Four Mile Creek (and certainly to the Savannah River) from the F-Area and H-Area seepage basins appears negligible relative to the discharge rate of mercury by the Olin Corporation directly to the Savannah River during the late 1960s.

Water in H-Area seepage basin 1 was sampled in 1970, and concentrations ranged from 100–150 ppb with a mean of 114 ppb (n [number of samples] = 5). Basin 4 was also sampled, and concentrations ranged from 3–8 ppb with a mean of 6.3 (n = 4). One sample was collected from basin 2 and it had a concentration of 15 ppb (<u>Bebbington</u> 1971).

Data from trebler samplers, which were used to collect liquid samples in F-Area and H-Area effluent streams from October 1980 through October 1981, provided average effluent concentrations of 2.9 for the F-Area and 25.6 ppb for the H-Area (attachment to <u>Horton</u> 1974b). These data appear to have been composited weekly and apparently were used to estimate annual releases of mercury to the basins.

In 1981, two National Pollutant Discharge Elimination Systems (NPDES) effluent outfalls from F-Area and H-Area facilities that flow directly into Four Mile Creek (F-008 and H-012) contained measurable mercury concentrations of 0.2 and 0.7 ppb, respectively. <u>Dixon and Rogers</u> (1994) concluded that a water concentration of 0.5 ppb was in the background range based on samples taken upstream from the separations areas, so it would be difficult to conclude that these effluent concentrations were elevated above background.

Well Water

Concentrations measured in two water samples taken from 200-H well #4 (just east of seepage basin 1) in 1970 were 5 and 25 ppb (<u>Bebbington</u> 1971). The 25-ppb sample was analyzed with solids removed (the report does not specify a definition for solids) and a concentration of 2 ppb was recorded, indicating most of the mercury was associated with suspended sediment. A sample collected from this well on May 26, 1973, had a concentration less than 2 ppb (<u>Du Pont</u> 1973a). Water samples from seven H-Area seepage basin wells were collected on November 11, 1981, and five contained concentrations less than 0.05 ppb. The other two samples had concentrations of 0.5 and 3.4 ppb (attachment to <u>Horton</u> 1974b).

In general, maximum reported mercury concentrations in SRS groundwater have occurred in H-Area seepage basin wells (Mikol et al. <u>1988a</u>, <u>1988b</u>; Davis et al. <u>1989a</u>, <u>1989b</u>; Cummins et al. <u>1990</u>, <u>1991</u>; <u>Arnett et al</u>. 1992). Figure 20-3 shows mercury concentrations for H-Area seepage basin wells that have historically shown some of the highest concentrations. The highest concentrations in these wells have generally occurred in wells situated south and east (downgradient) of the seepage basins. Concentrations measured between 1984 and 1996 are also generally consistent with concentrations reported for wells sampled in 1970 and 1981 (discussed above) although data are very limited before 1984.

Seepage basin operations halted in November 1988, and rainfall infiltration between that time and completion of the cap raised the pH significantly in the immediate vicinity of the basins. Reduced hydraulic load in the basins combined with a higher pH would be expected to slow the

migration of mercury. Dissolved mercury concentrations were reported through the third quarter of 1992, after which total mercury concentrations have been reported. This makes interpreting the data somewhat difficult, but it appears that concentrations in the wells depicted in <u>Figure 20-3</u> have decreased since closure of the basins.

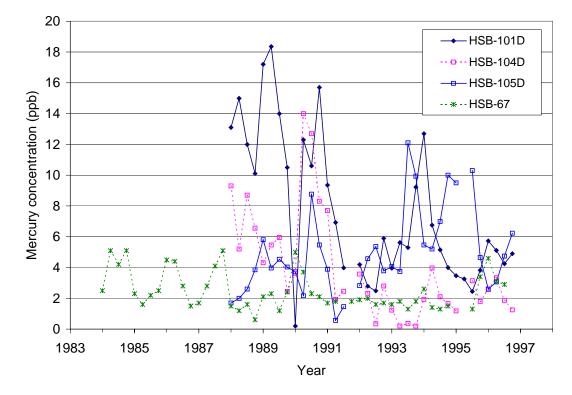


Figure 20-3. Mercury concentrations at four H-Area wells (HSB-101D, HSB-104D, HSB-105D, and HSB-67) that have historically had some of the highest measured concentrations. Link to <u>tabulated data</u>.

In 1991 and 1992, 65 and 67 F-Area seepage basin wells were sampled, respectively. Six seepage basin wells had water concentrations greater than the U.S. Environmental Protection Agency's (EPA's) Primary Drinking Water Standard (PDWS) of 2 ppb (Arnett et al. 1992; Arnett 1993). The maximum concentrations measured in these wells were 7.4 and 12 ppb, respectively. In 1991 and 1992, 108 H-Area seepage basin wells were sampled and 11 and 15, respectively, had concentrations greater than the PDWS. The maximum concentrations measured in these wells were 9.4 and 7.9 ppb, respectively.

Based on these data, it is clear that measurable but relatively small amounts of mercury from the F-Area and H-Area seepage basins are being leached into the groundwater. <u>Temporal trends</u> in groundwater concentrations for individual wells vary considerably, and it is difficult to draw many conclusions regarding the stability of mercury in groundwater below the seepage basins. However, elevated concentrations (above the PDWS) have only been measured in a small fraction (about 10%) of the total number of F-Area and H-Area seepage basin wells. The wells with water concentrations consistently above the PDWS are situated downgradient of both F-Area and H-Area seepage basins. Based on 1989 data, concentrations above the PDWS have only been measured in the upper saturated zone of the water table. Concentrations above the PDWS were not reported for any well in lower geologic layers, including the Dry Branch, McBean, Santee, and Congaree Formations.

Seepline and Swampy Outcrops of Four Mile Creek

Surface Sediment Monitoring

In 1972, 19 sediment samples were collected from the swampy outcrop along Four Mile Creek (Horton 1974b). Two samples collected in the vicinity of basins 1, 2, and 3 had concentrations of 30 and 20 ppb. Nine samples collected from the swampy outcrop south of basin 4 had an average concentration of 60 ppb, with concentrations ranging from 30 to 80 ppb. These concentrations are near background concentrations of 20 to 50 ppb reported by Horton (1974b). Similar values have been reported for uncontaminated lakes in South Carolina (Abernathy and Cumbie 1977). Similar background values have also been reported for river sediment in the Mt. Amiata region of Tuscany and sediment in Lake Michigan, with elevated values (in the vicinity of cinnabar mineralization) approaching or exceeding 1000 ppm (Dall'Aglio 1970, cited in Jonasson and Timperley 1973; Kennedy et al. 1971, cited in Reimers et al. 1973). Eight samples collected from the same swampy outcrop in the vicinity of the first side stream¹ into Four Mile Creek had an average concentrations by far were 10,100 and 19,400 ppb. These data appear to confirm migration of mercury to these outcrop areas, likely along a channel of high permeability leading to the first side stream.

Sediment samples were collected in 1988 and 1989 from the Four Mile Creek seepline in the vicinity of the F-Area and H-Area seepage basins (<u>Haselow et al. 1990</u>). In 1988, concentrations in the vicinity of the F-Area and H-Area seepage basins ranged from 40 to 310 ppb (mean = 166 ppb, n = 9) and from 70 to 220 ppb (mean = 131 ppb, n = 7), respectively. In 1989, concentrations at all F-Area (n = 6) and H-Area (n = 4) seepage basin vicinity seepline locations were less than 100 ppb (lower limit of detection [LLD]).

Water Monitoring

Three studies in recent years have analyzed for mercury in the groundwater intersecting the surface at the seepline along Four Mile Creek, downgradient from F and H-Areas. Water samples collected in 1987 from the seepline downgradient of F and H-Area seepage basins had maximum unfiltered mercury concentrations of less than 0.1 (LLD) and 0.14 ppb, respectively (Looney et al. 1988). The authors concluded that the majority of mercury was sorbed to subsurface materials or neutralized and that transport from both F-Area and H-Area seepage basins was very slow.

Water samples collected in 1988 from similar locations had maximum mercury concentrations of less than 0.2 (LLD) and 0.3 ppb, respectively (<u>Haselow et al.</u> 1990). Water samples collected in 1989 from similar locations had maximum mercury concentrations of less than 0.2 ppb (LLD).

¹ The frequently mentioned side streams in this chapter refer to the many small drainages or seeps that outflow into Four Mile Creek. The first side stream refers to the first of these encountered downstream of the Separations Area seepage basins.

Water samples collected in July 1992 from a "background" location upstream from the General Separations Areas had mercury concentrations ranging from less than 0.2 (LLD) to 0.47 ppb (Dixon and Rogers 1994). Water samples collected from the F-Area seepline had concentrations ranging from less than 0.2 (LLD) to 0.54 ppb (average of two measurements). The authors concluded that this was within the range of "background" concentrations (<0.2 to 0.47 ppb). Water samples collected from the H-Area seepline had concentrations ranging from less than 0.2 (LLD) to 1.7 ppb (average of three measurements). The 1992 data appear to confirm some measurable migration of mercury in the groundwater at localized areas of the H-Area seepline, but concentrations at the F-Area seepline do not appear elevated above background.

Four Mile Creek

Surface Sediment Monitoring

In 1972, sediment samples were collected from nine locations in Four Mile Creek from Road 4 to Road C (Horton 1974b). These samples had an average concentration of 240 ppb. The two highest concentrations, 620 and 590 ppb, were in sediment collected from locations at the first side stream and at Road C, just below F-Area effluent, respectively. This suggested maximum introduction of mercury from H-Area seepage basin 4 and F-Area cooling water. There is little question that mercury has been introduced to the Four Mile Creek swampy outcrop along the first side stream based on the seepline sediment concentrations discussed earlier. However, subsequent analyses of sediment collected at Road C indicated concentrations of 100, 190, <30, and <1 ppb, which are not elevated above average concentrations measured in 1972 (Horton 1974a; Du Pont 1972b; Du Pont 1973a; Mikol et al. 1988a). Sediment concentrations appear quite variable, and it would be difficult to conclude with confidence that discharge of F-Area cooling water has resulted in increased sediment concentrations at Road C.

