CHAPTER 17

RELEASES OF CHEMICALS TO AIR

ABSTRACT

This chapter discusses releases of chemicals to the atmosphere from Savannah River Site (SRS) facilities. Releases were determined using emissions estimates from the air emissions inventory, Operating Permit Application, Toxic Release Inventory; environmental and effluent monitoring data, process records and/or information obtained by interviewing SRS personnel. Releases from manufacturing and processing facilities, power plants, generators, open burning, construction and maintenance work were included in the release estimates. Large amounts of sulfur dioxide, nitrogen dioxide and particulates (ash) were released from seven coal-fired power plants. Thousands of tons of chlorinated solvents were released from the raw materials area (M-Area). Releases of mercury, lead, manganese, nickel, nitric acid, chromium, cadmium and hydrogen sulfide from the SRS were estimated. Release estimates are summarized in the tables and conclusions at the end of this chapter.

INTRODUCTION

We determined releases of chemicals to air at the SRS using several types of information, including the air emissions inventory; estimates in the SRS's Air Information Reporting System (AIRS) database; estimates made in support of the Title V Operating Permit Application submitted to the State of South Carolina in 1996; the Toxic Release Inventory (TRI); special stack monitoring or ambient air monitoring studies; and worker knowledge of processes, operations, and releases. Information obtained from interviews with current and former workers has been particularly important for understanding how chemicals were used, disposed of, and may have been released in the 1950s and 1960s. A limited amount of attention was given to chemical spills and releases to Site streams in reports from the 1970s. Most of the information and records we have found on chemical use and release pertains to operations after 1985. If we assume that the amounts and types of materials used and the processes did not change significantly over the years, then we can extrapolate this data back in time from the mid- and late-1980s.

Most of the release estimates are based on very limited information. The emissions estimates in the Air Emissions Inventory, the TRI and the Operating Permit Application are reported in units of tons per year. Throughout this chapter, amounts are given in tons, pounds, and kilograms (1 ton = 2000 lb and 1 kg = 2.2 lb), whichever units best facilitate comparisons.

Key Records and Resources Used to Reconstruct the Use and Release of Chemicals

There are many regulatory requirements for air pollution characterization and reduction, such as the Clean Air Act; the State of South Carolina's Air Toxics Rule; the Superfund Amendments and Reauthorization Act of 1986 (SARA), which require emergency planning and annual reporting of potentially hazardous chemicals; the 1970 National Emission Standards for

Hazardous Air Pollutants (NESHAPs) Program; and the Clean Air Act Amendments of 1990. Because of these requirements, the Site must submit to the State and the State must submit to the U.S. Environmental Protection Agency (EPA), emission inventories, operating permits, annual reports of toxic chemical releases to the environment, and chemical inventories—all of which have been useful to this study. The reports have only been required since the mid- to late-1980s, and data on the use, storage, and release of chemicals before this time were not common.

Several sources of information on air emissions were used to determine source terms. This section describes data found in the following recent reports on air emissions: (a) the air emissions inventory and the AIRS database maintained by the SRS to help prepare reports needed to comply with EPA and South Carolina Department of Health and Environmental Control (SCDHEC) regulations, (b) the Standard 8 and Standard 2 Air Pollutant Reports sent to SCDHEC to comply with operating and permitting regulations, (c) the Title V, Part 70 Permit Application submitted to the SCDHEC in 1996, (d) available calculational notebooks, worksheets, and other records used to derive the emissions in the AIRS database and the Part 70 Permit Application, and (e) the Toxic Release Inventory (TRI) reported to the EPA. Information in these reports and database may be the only information available on the potential release of some of the chemicals of concern. Although they pertain to operations after 1985, and in some cases, after 1990, the information may be applied to earlier time periods and has been useful for determining hypothetical maximum emissions estimates.

Air Emissions Inventory and AIRS Database

Following promulgation of the South Carolina Air Pollution Control Regulation for Air Toxic Pollutants (Standard 8) in 1991, the SRS began to conduct an air emission inventory for all facilities onsite. The inventory was intended to

- Help demonstrate compliance with the requirements of Standard 8
- Fulfill the requirements of the Air Toxics Rule promulgated by the SCDHEC
- Provide information, required by the State and EPA, on release points for air pollutants
- Account for sources of pollution
- Better characterize releases from Site processes.