The four above reports also provided sediment concentrations measured at other locations along Four Mile Creek and at other SRS locations (<u>Table 20-1</u>). <u>Du Pont</u> (1973a) provided concentrations at 12 locations in Four Mile Creek. The average concentration was 310 ppb, with the two highest concentrations (800 and 1060 ppb) occurring at Cassel's Pond above the weir and in sediment from C-Area cooling tower effluent at Road 3, respectively. <u>Du Pont</u> (1971a) provided concentrations at three locations in Four Mile Creek. One sample collected downstream from Road 4 had a concentration of 50 ppb, and the other two samples had concentrations less than 30 ppb. A 1974 memorandum (<u>Horton</u> 1974a) provided concentrations at 11 locations. The average concentration was 500 ppb, with the two highest concentrations (1860 and 810 ppb) occurring at Cassel's Pond above the weir and in sediment associate with H-Area cooling tower effluent.

Stream sediment concentrations measured in the vicinity of the F-Area and H-Area seepage basins were generally lower than concentrations measured at other locations, and the data for various stream locations are variable. Elevated concentrations measured at locations upstream from Road 3 can possibly be attributed to migration from the F-Area and H-Area seepage basins because Savannah River water was pumped to C Reactor, which only discharged water into Four Mile Creek below Road 3. The H-Area cooling tower received water pumped from groundwater wells, which could have contained elevated mercury concentrations based on groundwater concentrations in the H-Area water table. However, well water used at the Site comes from fairly

deep aquifers (in H-Area as well as other areas). None of the water supply wells is located between the basins and Four Mile Creek, and, in H-Area, the aquifer that supplies the production wells has higher pressure than its overlying aquifer (<u>Heffner</u> 1997). In general, sediment concentrations in Four Mile Creek appear higher below Road 3, indicating Savannah River contributions through C-Area cooling water.

The high concentrations reported for Cassel's Pond above the weir are likely the result of increased deposition of suspended sediments above the dam. Sediments at the discharge points for H-Area cooling tower effluent and C-Area cooling water and from cooling water settling basins (C-Area, K-Area, and L-Area) also appear to have elevated concentrations. Aside from these areas, onsite sediment concentrations are similar to the concentrations reported for Savannah River locations (see <u>Table 20-2</u>).

v	** /	February		June	
Location	1972 ^a	1972 ^b	May 1973 ^c	1974 ^d	1987 ^e
Four Mile Creek					
Effluent at Road E		130	<30	210	
Cooling tower effluent		540		810	
Downstream from Road 4	70	175	50	250	
Above entry of F-Area effluent	190	70		100	
F-Area effluent at Road E		150		210	
Below F-Area effluent at Road C	590	100	<30	190	<1
Downstream at Road A7		80		120	<1
Downstream at Road 3		240		600	
C-Area cooling water at Road 3		1060			
Downstream at Road A		250		430	<1
Cassel's Pond, above weir		800		1860	
Cassel's Pond, below weir		220		690	
Steel Creek					
At Road B				20	
At Road A-14				210	
At Road A		160			
At Road A-17		6			
Par Pond					
At pump house				60	
At hot dam				170	
At cold dam				210	
Cooling water settling basins					
C-Area		320		700	
K-Area		400		850	
L-Area				1410	
R-Area				200	
^a Source: <u>Horton</u> (1974b).					
^b Source: Du Pont (1972b).					
^c Source: Du Pont (1973a).					
^d Source: Horton (1974a).					
^e Source: Mikol et al. (1988a).					
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 Table 20-1. Mercury Concentrations (ppb) in Sediment Collected at Various SRS Locations

In 1987, sediment concentrations in Four Mile Creek at the locations shown in Table 20-1 and at two additional locations (where the stream enters the river swamp and at the mouth) were all less than 1 ppb (Mikol et al. 1988a). This makes it difficult to conclude with any confidence that migration of mercury from seepage basins has resulted in contamination of Four Mile Creek sediments except in areas associated with the swampy outcrop soil samples collected in the vicinity of the first side stream (previously discussed). The fact that sediment concentrations appear to have decreased by over 2 orders of magnitude since the early 1970s suggests that much of the sediment-bound mercury in Four Mile Creek has been buried or eroded into the Savannah River. The decrease also illustrates the decreased mercury discharges from the Olin Corporation. However, similar decreases were apparent at locations both upstream and downstream from Road 3. This is not consistent with the fact that Savannah River water has never been introduced to locations above Road 3. These stream surface sediment concentrations are also significantly lower than concentrations measured in F-Area and H-Area seepline sediment in 1988 (previously discussed). This suggests that mercury migration from the F-Area and H-Area seepage basins may be resulting in measurable contamination of the local seepline sediment but not widespread contamination of Four Mile Creek. It is also possible that seepline sediments are not as susceptible to erosion as stream sediments, and the mercury in these sediments is less mobile.

The data for sediment concentrations in Four Mile Creek are quite variable, and sediment samples collected from the Savannah River indicate that mercury concentrations may vary by more than a factor of 2 for sediment collected in similar locations (GWQCB 1971). These differences are likely due to natural heterogeneity in sediment composition. In addition, based on samples collected in 1972 and 1974, stream sediment concentrations in the vicinity of the F-Area and H-Area seepage basins appear lower than sediment concentrations below Road 3, which were impacted by C-Area cooling effluent. Based on 1972 measurements, there is little question that small amounts of mercury have migrated from the seepage basins, resulting in significantly elevated seepline sediment concentrations in the vicinity of the first sidestream (Horton 1974b). However, given the general variability in the data and the lack of an apparent disparity between Savannah River and Four Mile Creek sediment, it would be difficult to conclude with very much confidence that the F-Area and H-Area seepage basins have introduced sufficient amounts of mercury to measurably impact the Savannah River.

Water Monitoring

A water sample collected from the Four Mile Creek river swamp area (confluence with the Savannah River) in September 1970 had a mercury concentration less than 0.1 ppb. Water samples collected from Four Mile Creek at Roads E, 4, and C in May 1973 all had mercury concentrations less than 2 ppb, the apparent LLD (<u>Du Pont</u> 1973a). In 1973 and 1974, maximum concentrations of mercury were less than 1 ppb. Between 1984 and 1990, maximum concentrations of mercury in Four Mile Creek at Roads A7 and A were below the LLD of 0.2 ppb, except in 1988 (Road A7) and 1989 (Road A) when maximum concentrations were 0.22 and 0.4 ppb, respectively. In 1991, maximum mercury concentrations were below the LLD of 0.0001 ppb at these two locations.

Savannah River

Surface Sediment Monitoring

Sediment samples collected from the Savannah River have had similar mercury concentrations to those collected from many of the onsite streams (<u>Table 20-2</u>). However, the data that have been available for review are somewhat limited, and a significant gap exists between 1974 and 1992–1994.

	1970—	Echmony		-	
		February		June	1992–
Location	1971 ^a	1972 ^b	May 1973 ^c	1974 ^d	1994 ^e
River mile (RM) 187	272				< 0.13
RM 183	85				
Jackson's Landing (RM 165)		60	<30	90	
Shell Bluff Landing RM 162	346				
Upper Pumphouse (RM 158)		290			
Lower Pumphouse (RM 155)		320			
Griffin's Landing (RM 147)	875				
Steel Creek Landing (RM		60	<30	210	
142)					
Highway 301 bridge (RM	667	80	<30	210	< 0.13
119)					
RM 78	811				
RM 61	143				
RM 45	277				
RM 22	175	_			
^a Source: <u>GWQCB</u> (1971).					
^b Source: <u>Du Pont</u> (1972b).					
^c Source: <u>Du Pont</u> (1973a).					
^d Source: <u>Horton</u> (1974b).					
^e Source: <u>Westinghouse</u> (1996).					

Table 20-2. Mercury Concentrations (ppb dry weight) in Sediment Collected at Various	
Savannah River Locations Shown with the Approximate River Mile Designation	

In 1970–1971, the GWQCB, in cooperation with the Georgia Game and Fish Commission and the EPA, surveyed several media (including sediment) collected at various locations along the Savannah River (<u>GWQCB</u> 1971). Sediment concentrations ranged from 85 ppb, at a location just downriver from the Olin Corporation's discharge points (between river miles [RMs] 187 and 183), to 875 ppb, at a location near Griffin's Landing (RM 147). Given the general variability in sediment concentrations, it is difficult to make many conclusions other than that mercury concentrations appear elevated at distances greater than 100 mi downriver from the Olin Corporation's points of discharge. In addition, concentrations are similar to those reported for Four Mile Creek and other onsite locations in 1972–1974 (<u>Table 20-1</u>).

<u>Westinghouse</u> (1996) provided data for three- and four-sediment samples collected from the Savannah River between 1992 and 1994 at RMs 120 and 187, respectively. All seven samples had concentrations below the detection limit of 0.13 ppb. These concentrations are significantly lower (about 3 orders of magnitude) than the concentrations that were measured in the 1970s.

This suggests that much of the sediment-bound mercury in the Savannah River has been buried or eroded downriver; however, additional information would be helpful to more conclusively assess this situation. A similar decrease in sediment concentrations was noted for Four Mile Creek. It is interesting to note that the mercury concentrations measured in Four Mile Creek sediment in 1987 (<1 ppb) and Savannah River sediment in 1992–1994 (<0.13 ppb) are significantly less than background concentrations (20–60 ppb) reported for sediment in the SRS vicinity and in other areas. Further analysis of these data is hindered by the general spatial variability of mercury deposition in the river and the fact that precise sampling locations for different years are not known.

Water Monitoring

On July 9, 1970, mercury concentrations were measured in 25 water samples collected from the Savannah River between Augusta to Savannah, GA. Analyses indicated concentrations less than 0.2 ppb (the apparent LLD) for all of the samples. <u>Westinghouse (1996)</u> provided data for 16 water samples collected from RM 120 of the Savannah River. These samples all had concentrations below the detection limit of 0.2 ppb.

In 1973 and 1974, maximum concentrations of mercury in Savannah River water collected from locations above and below the SRS were less than 5 and 2 ppb (the apparent LLDs), respectively. Between 1984 and 1990, maximum concentrations of mercury in Savannah River water collected from locations above the SRS, below plant Vogtle, and below the SRS were below the apparent LLD of 0.2 ppb; however, in 1988 maximum concentrations at these three locations were 0.7, 0.39, and 0.26, respectively. In 1991, maximum concentrations at all three locations were less than 0.05 ppb. For comparison, wastewater from the Olin Corporation contained 50 ppb of mercury on July 17, 1970 (St. John 1970).

Fish

We examined three sets of routine SRS annual environmental monitoring reports spanning the years 1971 through 1991 to summarize mercury concentrations in fish collected from locations on or in the vicinity of the SRS:

- Environmental Monitoring at the Savannah River Plant, 1971–1984 (<u>Ashley 1972</u>; Ashley and Zeigler <u>1973</u>–1984; Ashley et al. <u>1984a</u>, <u>1984b</u>; <u>Zielger et al.</u> 1985)
- Environmental Monitoring in the Vicinity of the Savannah River Plant, 1971–1983 (Du Pont <u>1972c</u>, <u>1973b</u>, <u>1974–1984</u>)
- Savannah River Plant Environmental Report, 1985–1991 (Zeigler et al. <u>1986a</u>, <u>1986b</u>, <u>1987a</u>, <u>1987b</u>; Mikol et al. <u>1988a</u>, <u>1988b</u>; Davis et al. <u>1989a</u>, <u>1989b</u>; Cummins et al. <u>1990</u>, <u>1991</u>; <u>Arnett et al.</u> 1992).

Monitoring for mercury in fish by the SRS began in 1971, and, in general, values reported in the three sets of monitoring reports were consistent during this time period.

Sample Collection and Preparation

In July 1971, the SRS began monitoring fish for mercury. Collected fish were composited quarterly for analysis through 1972 and semiannually from 1973 through 1975. In 1976, analysis of individual fish began and has continued through 1991. Du Pont (1972a) described the method of analysis for fish and indicated that 1-g samples of flesh were used for analysis. A LLD of 20 ppb was also reported. A 1975 memorandum indicated that 2-g portions of flesh taken from behind the dorsal fin were used for analysis <u>Cumbie</u> 1975). A 1990 document (Loehle and Paller 1990) indicated that 0.3-g plugs of fish flesh were routinely collected for analysis. Concentrations were consistently reported for Savannah River locations, but the Clark Hill control location and onsite location concentrations were reported more sporadically. Concentrations have generally been reported as micrograms mercury per gram of flesh wet weight (ppm).

Basis for Analysis

For brevity and clarity, only average concentrations for all species are graphically depicted in this report. However, based on the reported concentrations for various species of fish, there is evidence to suggest that bass (and other predatory fish as well as bottom-dwelling fish) typically accumulate higher concentrations of mercury than other species. Concentrations for bream, catfish, and other species relative to those for bass at all locations between 1971 and 1991 (1981 through 1991 for other species) were 0.49, 0.50, and 0.70, respectively. These data suggest that bass may exhibit concentrations by at least a factor of 2 greater than bream or catfish. In 1973, bass from Four Mile Creek and Steel Creek had concentrations more than a factor of 5 greater than bream collected at the same locations (<u>Du Pont</u> 1974; <u>Ashley and Zeilger</u> 1974). In 1976, bass from Four Mile Creek had concentrations more than a factor of 10 greater than bream or catfish collected at the same location (<u>Du Pont</u> 1977; <u>Ashley and Zeilger</u> 1978a).

Because average concentrations and concentrations for individual species are discussed, it is helpful to look at the relative numbers of each species of fish collected at the various sampling locations (Table 20-3). In general, a larger percentage of bass has been collected from onsite locations, particularly Par Pond and Pond B. This is considered when evaluating concentrations measured in fish from the Savannah River and various onsite locations.

The total number of fish collected yearly from the Savannah River and from onsite locations has varied significantly since 1971 (Figure 20-4). Onsite and Savannah River locations are the same as described in <u>Table 20-3</u> (see <u>Chapter 14</u> for a map illustrating specific locations). Very few fish were collected from the Savannah River and onsite locations from 1976 through 1980. Additionally, concentrations were reported for onsite locations in 1974 and 1975, but sample numbers were not provided. No fish were analyzed in 1987 because of the construction of a new laboratory.

	the SKS Between 1971 and 1991							
Bream	Catfish	Bass	Other	Total #				
45.7	26.7	15.7	11.9	210				
43.4	45.0	5.2	6.3	553				
40.8	43.3	5.9	9.9	573				
44.7	44.6	5.3	5.4	704				
43.1	44.3	5.5	7.1	1830				
37.8	34.6	16.2	11.4	185				
76.3	3.6	17.7	2.4	413				
44.0	29.5	23.5	3.0	366				
54.3	29.6	13.5	2.7	223				
34.5	8.1	38.6	18.8	197				
33.1	8.8	52.9	5.1	136				
51.3	18.5	24.1	6.1	1520				
46.8	32.2	14.0	6.9	3560				
	45.7 43.4 40.8 44.7 43.1 37.8 76.3 44.0 54.3 34.5 33.1 51.3	45.7 26.7 43.4 45.0 40.8 43.3 44.7 44.6 43.1 44.3 37.8 34.6 76.3 3.6 44.0 29.5 54.3 29.6 34.5 8.1 33.1 8.8 51.3 18.5	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				

Table 20-3. Percentage of Bream, Bass, Catfish, and Other Fish and the Total Number of Fish Collected for Mercury Analysis at Various Sampling Locations on or in the Vicinity of the SRS Between 1971 and 1991

^a This total does not include fish collected from Four Mile Creek at Road 3 or the mouth of Steel Creek because these locations were sampled very infrequently.

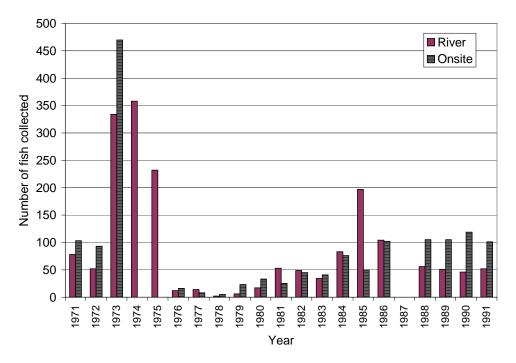


Figure 20-4. Total number of fish collected annually for mercury analysis from three Savannah River locations and five onsite locations. Link to <u>tabulated data</u>.

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Mercury Concentrations Reported in SRS Annual Monitoring Reports

To establish whether the SRS has been responsible for introducing mercury to Savannah River fish, it is instructive to examine concentrations measured in fish from Clark Hill (a control location upriver from the SRS) and three Savannah River locations (above, adjacent to, and below the SRS) (Figure 20-5). Figure 20-5 also shows the Food and Drug Administration (FDA) guide for daily intake of mercury in edible fish. Concentrations have fluctuated somewhat since inception of the monitoring program, but they have fluctuated rather consistently at all locations. This is indicative of similar mercury levels in fish from various locations along the Savannah River. In addition, average concentrations in Savannah River fish (at all three locations) between 1971 and 1991 (see Table 20-3) are not statistically different from the average fish concentrations measured at Clark Hill. This is not consistent with the fact that Olin Corporation discharges to the Savannah River are well downriver from the Clark Hill Reservoir, and concentrations of mercury in fish from Clark Hill Reservoir would not be expected to be the same as for fish from the Savannah River. An explanation for the lack of a difference is not apparent, but differences in fish size and age as well as differences in mercury methylation rates for different locations could be factors.

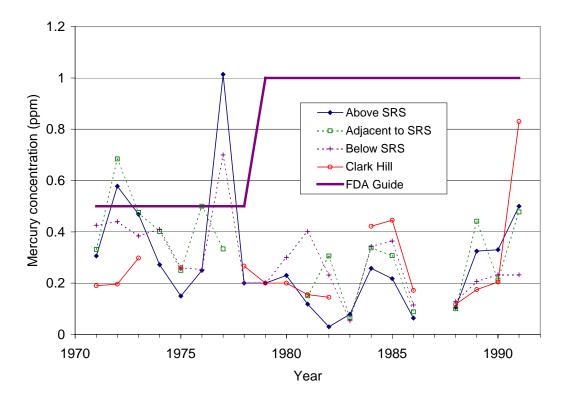


Figure 20-5. Average mercury concentrations measured in fish collected from Clark Hill and the Savannah River at locations above, adjacent to, and below the SRS. Link to tabulated data.

It is also instructive to examine average onsite concentrations and average Savannah River concentrations relative to those reported for Clark Hill (Figure 20-6). Very few fish were

collected at any location from 1976 through 1980, but mercury concentrations in fish collected from onsite locations are clearly elevated relative to concentrations in fish collected from the Savannah River and Clark Hill locations. In general, onsite concentrations are about a factor of 2 greater than Savannah River concentrations. It should be noted that a greater percentage of bass has typically been collected from onsite locations. This may contribute somewhat to the higher onsite concentrations, but there was likely some other mechanism that resulted in higher concentrations in onsite fish.

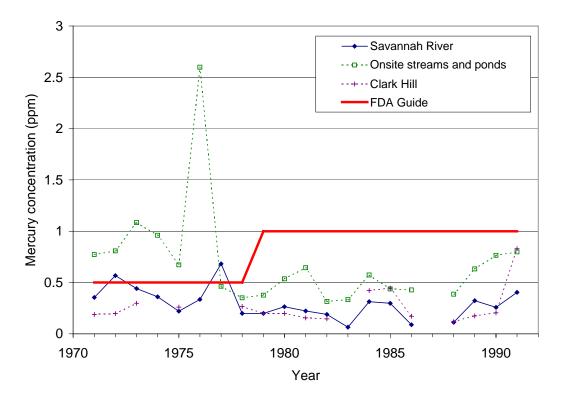


Figure 20-6. Average mercury concentrations measured in fish collected from Clark Hill, Savannah River, and onsite locations. Link to <u>tabulated data</u>.