The inventory includes information on each source, such as stack height, diameter, location, pollutant emission rate, production, and operating rate. Data collection forms (referred to by site personnel as the Air Emissions Inventory Worksheets) were used in this effort. Information from the forms was entered into the AIRS database. The initial air emissions inventory was finished in 1993, and it estimated air emissions for the years 1985 through 1991. Air emissions estimates for 1990 were used, along with air dispersion modeling, to demonstrate compliance with Standard 8. The Air emissions inventory has been updated annually since 1993. The air emissions inventory data for 1994 were used for the 1996 Part 70 Operating Permit Application (Westinghouse 1996a).

In 1985 and 1986, the EPA and the State environmental agencies conducted a comprehensive audit of the Site. They asked that all stacks, vents, and other discharge points for atmospheric emissions be identified for all areas. The AIRS database also fulfilled this requirement. The AIRS information goes back to 1985, a year when the last four reactors in use were still running and both canyons were operating. With time, the information in the database

has become more complete and more effort has been put into calculating the estimates, resulting in improved estimation methods. The estimates for recent years are considered to be more defensible (Faugl 1996a).

SARA Section 313 requires annual reporting of releases to all media of toxic chemicals with usage exceeding 10,000 lb y^{-1}. The emissions inventory and AIRS database was put in place at the SRS to

- Respond to SCDHEC requests for a air toxic emissions inventory
- Provide a basis for operating permits
- Estimate air emissions for SARA regulations and reporting
- Provide baseline estimates to evaluate emissions reductions.

The Site has put all of the emissions estimates used for the various reports just described in an ORACLE database called the AIRS database. The emission estimates for each year are compiled in the database. Several reports use the information in the database, but the estimates are not available in a hardcopy report. Estimates must be extracted from the database. We requested several database excerpts.

The database has space for four types of emission estimates:

- Uncontrolled actual emissions
- Uncontrolled maximum design capacity emissions
- Controlled actual emissions
- Controlled maximum design capacity emissions.

Uncontrolled emissions are theoretical emissions that might occur if pollution control equipment was not in place or not operating. Controlled emissions account for the pollution control equipment in place and working. The actual emissions are those predicted under normal operating capacities and times. Maximum design capacity emissions are theoretical for 24 hours a day, 365 days a year, 8760 hours a year operations. Of most interest for this study for determining a best estimate of a source term are the controlled actual and controlled maximum design capacity emissions. These reflect likely actual emissions under real or typical operating conditions and maximum theoretical emissions at full production capacity after reduction by any pollution abatement equipment. The uncontrolled maximum design emissions represent an unrealistic, extreme upper bound scenario. All of these emissions were calculated, rather than measured; however, some measurements for sulfur dioxide and nitrogen dioxide (opacity) have been used to corroborate the estimates. The database includes a code to reference how the estimates were calculated. The codes for the estimation methods were

01 EPA AP-42
02 EPA speciate
03 Engineering calculations
04 Material balance
05 Stack test data
06 Monitor—sampler data
07 EPA CHEMDAT7-LAND7
08 EPA SIMS Model
09 MSDS Data Sheet
10 Other.

Almost all of the estimates were calculated with method 03, engineering calculations.

After reviewing the air emission inventory forms and worksheets that show the fields of data potentially available from the AIRS database, *RAC* requested an initial search for process releases from any facility for the chemicals of concern. We asked for a search of the emissions for 1985, 1987, 1990, and 1992 and a printout of the following fields for benzene, cadmium, chromium, hydrogen sulfide, lead, manganese, mercury, nickel, nitric acid, nitrogen dioxide, sulfur dioxide, tetrachloroethylene, trichloroethane, and trichloroethylene: chemical (pollutant); source ID; building number; building name; source type; source description; form (solid, gas, liquid); controlled maximum; and controlled actual emissions in tons per year. Some of the information on the location of the source was sensitive, so the request was abbreviated to eliminate this information to expedite security review. For some chemicals, known emissions from a source, for example mercury from the 291-H stack, were not in the database, so a search for 1994 and 1995 emissions was done for these missing estimates. Although more emissions estimates have been calculated each year, not all of the emissions of interest for the historical dose reconstruction study have been estimated.

After examining these data, another request for database information was made for key emission points and sources. We asked for emission type (point, volume or fugitive); height aboveground; height above building, diameter (of vent, stack etc.); exit velocity; exit temperature; release height; continuous detection (monitoring in place); estimation method (key 1-10); raw materials (used in process); process rate; product; pollution abatement equipment data; and control device (key). Not all of this information was available for all of the emission points. The results of the AIRS database runs for each chemical (except sulfur compounds, which were grouped together) were given *RAC* document numbers. This report references database runs as Faugl 1996a, Faugl 1996b, Faugl 1996c, Faugl 1996d, etc. because Timothy Faugl, with the Environmental Protection Department at the SRS, conducted the database searches or arranged for them to be done by a subcontractor.