Onsite concentrations appear significantly elevated in 1976. However, few fish were collected and the majority of fish collected onsite were bass, which had concentrations roughly an order of magnitude greater than bream and catfish collected at the same locations. No bass were collected from the Savannah River in 1976.

To assess the credibility of a significant F-Area and H-Area seepage basin <u>source term</u> for mercury, it is instructive to look at mercury concentrations measured in fish from various onsite locations (Figure 20-7). Concentrations appear similar at all locations, which suggests that F-Area and H-Area seepage basins have not contributed significantly to elevated mercury concentrations in Four Mile Creek. In fact, with the exception of 1971 and 1973, concentrations in fish from Four Mile Creek are lower than concentrations in fish from other onsite streams. Concentrations measured in onsite fish appear significantly elevated in 1976 at all locations. As <u>discussed above</u>, measured mercury concentrations in 1976 were heavily influenced by the fact that the majority of

fish sampled were bass, which had significantly higher mercury concentrations that other species collected at the same locations.

Unfortunately, the routine sampling location in Four Mile Creek was at Cassel's Pond, which is below the C-Area cooling tower effluent discharge point. Concentrations were reported from 1971 through 1973 for fish collected from Four Mile Creek at Road 3, which is above the C-Area cooling tower effluent discharge point. During this time period, concentrations in fish at Road 3 averaged 0.66 ppm, and concentrations in fish at Cassel's Pond averaged 1.15 ppm. This suggests that C-Area cooling water discharges (water originating from the Savannah River) had a larger impact on mercury concentrations in Four Mile Creek fish than did F-Area and H-Area seepage basins. The fact that fish from other onsite streams have historically had mercury concentrations similar to those measured in Four Mile Creek also suggests limited impact from F-Area and H-Area seepage basins.

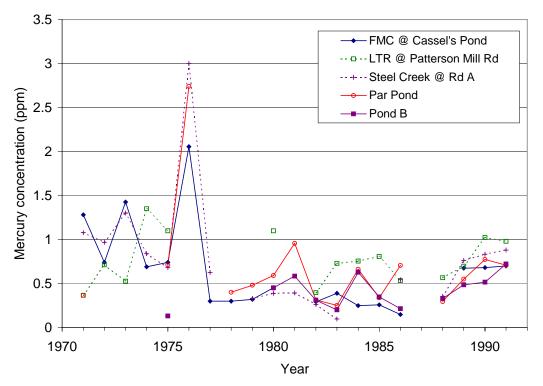


Figure 20-7. Average mercury concentrations in fish collected from five onsite locations. Link to <u>tabulated data</u>.

<u>Table 20-4</u> shows average mercury concentrations for Savannah River and onsite locations from 1971 through 1991. Average concentrations for each individual species (i.e., bass, bream, catfish, and other) are shown as well as mean concentrations for all species and normalized mean concentrations for all species after normalization to bass concentrations. Normalized mean concentrations were calculated by dividing the bream, catfish, and other species concentrations by an adjustment factor (0.49, 0.50, 0.70, respectively). These adjustment factors were calculated by dividing the concentrations measured in bream, catfish, and other species by the concentrations measured in bass. There is little question that average mercury concentrations in all species of fish collected from onsite locations appear higher than the concentrations in fish collected from

the Savannah River. The concentrations appear, on average, to be about a factor of 2 greater in onsite fish. The mean concentration for all species from onsite locations is a factor of 2.0 greater than for Savannah River locations. The mean concentration for all species after normalization to bass concentrations is a factor of 1.6 greater than for Savannah River locations. These mean concentrations were calculated considering the number of each species. Therefore, the difference in relative numbers of each species collected from the Savannah River and onsite locations (Table 20-3) likely contributed to the disparity in mercury concentrations. However, it does not appear that this is the only factor that contributed to higher onsite fish concentrations. Concentrations measured in fish collected from Four Mile Creek and from other onsite locations that would have been exposed to water pumped from the Savannah River (Steel Creek, Lower Three Runs, and Par Pond) do not appear to be significantly different.

Location	Bass	Bream	Catfish	Other	Mean	Mean ^a		
Clark Hill	0.35	0.20	0.16	0.39	0.27	0.40		
River above SRS	0.51	0.26	0.30	0.26	0.28	0.53		
River adjacent to SRS	0.52	0.28	0.30	0.27	0.32	0.58		
River below SRS	0.60	0.21	0.32	0.32	0.29	0.54		
Savannah River average	0.54	0.25	0.30	0.28	0.30	0.55		
Upper Three Runs at Road F	0.98	0.38	0.45	0.51	0.44	0.78		
and Highway 278								
Upper Three Runs at Road A	0.58	0.33	0.30	0.39	0.35	0.55		
FMC at Cassel's Pond	1.22	0.48	0.44	0.18	0.65	0.94		
Steel Creek at Road A	1.43	0.52	0.54	0.40	0.78	1.09		
Lower Three Runs at Patterson	1.31	0.51	0.83	0.60	0.78	1.12		
Mill Road								
Par Pond	0.94	0.52	0.42	0.49	0.68	0.88		
Pond B	0.59	0.23	0.28	0.45	0.41	0.48		
Onsite average	1.02	0.45	0.46	0.43	0.59	0.89		
^a Mean concentrations for all species normalized to bass concentrations.								

Table 20-4. Average Mercury Concentrations (µg mercury g⁻¹ flesh wet weight) Reported for Clark Hill, Savannah River, and Onsite Locations from 1971 through 1991

Examining the maximum reported concentrations from 1981 through 1991 (the reports did not provide maximum concentrations before 1981) reveals similar maximum reported concentrations for Clark Hill, Savannah River, and onsite locations (Figure 20-8). However, maximum concentrations appear consistently higher for the Savannah River and SRS streams and ponds than for Clark Hill. The highest reported concentration during this time period was at Clark Hill.

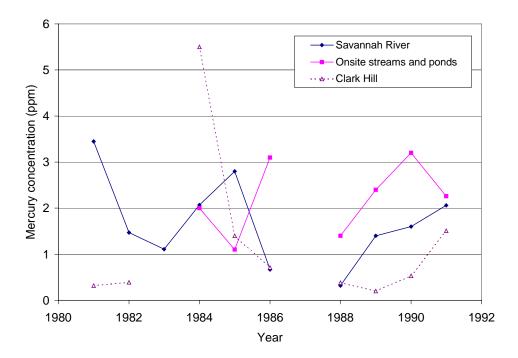


Figure 20-8. Maximum reported mercury concentrations for Clark Hill, the Savannah River, and onsite locations from 1981 through 1991. Link to <u>tabulated data</u>.

There appears to be little evidence to suggest that mercury introduced to Four Mile Creek from the F-Area and H-Area seepage basins has resulted in the elevated concentrations measured in Four Mile Creek based on concentrations measured by the SRS. It is not clear why onsite fish have consistently had higher concentrations than fish from the Savannah River, but potential explanations will be explored later in this section.

Other SRS and Savannah River Studies

In 1970–1971, the GWQCB, in cooperation with the Georgia Game and Fish Commission and the EPA, conducted an extensive survey of several media, including fish. Concentrations for bass, bream, suckers, and shad collected at various locations along the Savannah River and from seven other major river basins in Georgia are reported in <u>Table 20-5</u>. Concentrations in fish collected from various locations along the Savannah River below the Olin Corporation's discharge points (between RMs 183 and 187) appear very similar, and they are significantly elevated relative to concentrations in fish collected below Clark Hill dam. This suggests that mercury contamination extends at least 150 mi below the Olin Corporation's discharge points. A study on mercury accumulation in fish of the North Fork Holston River in Virginia and Tennessee reported elevated mercury concentrations in fish more than 80 mi below an inactive chlor-alkali plant (<u>Hildebrand et al.</u> 1980). Similar concentrations (between 1 and 2 ppm) were reported for fish collected upriver of the Olin Corporation's discharge points (below the Clark Hill dam) were significantly less than for fish collected below the discharge points and similar to average mercury concentrations measured for fish collected from the seven other major river basins in Georgia. The average concentration across all species (not just those listed in <u>Table</u> <u>20-5</u>) was 0.34 ppm for the seven major river basins exclusive of the Savannah River and 0.95 ppm for the Savannah River from Augusta to Savannah.

Location	Bass	Bream	Suckers	Shad
Savannah River				
RM 238 ^{b, c}	0.47	0.06		0.04
RM 162	1.53	0.70	1.30	0.52
RM 119	1.72	0.70	1.41	0.50
RM 78	1.63	1.06	1.36	0.52
RM 22	1.80	0.80	1.80	0.36
Other river basins ^d	0.37	0.37	0.44	0.38
^a Source: <u>GWQCB</u> (197	1).			
^b RM = river mile.				
^c Below Clark Hill dam.				
d Seven major river basi	ns in Georgia ex	clusive of the Sava	nnah River.	

 Table 20-5. Average Mercury Concentrations (ppm mercury wet weight) in Fish Collected in 1970–1971 by the GWOCB^a

Concentrations measured in bass and suckers were significantly higher than for bream and shad, and the data indicated that piscivorous fish at the top of the food chain (e.g., largemouth bass) had the highest mercury concentrations. However, suckers were found to contain mercury concentrations comparable to concentrations in the piscivorous species. Because suckers are bottom feeders, they may ingest greater amounts of sediment than other species of fish and, therefore, may have accumulated higher mercury concentrations. In addition, large specimens of a species were generally found to contain higher concentrations than smaller specimens of the same species from the same area.

Newman and Messier (1994) conducted an extensive study to address the consistently higher reported mercury concentrations for mosquitofish collected from SRS streams relative to fish collected from the Savannah River. The results indicated no significant differences in mercury concentrations between onsite and offsite fish. There were, however, significant differences in mercury concentrations between fish from locations associated with Savannah River water input and fish from locations isolated from river water input. Additionally, mosquitofish collected from the Olin Plant Canal had concentrations roughly an order of magnitude greater than fish from other locations. Furthermore, the authors examined Westinghouse Savannah River Company data (which is reported in the annual environmental monitoring reports) and concluded that fish size and age were confounding factors in interpreting the data. This is the only study that *RAC* has been able to locate that was designed specifically to address the question of higher concentrations reported for onsite locations.

<u>O'Connell</u> (1971) compared mercury concentrations for several species of fish collected from Four Mile Creek to concentrations in fish from other "control" locations, including Upper Three Runs Creek, Tinker's Creek, Dick's Pond, Skinface Pond, and an unnamed creek. There were no statistically significant differences for any species except largemouth bass. Concentrations in largemouth bass from Four Mile Creek were approximately an order of magnitude greater than in bass from the "control" locations. Only three bass were collected from Four Mile Creek, and detailed information regarding fish size and age was not provided, although the authors reported that the sizes of fish varied greatly. Based on the results of this study, concentrations in fish from Four Mile Creek do not appear higher than in fish from "control" locations, and the difference noted for largemouth bass may have resulted from collecting larger or older fish from Four Mile Creek. Samples of homogenized whole fish and, when possible, fish muscle were analyzed, and the limit of detection was reported as 0.01 ppm.

In July 1990, fish were collected from six locations in Four Mile Creek and one location in Pen Branch (Loehle and Paller 1990). Fish were gutted, and the entire fish was homogenized before analysis. The detection limits were reported as 0.004 to 0.019 mg g^{-1} , depending on the fish weight. It is assumed that the detection limit units were erroneously reported as milligrams per gram and should have been reported as micrograms per gram (ppm) because concentrations well below the reported limit were measured.

Concentrations of mercury in fish collected from Four Mile Creek at Road F, which is upstream from the seepage basin outcrops, and at Road 4 and Road C, which are in the vicinity of H-Area and F-Area seepage basins, were below the detection limits. Concentrations in all fish collected at Road 3 were also below the detection limits. Four out of six fish collected from Four Mile Creek at the west end of Banana Road had concentrations greater than the detection limit and a mean of 0.017 ppm. Seven out of ten fish collected from Four Mile Creek at Cassel's Pond had concentrations greater than the detection limit and a mean of 0.008 ppm. Two out of eight fish collected from Pen Branch at Road B had concentrations above the detection limit (0.24 and 0.038 ppm). All fish with concentrations greater than the detection limit were sunfish.

One fish from Pen Branch (0.24 ppm) had a concentration similar to concentrations reported in the annual environmental monitoring reports in 1989 and 1990. However, the concentrations reported for Four Mile Creek location are nearly 2 orders of magnitude lower than concentrations reported in the annual monitoring reports and significantly lower than concentrations reported in other studies. For comparison, mean concentrations reported for bream collected from Four Mile Creek at Cassel's Pond in 1989 and 1990 were 0.48 and 0.52 ppm, respectively. An explanation for the large discrepancy between concentrations for fish collected by Loehle and Paller and fish collected routinely by the Westinghouse Environmental Protection Department is not apparent. The method of analysis may account for some of the difference because Loehle and Paller analyzed individual homogenized fish, and the SRS reportedly analyzed 0.3 g plugs of flesh.

As part of the National Pesticide Monitoring Program, the Bureau of Sport Fisheries and Wildlife collected fish from the Savannah River near Savannah, Georgia, in 1969 and 1970 (<u>Henderson et al.</u> 1972). In 1969, mercury concentrations ranged from 0.36 to 1.00 ppm wet weight; in 1970, concentrations ranged from 0.17 to 1.80 ppm. Composite samples of homogenized tissue from two to four fish were analyzed, and the LLD was reported as 0.05 ppm. Species of fish included carp, bluegill, and largemouth bass.

As part of the same program, the U.S. Fish and Wildlife Service collected fish from the same location in 1971 through 1973 (<u>Walsh et al.</u> 1977). In 1971, mercury concentrations ranged from <0.05 to 0.72 ppm wet weight; in 1972, concentrations ranged from 0.14 to 1.25 ppm; and in 1973, concentrations ranged from 0.08 to 0.73 ppm. Composite samples of homogenized tissue from two to five fish were analyzed, and the LLD was reported as 0.05 ppm. Species of fish included carp, bluegill, catfish, sunfish, and largemouth bass.

As part of the National Contaminant Biomonitoring Program (formerly the National Pesticide Monitoring Program), the U.S. Fish and Wildlife Service collected fish from the Savannah River near Savannah, Georgia, in 1978 and 1980 (Lowe et al. 1985). Mercury

concentrations ranged from 0.08 to 0.19 ppm wet weight in 1978 and from 0.06 to 0.57 ppm wet weight in 1980. Three composite samples were analyzed in both years of collection, and each composite contained homogenized tissue from three to five fish. The LLD was reported as 0.01 ppm. Species of fish included catfish, bowfin, and largemouth bass.

Concentrations reported through the National Pesticide Monitoring Program and the National Contaminant Biomonitoring Program indicate significantly elevated mercury concentrations in the Savannah River near Savannah, Georgia. These data also suggest that mercury discharges from upriver industries may have resulted in widespread contamination extending more than 150 mi downriver from the source.

In February 1984, spotted gar and largemouth bass collected from the Savannah National Wildlife Refuge near Savannah, Georgia, had mercury concentrations ranging from 0.17 to 0.41 ppm wet weight (Winger et al. 1990). A follow-up study in August 1985 collected and analyzed fish and other organisms from the Savannah National Wildlife Refuge and the lower Savannah River. Mercury concentrations in these specimens ranged from 0.02 (fiddler crab) to 0.78 (bowfin) ppm wet weight. <u>Aliquots</u> of homogenized whole organisms were analyzed, and the limit of detection was reported as 0.01 ppm.

Information obtained from the Georgia Department of Natural Resources (GDNR 1994) included data regarding a summary of toxic substances found in fish fillet composite samples collected in the fall of 1993. However, a very limited number of samples were collected. Fish collected from the Savannah River in Richmond County (above the SRS) included one largemouth bass and three suckers with mean concentrations of 0.20 and 0.18 mg kg⁻¹ (ppm) wet weight, respectively. Concentrations ranged from 0.10 to 0.25 ppm. Fish collected from the Savannah River in Chatham County (near Savannah, Georgia) included three channel catfish and three largemouth bass with mean concentrations of 0.06 and 0.04 ppm, respectively. Concentrations ranged from 0.02 to 0.08 ppm. Samples of fish muscle tissue were analyzed, and the detection limit was reported as 0.01 ppm.

Other South Carolina and Georgia Studies

Various species of fish were collected in 1974 from several South Carolina lakes and rivers (Koli et al. 1977). These locations included the Savannah River and Clark Hill, but relatively few fish were sampled. Because of the small number of fish collected and the fact that different species were collected from the various lakes and rivers, it is difficult to make many conclusive comparisons to SRS data. Mercury concentrations in fish from the Savannah River were similar to concentrations in fish from Clark Hill and generally lower than concentrations in fish from other locations. However, the collection location along the Savannah River was not specified and may have been upriver from Augusta, Georgia. Only two fish (both catfish) were collected from the Savannah River, and concentrations were about a factor of 5 less than concentrations measured by the SRS in catfish from the Savannah River in 1974. Concentrations generally increased with fish size, and liver, kidney, and muscle had the highest concentrations among various tissues.

Largemouth bass were collected from three unpolluted South Carolina reservoirs between March 1973 and November 1975 (<u>Abernathie and Cumbie</u> 1977). Fish muscle tissue was analyzed and the reported detection limit was 0.05 ppm. Fish were grouped according to length, and mean concentrations ranged from 0.34 to 4.49 ppm. Variations in concentrations between the

three reservoirs (differences were statistically significant) were attributed to the ages, trophic states, and water quality characteristics of the reservoirs.

Various species of fish were collected from the Suwannee River below Okefenokee Swamp in Georgia in 1973 (<u>Cumbie</u> 1975). This river was not associated with a recognized point source of mercury contamination. Fish axial muscle was analyzed, and the LLD was reported as $0.02 \,\mu g$ total mercury per specimen. Average mercury concentrations ranged from 0.14 (chubsucker) to 0.81 ppm (chain pickerel), with a maximum measured concentration of 1.40 ppm in a chain pickerel.

Factors Influencing Accumulation of Mercury in Fish

A number of water quality and biological factors can influence the degree to which mercury bioaccumulates in fish. <u>Eisler</u> (1987) presents a very detailed discussion of mercury in the environment. The majority (80 to 99%) of mercury found in fish tissue is organic in the form of methylmercury (Phillips and Russo 1978; Hildebrand et al. 1980; Grieb et al. 1990; Winfrey and Rudd 1990). Accumulation of mercury is generally greatest in liver, kidney, and muscle tissue (Wojtalik 1971; Koli et al. 1977; EPA 1992). A study by the EPA (EPA 1992) generally found higher mercury concentrations in fillet samples than in whole body samples, but the opposite was also true for several locations. This disparity may have resulted from a number of factors, including species variability and stomach content, which can include significant quantities of contaminated sediment.

It is widely accepted that mercury can be bioconcentrated in organisms and biomagnified through food chains. Estimated biomagnification factors (water concentration divided by fish concentration) range from 10^3 to $10^{6.5}$ (Wojtalik 1971; Watras and Huckabee 1994). Consequently, fish living in waters with mercury concentrations well below the PDWS (2 ppb) can accumulate mercury levels in muscle tissue exceeding the FDA "Action Level" of 1.0 µg g⁻¹ (ppb) mercury.