The AIRS database includes emissions from maintenance and fabrication shops, controlled burns, welding operations, batteries, combustion engines, compressors, and generators. The uncertainties associated with the total release estimates are large enough to justify subtracting from our analysis all the emission points that are not process related (such as minor maintenance operations, small emergency generators, portable grinders, or welders) or those that contribute little to the total emissions. Many sources of chemical releases are very minor and localized and these were not considered by *RAC*, for example, electric oven exhausts, paper shredders, painting stations, brush cleaners, paint rollers, small diesel pumps, and mobile air compressors.

A typical diesel engine will release lead, oxides of nitrogen, oxides of sulfur, benzene, arsenic, cadmium, chromium, manganese, mercury, nickel, and organic pollutants. Emissions estimates for some individual diesel engines were also made in the Title V Operating Permit Application. Worksheets from the M-Area Air Emissions Inventory indicate that emissions of sulfur dioxide, nitrogen oxides, arsenic, beryllium, cadmium, chromium, mercury, manganese, nickel, and benzene were calculated for generators using AP-42 emission factors (Radian 1992a).

In the case of nitrogen oxides and benzene, the emissions estimates from generators and other engines are some of the highest at the SRS. The most numerous sources of cadmium, chromium, mercury, and nickel emissions to the air were generators. The emergency generators are used in emergency power failure situations and most are usually started and run once or twice

a year and tested. Some are tested monthly or quarterly. Many are tested for about 1 hour each week to keep batteries charged. Generally, all emergency generators are run less than 100 hours per year. A few generators are the main power source for equipment, and some run continuously at a maximum of 8760 hours per year assumed for the estimates in the AIRS database. Emissions from generators are addressed in a section of this chapter called, "Diesel-powered Generators."

Most of the emissions points for metals were grinding, cutting, torch cutting, belt sanders, lathes, drilling, and other similar maintenance facility and machine shop operations. Estimates for releases of cadmium, manganese, mercury, and nickel were estimated for the H-Area and K-Area coal pile and transfer operations, and chromium and lead were included in estimates for the K-Area coal pile. Manganese releases were included for the D-Area coal pile. It appears that the contractor or Westinghouse Savannah River Company department responsible for the K-Area coal pile estimates provided the most comprehensive estimates. The K-Area coal pile releases included all of the metals, while the H-Area coal pile estimates included four metals, and the other coal piles included none or no emissions estimates were reported. Why other metal releases were not included for each coal pile is unknown.

Estimates of total emissions generally increased with time after 1985 because more processes were included in the inventory. For example, nickel emissions for 232-H included six processes in 1985 and eight in 1987 and 1990. All eight processes operated in 1985, but emissions were not estimated for metallography and cutting operations before 1987. In 1992, the number of emissions points reported more than doubled because release points were added from the vitrification process and there was an increased reporting of tanks, generators, and other sources.

Because different contractors may have been responsible for calculating emission estimates from different facilities or areas, similar processes may have different estimates and some emissions may be reported for one facility but not another. The emission estimates for F-Area and H-Area were developed by two different contractors. The pollution control equipment, maximum design rates, tank capacities, etc. should have been the same, but emission estimates were different. For example, the highest benzene emissions for 1985 were for the two paraffin tanks in the F-Canyon building. H-Area did not report such tanks. The highest emission for oxides of nitrogen in 1985 was the second uranium cycle discharge to the 291-F stack (an emission of 49.3 ton y^{-1}). No emission for oxides of nitrogen was listed for H-Canyon stack in 1985 or any H-Canyon processes except the diesel generators for the canyon exhaust fan house, two generators used in the HB-Line and the metal manufacturing processes.