In general, mercury concentrations tend to increase with fish age, length, and weight (Grieb et al. 1990; GWQCB 1971; Doi and Ui 1973; Hildebrand et al. 1980; Abernathy and Cumbie 1977; Koli et al. 1977; and Stiefel 1976). Other factors that may influence the formation of methylmercury and subsequent accumulation by fish include pH, dissolved organic carbon, temperature, microbial activity, sulfate, chloride, calcium, suspended sediment load, and sedimentation rates (Wren and MacCrimmon 1983; Bisogni and Lawrenece 1975; Hildebrand et al. 1980; Grieb et al. 1990; Watras and Huckabee 1994; Tsai et al. 1975; Rodgers and Beamish 1983; and Eisler 1987). In addition, piscivorous (e.g., largemouth bass) and bottom dwelling fish have been shown to contain higher mercury concentrations than other species of fish; however, top predatory species generally accumulate mercury to the highest concentrations (GWQCB 1971; Grieb et al. 1990; Koli et al. 1977). The construction of artificial reservoirs has also contributed to elevated mercury concentrations resulting from mercury releases from flooded soils when the reservoirs are first filled (Eisler 1987). Concentrations in fish collected from various reservoirs have been shown to decrease with increasing reservoir age (Abernathy and Cumbie 1977). It is also likely that the rate of mercury methylation is different for reservoirs and streams, resulting in different rates of bioaccumulation.

<u>Miettinen</u> (1973) described a biexponential equation for mercury excretion in aquatic animals. The biological <u>half-life</u>. of the fast component usually varies from 1 to 10 days, while

the slow component ranges from 200 to 1200 days. <u>Tollefson and Cordle</u> (1986) described accumulation of mercury in fish muscle tissue over a period of a few weeks, and a biological halflife of 2 years. In addition, methylmercury has been shown to have the slowest rate of elimination among different mercury species. Methylmercury production is greatest at the sediment-water interface. Methylation generally takes place only in the top few centimeters of sediment (Jernelöv and Åséll 1973), and methylation of mercury by microorganisms can occur under both anaerobic and aerobic conditions (Bisogni and Lawrence 1975; Eisler 1987).

The factors that appear to consistently be correlated with mercury accumulation in fish include species, age, length, weight (positively correlated), and pH (negatively correlated). Other water quality characteristics have been shown to have varying effects in different aquatic systems. In addition, much of the research on factors affecting mercury accumulation in fish has been conducted in lakes and not streams or rivers.

Potential Explanations for Higher Mercury Concentrations Measured by the SRS in Onsite Fish

A definitive explanation for higher mercury concentrations measured by the SRS in onsite fish is not readily apparent. However, based on the vast amount of information in the open literature regarding mercury in aquatic ecosystems, there appears to be a number of potential explanations.

A study conducted by the GWQCB (GWQCB 1971) indicated significantly higher mercury concentrations in Savannah River fish below the Olin Corporation's discharge points than above the discharge points. This appears consistent with the fact that the Olin Corporation has historically discharged significant amounts of mercury to the Savannah River. Information reported in the SRS annual environmental monitoring reports indicates very similar average concentrations in fish from the Clark Hill reservoir and the Savannah River (Table 20-4). This is not consistent with the fact that the reservoir is located a significant distance upriver from the Olin Corporation's discharge points or with the results presented by the GWQCB. Very similar concentrations were measured by the GWQCB in Savannah River (Table 20-6). In addition, concentrations in fish from onsite locations that did not receive Savannah River water appear similar to concentrations measured in fish from Clark Hill. Concentrations measured in Savannah River fish by the SRS in 1971 are significantly lower than concentrations measured by the GWQCB in 1970–1971.

Average concentrations measured by the SRS in fish from Upper Three Runs at Highway 278 (which would not have been affected by SRS activities or received any pumped Savannah River water) are actually higher than concentrations measured in Savannah River fish (Table 20-4). The concentrations measured in Upper Three Runs at Highway 278 are similar to concentrations measured in other river basins in Georgia (GWQCB 1971) and in "background" locations throughout the United States (EPA 1992). Newman and Messier (1994) reported significant differences between mercury concentrations in fish from locations associated with Savannah River water input and locations isolated from Savannah River water input.

by the G W Q OD and BKS in 1971								
Species of	GWQCB (1970–19-71)		SRS (1971)					
fish	River mile 162	Clark Hill	River	Clark Hill	Onsite ^b	Onsitec		
Bass	1.53	0.47	nsa	0.25	1.74	ns		
Bream	0.7	0.06	0.34	ns	0.72	0.30		
a ns = no sa	mple collected.							
^b Onsite streams that received pumped Savannah River water (FMC, Steel Creek, and Lower								
Three Runs								

Table 20-6. Mean Mercury Concentrations (ppm) Reported for Bass and Bream Collected by the GWOCB and SRS in 1971

^c Onsite streams that did not receive pumped Savannah River water (Upper Three Runs).

Savannah River and onsite stream water quality data were examined for the years 1984 through 1991. The pH appears lower for onsite streams (this is based on minimum and maximum yearly values that were provided in the annual monitoring reports), and sulfate and chloride concentrations were consistently lower for onsite streams. Calcium concentrations were significantly higher in Lower Three Runs Creek than in other onsite streams, but mercury concentrations do not appear significantly different in fish from Lower Three Runs than in fish from other onsite streams that received pumped Savannah River water. More acidic conditions in onsite streams may result in increased accumulation of mercury by fish.

It appears likely that the lower concentrations measured in Savannah River fish by the SRS may, in part, be the result of a combination of factors. However, the fact that average concentrations in Upper Three Runs fish have been consistently higher than Savannah River fish and that average concentrations in Savannah River fish have been similar to Clark Hill fish suggests that variations in fish size or age may account for much of the discrepancy. Concentrations have been shown to vary by more than a factor of 3 between fish ages 2 and 9 (Grieb et al. 1990). Concentrations in largemouth bass collected from a South Carolina reservoir have also been shown to vary by more than an order of magnitude between fish less than 230 mm and fish greater than 380 mm (Abernathy and Cumbie 1977). If smaller and younger fish were consistently collected from the Savannah River relative to fish collected from onsite streams and the Clark Hill reservoir, differences in mercury concentrations would result. This certainly seems possible since the Savannah River is commercially fished, while onsite streams and ponds are restricted from public access. Unfortunately, information regarding the size and age of fish collected by the SRS is not available for examination. However, Newman and Messier (1994) concluded that fish size and age were confounding factors in interpretation of SRS fish data. A larger percentage of bass has also consistently been collected from onsite streams and likely accounts for some part of the discrepancy between onsite and Savannah River fish. It is also possible that differences in analytical techniques (e.g., analysis of muscle tissue or homogenated whole fish) have resulted in different concentrations.

It is not clear why fish concentrations measured by the SRS do not appear to have mimicked the decreases noted for sediment concentrations based on data reported by the SRS. <u>Hildebrand et al.</u> (1980) reported a linear relationship between fish and sediment mercury concentrations, with a two-fold reduction in fish mercury concentrations roughly corresponding to a three-fold reduction in sediment mercury concentrations. However, a study of the distribution and accumulation of mercury in the Ottawa River (<u>Miller</u> 1977, cited in <u>Hildebrand et al.</u> 1980) indicated that fish concentrations did not decrease as rapidly as sediment concentrations. This is apparently related to the slower turnover rate of mercury in fish relative to sediment. <u>Eisler</u> (1987) stated that

elevated levels of mercury in aquatic <u>biota</u> can persist for up to 100 years after the pollution source is eliminated. Concentrations reported for mosquitofish collected from an Olin Corporation canal in 1993 suggest that significant mercury contamination remains in this area and may contribute to continued elevated mercury concentrations in Savannah River fish (<u>Newman</u> and <u>Messier</u> 1994). Inconsistencies in fish size and age from year to year may also hinder definitive interpretation of the SRS data.

Conclusions Regarding Mercury

In an attempt to determine whether SRS operations have resulted in elevated mercury concentrations, reported concentrations for several environmental media have been examined. In general, water concentrations measured in onsite streams and in the Savannah River have consistently been near or below the detection limits and well below the PDWS of 2 ppb. There have been no apparent differences between concentrations in the various onsite streams and the Savannah River. Based on water concentrations, there is little evidence to suggest that mercury from F-Area and H-Area seepage basins has resulted in elevated mercury concentrations in any onsite (except at the Four Mile Creek groundwater seepline near the H-Area seepage basin) or Savannah River surface water.

There is little question that small amounts of mercury have migrated from F-Area and H-Area seepage basins into the groundwater. Monitoring of seepage basin wells has confirmed this, but the majority of seepage basin wells (~90%) have consistently had concentrations below the PDWS (2 ppb). In general, the highest groundwater mercury concentrations have been measured in H-Area seepage basin wells. This suggests that migration of mercury through the groundwater to any onsite stream has likely been greatest to Four Mile Creek in the vicinity of the H-Area seepage basins. Seepage basin closure in 1988 and the reporting of total mercury beginning in the third quarter of 1993 (instead of dissolved mercury) hinders complete interpretation of temporal trends.

It appears likely that much of the F-Area and H-Area seepage basin mercury inventory (about 4500 lb) has remained in the environs of the basins, and that the rate of mercury migration into Four Mile Creek (and certainly into the Savannah River) has been small relative to the rate of mercury discharge from the Olin Corporation. At one time, the rate of discharge was reported to be 12 lb d^{-1} . At this rate, Olin plant operations would result in an annual discharge of about 4400 lb of mercury directly to the Savannah River. For comparison, approximately the same amount was discharged by the SRS to F-Area and H-Area seepage basins between 1959 and 1982.

Sediment samples collected from the swampy outcrop along the first sidestream into Four Mile Creek have indicated migration of mercury to this area. However, sediment samples taken from various locations in Four Mile Creek imply that the mercury has remained in rather localized areas. In general, the highest sediment concentrations have been measured in ponds, reservoirs, and settling basins. This suggests accumulation of mercury from increased deposition of suspended sediments in these areas. Sediment concentrations measured in the Savannah River were similar to concentrations measured in sediment collected from many onsite locations, including Four Mile Creek, in the early 1970s. In addition, mercury concentrations in sediment samples collected from Four Mile Creek in 1987 and from the Savannah River between 1992 and 1994 indicate significant decreases since the early 1970s. While this is based on limited data, it

suggests that much of the sediment-bound mercury has been buried or eroded. It also reflects the significant decreases in mercury discharge to the Savannah River from upriver industries.

Sediment concentrations in Four Mile Creek appear to have decreased significantly since the early 1970s. However, concentrations reported for sediment samples collected from the Four Mile Creek seepline near the F-Area and H-Area seepage basins in 1988 and 1989 were more than 2 orders of magnitude greater than concentrations reported for Four Mile Creek stream sediment in 1987. This may be the result of more stable seepline sediments (i.e., not as exposed to erosive forces) as well as localized accumulation of mercury leached from the seepage basins. Based on mercury concentrations measured in Savannah River and Four Mile Creek sediment, however, SRS activities have not resulted in an appreciable mercury releases to the Savannah River.

Based on concentrations of mercury measured in fish collected from the Savannah River at locations above, adjacent to, and below the SRS, which were very similar, SRS activities have not resulted in measurable mercury releases to the Savannah River. Mercury concentrations measured by the SRS in fish collected from the Savannah River have also been very similar to concentrations measured in fish from Clark Hill, which would not have been impacted by Olin Corporation discharges. This is inconsistent with other studies and suggests that collecting smaller or younger fish from the Savannah River may have resulted in lower measured concentrations.

Mercury concentrations measured in fish collected from onsite ponds and streams have consistently been elevated (by about a factor of 2) relative to Savannah River fish concentrations. However, concentrations in fish from Four Mile Creek are similar to or lower than concentrations in fish from other onsite locations. There is little evidence to suggest that mercury from F-Area and H-Area seepage basins has resulted in elevated fish concentrations in Four Mile Creek or any other onsite stream. The highest concentrations appear to be in streams and reservoirs that have received reactor cooling effluent. It is unlikely that cooling effluent would contain mercury resulting from reactor operations, and it appears that the primary source of mercury at the SRS has been the continuous pumping of Savannah River water for use as reactor coolant. In addition, several studies have reported elevated mercury concentrations in fish (approaching and exceeding concentrations measured in onsite fish) collected from South Carolina and Georgia reservoirs lacking a known mercury point source of contamination. A number of factors may be related to the higher measured onsite concentrations. Given the general variability that occurs between fish of various sizes and ages and the variability that appears to occur between fish from various water systems in South Carolina and Georgia, it would be almost impossible to develop a credible SRS mercury source term based on fish concentrations.

It is difficult to determine the exact source of the onsite mercury, but it is certainly possible (and seems likely) that suspended sediment in water pumped from the Savannah River for use as cooling water has accumulated in onsite streams, reservoirs, and settling basins. However, concentrations measured in fish collected from Upper Three Runs Creek at Road F and Highway 278 were also elevated above concentrations in fish from the Savannah River. These locations are upstream from SRS operations and were not impacted by continuous circulation of Savannah River water for use as reactor coolant. Clearly, the Savannah River is not the sole source of onsite mercury contamination, and other anthropogenic (coal burning) and natural (volcanoes and igneous rock) mercury sources contribute to accumulation in onsite fish. It is not clear why fish from Upper Three Runs Creek would have higher concentrations than fish from the Savannah

River, which have been exposed to industrial mercury sources. Differences in fish size and age, however, are likely factors.

In addition, mercury concentrations in fish measured by the SRS have been relatively constant between 1971 and 1991. This is inconsistent with the significant (2 or 3 orders of magnitude) decreases apparent in Four Mile Creek and Savannah River sediment concentrations. If sediment-bound mercury has been buried or eroded, as recent analyses of FMC and Savannah River sediment suggest, it is possible that a consequent reduction in fish concentrations would not be evident for several years. It is also possible that seepage from waste disposal areas at the Olin Corporation continues to release mercury to the Savannah River.

It is clear that some mercury has been leached from the H-Area seepage basins and has migrated at least to the seepline area at Four Mile Creek. However, even if SRS activities have resulted in some mercury releases to onsite streams, Four Mile Creek in particular, they do not appear to have impacted concentrations in Savannah River media, including water, sediment, and fish. Regardless, continued monitoring of environmental media for elevated mercury concentrations is warranted because of the small difference between tolerable natural background levels of mercury and possible harmful effects in the environment.

CHROMIUM

SRS Seepage Basins

In 1975, non<u>radioactive</u> releases included about 270 and 5100 lb of chromium to F-Area and H-Area seepage basins, respectively (<u>Holcomb and Emslie</u> 1984). Data from trebler samplers in the H-Area effluent stream from October 1980 through October 1981 provide an average effluent concentration of 2200 ppb (addition to <u>Horton</u> 1974b).

SRS Well Water

Water samples from seven H-Area seepage basin wells were collected on November 10, 1981, and four contained concentrations less than 5 ppb. The other three samples had concentrations of 7, 16, and 16 ppb (addition to <u>Horton</u> 1974b).

Data reported in SRS environmental monitoring reports from 1984 through 1991 indicate F-Area and H-Area well water concentrations to be near or below the PDWS of 50 ppb (the PDWS was raised to 100 ppb in 1991) (Figure 20-9). An abnormally high concentration was measured in an H-Area well (HSB 68) in 1984 (1188 ppb), but subsequent analyses of water from this well have indicated concentrations less than 4 ppb. However, considerably higher concentrations have consistently been measured in other areas, particularly in the C-Area burning/rubble pit and D/TNX coal pile runoff basin areas (D-Area). Concentrations in D-Area groundwater have been as high as 2760 ppb (Cummins et al. 1990).

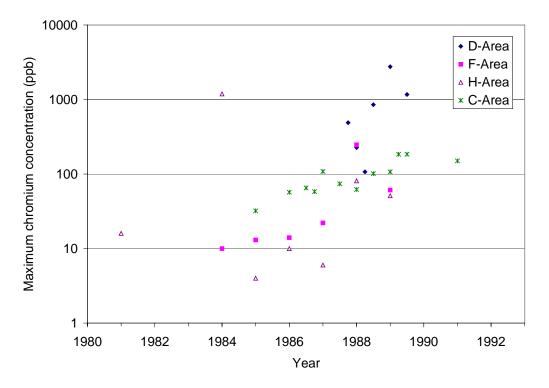


Figure 20-9. Maximum chromium concentrations measured in F-Area, H-Area, C-Area, and D-Area groundwater wells. Link to <u>tabulated data</u>.

Onsite Streams and Ponds and the Savannah River

Water

<u>Geisy and Weiner</u> (1977) measured chromium concentrations in Par Pond water collected between December 1974 and March 1976. The mean concentration for all samples was reported as 0.35 ppb and was described as characteristic of relatively uncontaminated lentic systems in the southeastern United States. Concentrations were determined by flameless atomization.

From 1984 through 1986, maximum measured chromium concentrations in Upper Three Runs, Four Mile Creek, Steel Creek, and Lower Three Runs Creek were reported as less than 10 ppb. In 1987, maximum measured concentrations in the same onsite streams were reported as less than 50 ppb. From 1988 through 1991, maximum measured concentrations in these streams were reported as less than 20 ppb and were generally indistinguishable from maximum concentrations for Savannah River water.

An April 1985 report (Lower 1985) provided mean chromium concentrations of <6 ppb in Savannah River water collected at RMs 155.5 and 157.5. In 1980, Savannah River water samples collected at six stations along the SRS boundary all had concentrations less than the 1 ppb detection limit, except one sample that had a concentration of 2 ppb (ANSP 1980). A September 1996 report (Westinghouse 1996) provided data for 36 samples (12 at each location) collected from the Savannah River between 1992 and 1994 at RMs 120, 150, and 160, which all had concentrations less than 7.5 ppb, the apparent LLD.

Water samples collected in 1987 from Four Mile Creek upstream and downstream of F-Area and H-Area seepage basins and from the seep area downgradient of F and H-Area seepage basins all had chromium concentrations less than 1 ppb (Looney et al. 1988). The authors concluded that the majority of chromium was sorbed to subsurface materials and that transport from both F and H-Area seepage basins was very slow.

Water samples were collected from the Four Mile Creek seepline in the vicinity of the F-Area and H-Area seepage basins in 1988 and 1989 (Haselow et al. 1990). Concentrations in water samples collected from the seepline in the vicinity of the H-Area seepage basins were less than 10 ppb (LLD) in 1988 and ranged from 2.1 to 3.4 ppb in 1989. Concentrations in water samples collected from seepline areas between the F-Area and H-Area were less than 10 ppb (LLD) in 1988 and ranged from less than 3 (LLD) to 4.3 ppb in 1989. Concentrations in water samples collected from the seepline in the vicinity of the F-Area seepage basins ranged from less than 10 (LLD) to 27 ppb in 1988 and from less than 3 (LLD) to 4.8 ppb in 1989.

Water samples were also collected from the Four Mile Creek seepline in the vicinity of the F-Area and H-Area seepage basins in July 1992. Concentrations were reported to be less than the LLD of 4 ppb at the F-Area seepline, Four Mile Creek stream water in the vicinity of the seepage basins, and in seepline and stream water collected upstream from the general separations areas. Water samples collected from the seepline in the vicinity of the H-Area seepage basins had concentrations below the 4 ppb LLD, except one that had a concentration of 13 ppb (an average of three measurements) and one that had a concentration of 4.4 ppb (an average of two measurements).

Sediment

Surface sediment samples were collected and analyzed for chromium from five locations in Four Mile Creek during 1987 (Mikol et al. <u>1988a</u>, <u>1988b</u>). Sample locations were Road C, Road A7, the Road A7 flood plain, the place where FMC enters the river swamp, and the mouth of FMC. The respective concentrations were 6, 5, 4, 3, and 7 ppm.