Some of the processes and the locations of some of the emissions points are sensitive and they may not be identified specifically in this analysis; however, all of their emissions are included in the source term estimates for individual compounds. In the AIRS database, all of the emissions points at the SRS are given an identification number. For example, F-Canyon emission points are numbered 001–0059, for a total of 59 emission points for that one building, 221-F. The emission points include major points, such as the stack, vents and hood exhausts, and minor points, such as welding booths, grinding areas, and various tank and vessel vents. The pollution control equipment is described, for example scrubbers, high-efficiency particulate air (HEPA) filters, adsorbers, sand filters, and dust filters designed to remove particulates and oxides of nitrogen (Faugl 1996a). Almost all of the radionuclides and chemicals of concern were discharged from the stacks. For the purposes of this study and to avoid identifying emission sources that are sensitive, all of the emissions from the canyon building were combined. The SRS

emission point identification numbers and all of the sources going into each emission point were made available to *RAC*, but this information was not compiled here because of the sensitive nature of some of the information. For the purposes of this study and transport modeling and dose calculation in subsequent phases of the dose reconstruction, it should be sufficient to combine the emissions for each area to one or several points with appropriate release heights.

Data from the AIRS database runs were reviewed and useful information was compiled for each chemical of concern. We compiled a description of the types of emissions reported, the controlled maximum design emissions estimates, and the controlled actual emission estimates in tons per year for major sources from the AIRS database. This information is presented in tables for each chemical in this chapter.

Part 70 Operating Permit Application

The Title V Clean Air Act amendments promulgated in 1990 required that estimates of possible releases at maximum capacity be developed and the SRS was required to submit a permit application, under R61-62.70 Title V Operating Permit Program, Clean Air Amendments for Title III, Part 70 Regulations. The SCDHEC Air Pollution Control Regulation, Title V Operating Permit Program requires that all of sources of air pollution subject to the regulations have a permit to operate that assures compliance with all applicable regulations. To obtain a permit, the regulation requires that each source must submit a Part 70 Permit Application that identifies all sources of air emissions at the facility and identifies all state and federal regulations and requirements pertaining to the sources. Many of the regulations are quite general and have been applied to the Site as a whole rather than to individual facilities or sources (Westinghouse 1996a).

The State of South Carolina requires new SRS construction permits to include emissions information and modeling analysis for air pollutants. The emission rates are calculated based on process knowledge and EPA Air Pollution Emission Factors (AP-42) or other models available through the EPA. The maximum potential emission rates used for the dispersion modeling are based on maximum estimates of operating capability based on process design capabilities while operating within permit restrictions. Some of the modeling for metal emissions has been done using actual operation times and emission rates rather than potential maximum values.

The permit currently on file for the SRS was prepared in March 1996 in 23 volumes with three additional binders of amendments from 1997 (Westinghouse 1996a, 1996c, 1997c). This document is kept by the Environmental Protection Department in 742-A. We reviewed these binders and photocopied sections relevant for Phase II of the project.

The SRS developed an emission source identification system for the air emissions inventory. Point sources, volume sources, and area sources were identified. Exhaust points, sources, and pollution control devices were numbered. Fortunately, the same codes were used in the air emissions inventory and the Part 70 Operating Permit Application. The identification code and procedure for implementing the identification system was included in Chapter 5 of the permit, which *RAC* photocopied. Some of the information about process throughputs and concentrations of chemicals is currently sensitive with respect to national security and was not photocopied as a part of the application or worksheets supporting it. *RAC* researchers with the appropriate clearance did review this and other classified information relevant to the dose reconstruction project.

Title V of the Clean Air Act amendments require operating permits that detail the emission rates of regulated pollutants, describe fuels and materials use, emission points, control equipment, monitoring equipment, stack or release point parameters, area sources, and fugitive sources. The Criteria Pollutants (nitrogen oxides, sulfur dioxide, ozone, lead, and particulates) are subject to the National Ambient Air Quality Standards (NAAQS) and were addressed in the Standard 2 report. Hazardous air pollutants regulated under the 1970 NESHAPs Program, such as asbestos, beryllium, and mercury were addressed in the Standard 8 Report (Westinghouse 1993a). These reports are described in more detail in the next section of this chapter.

The Part 70 Operating Permit Application included large sections of air emissions inventory-derived emissions calculation sheets that list the approach, assumptions involved, input data, and emissions for processes (such as abrasive cleaning, bulk material handling, cutting, grinding and metal fabrication, diesel combustion, open burning, tanks and vessels, and welding). Calculations associated with many of these processes are important for establishing emission estimates for the chemicals of concern for the dose reconstruction. Those calculations used to establish estimates for emissions of the chemicals of concern are discussed in the section for each chemical.

The permit application may also have information on the design capacity of process equipment; the major raw material and quantity used; and the product for individual process source, operating schedule and production rate, stack height, diameter, distance to the plant boundary, control equipment, and maximum uncontrolled and controlled emissions estimates for NAAQS pollutants and Hazardous Air Pollutants or Air Toxics. Monitoring devices and regulatory requirements and compliance status are also given if applicable.