Sediment samples were collected from locations along the Four Mile Creek seepline in the vicinity of the F-Area and H-Area seepage basins and analyzed for chromium in 1988 and 1989 (Haselow et al. 1990). Concentrations in sediment collected from the seepline in the vicinity of the F-Area seepage basins ranged from less than 1 to 11 ppm (mean = 5 ppm, n = 9) in 1988 and from less than 0.6 to 26.2 ppm (mean = 12, n = 6) in 1989. Concentrations in sediment collected from less than 2 to 15 ppm (mean = 8 ppm, n = 7) in 1988 and from less than 0.6 to 34.4 ppm (mean = 14, n = 4) in 1989.

In October 1976, sediment box core samples were collected from the Savannah River at a location 18 km above the mouth (Goldberg et al. 1979). Concentrations ranged from 150 ppm in the 0–1-cm depth interval to 110 ppm in the 44–48-cm depth interval. The maximum concentration in the core was 260 ppm in the 16–17-cm depth interval.

<u>Winger and Lasier</u> (1995) collected sediment samples from 26 sites along the Savannah Harbor between RMs 9.5 and 23.0. Acid-digested samples were analyzed by inductively coupled plasma emission spectrophotometry. Chromium concentrations ranged from about 10–80 ppm (values were estimated from a figure).

As part of the Savannah River Integrator Operable Unit Study (Westinghouse 1996), several data sets were compiled to provide chromium concentrations measured in Savannah River

sediment from 1992 through 1994. One data set provided concentrations of 0.0193 and 0.0158 ppm for RMs 120 and 184, respectively. Another data set provided concentrations of less than 0.01 ppm for RMs 120, 150.7, and 160. These concentrations are more than 2 orders of magnitude less than concentrations measured in Four Mile Creek in 1987, 1988, and 1989 and four orders of magnitude less than concentrations measured in the Savannah River in 1976.

Chromium concentrations in both water and sediment samples collected from the SRS vicinity are certainly within the ranges of "background" concentrations and well below concentrations measured in contaminated areas compiled for these media by <u>Eisler</u> (1986). <u>Lower</u> (1985) reported a typical soil and crustal rock chromium concentration of 100 ppm. Several of the above studies reported sediment concentrations well below expected background concentrations, which calls into question the <u>accuracy</u> of the detection techniques for chromium.

Fish

Limited data are available for chromium concentrations measured in fish. Ten catfish and two suckers collected from the Savannah River along the SRS boundary in 1980 had mean concentrations of 1.4 and 0.7 ppm dry weight, respectively (<u>ANSP</u> 1980). Five-gram samples of dried muscle tissue were analyzed, and the apparent detection limit was 0.05 ppm. Samples were analyzed by atomic absorption spectrophotometry. For comparison, <u>Mathis and Cummings</u> (1973) reported chromium concentrations in fish from industrialized areas of the Illinois River ranging from 0.02 to 1.06 ppm dry weight.

In August 1985, fish were collected from the Savannah National Wildlife Refuge near Savannah, Georgia, and from the lower Savannah River and analyzed for chromium content (<u>Winger</u> et al. 1990). Concentrations ranged from 0.50 to 10.2 ppm dry weight (converted from wet weight, assuming 80% moisture). Aliquots of homogenized whole fish were analyzed, and the limit of detection was reported as 0.1 ppm wet weight or 0.5 ppm dry weight.

Ten predatory fish, 19 bream, and 12 catfish collected from the Savannah River in the vicinity of RM 150 from 1992 through 1994 had mean concentrations of 3.0, 0.86, and 2.35 ppm dry weight, respectively (Westinghouse 1996). Based on these limited data, concentrations of chromium in fish from the Savannah River in the vicinity of the SRS appear to have remained relatively stable from 1980 through 1992–1994.

Between December 1974 and March 1976, 35 bluegill, 35 blueback herring, 29 brook silverside, 50 golden shiners, and 40 chain pickerel were collected from Par Pond located on the SRS (Geisy and Wiener 1977). Mean chromium concentrations were 0.16, 0.09, 0.28, 0.19, and 0.15 ppm dry weight, respectively. Aliquots of acid-digested, dried whole fish were analyzed by flameless atomization, and the LLD was not specified.

In July 1990, fish were collected from six locations in Four Mile Creek and one location in Pen Branch (Loehle and Paller 1990). Fish were gutted, and the remainder of the entire fish was homogenized before analysis by EPA standard methods (i.e., atomic absorption spectroscopy). The detection limits were reported as 0.1 to 0.2 μ g g⁻¹ wet weight (ppm), depending on the fish weight. Assuming 80% moisture, this corresponds to a detection limit of 0.5 to 1.0 ppm dry weight. Mean concentrations ranged from 0.33 to 0.49 ppm wet weight (1.65 to 2.45 ppm dry weight). There were no apparent <u>spatial trends</u>, and the lowest mean concentrations were recorded for fish collected from Four Mile Creek in the vicinity of the F-Area and H-Area seepage basins.

Differences in chromium concentrations in fish collected from the SRS and the Savannah River are not evident. Based on the data that have been examined, there is little evidence to suggest that SRS activities have resulted in elevated chromium concentrations in fish.

Eisler (1986) reported that tissue levels in excess of 4.0 ppm dry weight should be regarded as presumptive evidence of chromium contamination. Winger et al. (1990) reported a maximum chromium concentration in fish collected from the Savannah River Wildlife Refuge, a few miles upriver from the mouth of the Savannah River, of 10.2 ppm. This provides some evidence of chromium contamination in the Savannah River, but there is no indication that this contamination has resulted from SRS activities. In addition, there is some concern about the <u>uncertainties</u> involved with the analysis of some types of biological and environmental samples. Collaborating laboratories have reported order of magnitude differences in measured chromium concentrations in standard bovine liver.

Ecological Aspects of Chromium

In general, fish accumulate chromium to the largest extent in organs such as the spleen, kidney, gall bladder, and gill tissue, while relatively little chromium accumulates in muscle tissue (Knoll and Fromm 1960; Phillips and Russo 1978). No biomagnification of chromium in food chains has been observed, and concentrations are generally highest at the lowest trophic levels (Eisler 1986). In general, chromium compounds have a low fractional absorption from the gut (EPA 1980). Eisler (1986) provides a very thorough review of the ecological and toxicological aspects of chromium in the environment.

In aquatic environments, chromium is virtually always found in the trivalent (+3) or hexavalent (+6) states (EPA 1980). Hexavalent chromium is more toxic than trivalent chromium because of its oxidizing potential and biologic membrane permeability. In addition, biological interactions with chromium involve reduction to the trivalent form and eventual coordination to organic molecules (NAS 1974). Consequently, consumption of fish will involve exposure to primarily trivalent chromium in the form that functions as an essential element in mammals. Most investigators agree that chromium is almost always in the trivalent state in biological materials, and that no adverse effects have been reported for human populations from exposure to chromium in this state through the diet (Eisler 1986). Chromium is also widely accepted as an essential trace element, and a "safe" acceptable daily intake of 0.175 mg d⁻¹ was reported in EPA (1980).

Conclusions Regarding Chromium

It is clear that some groundwater wells have contained water with chromium concentrations far exceeding the PDWS (50 ppb through 1990 and 100 ppb since 1991), particularly in the vicinity of the D-Area coal pile runoff basin. However, based on data reported from 1984 through 1991, there do not appear to be significant differences in chromium concentrations measured in onsite stream and Savannah River water, which have both been well below the PDWS and near or below detection limits. In addition, maximum chromium concentrations measured in water collected from the Four Mile Creek seepline downgradient from the F-Area and H-Area seepage basins have also been well below the PDWS.

Chromium concentrations measured in sediment collected from the Savannah River in 1976 were about 4 orders of magnitude greater than concentrations measured in the Savannah River in

1992–1994. Chromium concentrations measured in sediment collected from Four Mile Creek in 1987 were more than an order of magnitude less than in sediment collected from the Savannah River in 1976. Maximum concentrations measured in sediment collected from the seepline in the vicinity of F-Area and H-Area seepage basins in 1988 and 1989 were nearly an order of magnitude less than concentrations measured in the Savannah River in 1976. These data suggest a significant decrease in chromium concentrations in the Savannah River between 1976 and 1992– 1994, but without additional data, it is difficult to ascertain the contribution of SRS activities based on sediment concentrations. Additionally, several studies have reported sediment concentrations significantly lower than typical "background" concentrations.

Fish concentrations appear to have remained relatively stable in the Savannah River at locations in the vicinity of the SRS between 1980 and 1992–1994, and concentrations measured in 1985 in the Savannah River near the mouth appear similar to or greater than concentrations measured in the vicinity of the SRS. In addition, concentrations measured in fish collected from Four Mile Creek in 1990 are similar to or less than concentrations measured in fish collected from the Savannah River.

Based on limited data, SRS activities do not appear to have affected chromium concentrations in the waters of onsite streams or the Savannah River. Chromium concentrations measured in fish collected from onsite streams and the Savannah River also provide no evidence for a chromium source term from the SRS. Given the chromium concentrations measured in the various SRS vicinity media and the potential uncertainties associated with these measurements, there is little evidence to suggest elevated levels of chromium in any media resulting from SRS activities. Because chromium does not bioaccumulate significantly in edible portions of fish and trivalent chromium (the form found in fish tissues) is essentially nontoxic to humans, it does not appear to present a health concern to people who may regularly consume fish from the Savannah River.

TABULATED DATA USED TO PRODUCE THE FIGURES IN THIS CHAPTER

The various data summarized in this chapter are electronically compiled in one workbook that contains the figures depicted in this chapter as well as the tabulated data that were used to produce the figures. In this workbook, there is a separate worksheet for each figure and one worksheet that contains the tabulated data for all of the figures. These data can be accessed by clicking on the following hyperlink: <u>Ch20-Figure_data.xls</u>.

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