The assumptions and values used to calculate the emission estimates were described in the Title V Operating Permit Application and accompanying material. The calculations were based on a review of process flowsheets, safety analysis reports, engineering notes, and interviews conducted in 1984, 1985 and 1986. For example, the F-Canyon Purex process dissolver and head end were evaluated for the permit based on interviews with F-Area engineers, historical process data, abatement devices and their efficiencies, stoichiometric calculations, and characteristics of the fuel dissolved. In most cases, the information used for the estimates appeared to be more detailed than any *RAC* could collect in 1997; therefore, we consider these data to be the best available for estimating releases. The assumptions about operations, throughputs, volumes, and usage seem conservative. The actual estimates are likely to be upper bound rather than central or best estimates.

Included in the permit, for most sources, were air pollution control equipment forms that include efficiency estimates, gas flow rate, pressure drops, gas temperature, and description of the unit. These data were used by the Site and contractors to estimate the controlled emissions. The information does not indicate when the equipment was first put into place.

After inquiring about where to find supporting documentation and calculations for the AIRS estimates, we were advised that similar, if not identical, methods were used by the Facilities and the Environmental Protection Departments to calculate emissions for the Title V Part 70 Air Permit Application.

Generally, these records were called Air Emissions Inventory Data Sheets, Worksheets, or Supporting Information. Most of these records have been kept in the Environmental Protection Department at the SRS. Calculations that the facilities may have used to make the estimates may have been submitted as worksheets and supplemental information to the information submitted for the AIRS database and the Operating Permit Application. The worksheets were sometimes

submitted with the estimates to the Environmental Protection Department, but often, supplemental information and worksheets were kept at the facility. Environmental Protection Department personnel thought that once their contractor had entered the annual AIRS information into the database, the supplemental data were usually sent to be microfiched and then to central records. Most the information used for this study was found in the Environmental Protection Department records. A few pertinent files were found in central records, and records that were kept at the facilities were also photocopied for this study.

The permit application also included useful descriptions of some of the most important processes and the air exhaust and liquid effluent discharges associated with them. Chapter 15 summarizes the useful process or facility descriptions. Many of the storage tanks addressed in the permit application were waste tanks and process chemical tanks associated with new facilities, such as the consolidated incineration facility, Defense Waste Processing Facility (DWPF), in-tank precipitation, saltcrete, and others. These processes are subject to air quality regulations designed to protect the offsite public.

Standard Two and Standard Eight Reports

SCDHEC Bureau of Air Quality Control promulgated Operating and Construction Permits Regulations in June 1991. This health-based regulation established maximum allowable ambient air concentrations at the facility boundary in micrograms per cubic meter for 256 identified pollutants. To comply with this rule, the SRS submits air emission source information and modeling input/output data and maintains the air emissions inventory and the AIRS database for all potential criteria and toxic air pollutant emission sources. The AIRS identified 138 Standard 8 air toxics with the potential to be emitted. Emissions calculations were based on process knowledge, EPA emissions factors (AP-42), and other EPA or vendor-developed models. Bowman's Industrial Source Complex-Short Term II (ISC-ST II) dispersion model was used to demonstrate whether any of the identified air toxics have compromised air quality standards. The first report submitted to comply with the regulation, (which was also the most recent report as of 1997), was sent to SCDHEC in 1993 and was based on the 1990 air emissions inventory data and 1991 meteorological data. The maximum emissions were based on maximum design capabilities or maximum potential while operating with permit restrictions in place. None of the air toxics concentrations modeled exceeded the standards. The modeling results showed that the SCDHEC standard boundary concentration would not be exceeded by maximum potential emissions from the SRS. However, the potential emissions for two of the criteria pollutants could be in excess of the air quality standards. Using maximum values, the modeled concentrations of sulfur dioxide and nitrogen dioxide exceeded the standards at the Site boundary near D-Area and TNX. The largest contributing source of emissions was predicted to be the D-Area powerhouse boilers. Minor exceedances were also predicted for the A-Area boundary for the 3-hour sulfur dioxide standard (Dukes 1993; Westinghouse 1993a).

The Environmental Protection Department staff submitting the report to SCDHEC believed that the exceedances were due to extremely conservative approaches being used in the modeling analysis. They planned to remodel for the standards using more accurate operating data and system configurations. They also said they planned to develop a control strategy plan for the D-Area powerhouses (Dukes 1993).

Table 17-1 lists the air pollution standard, estimated concentration in air at the Site boundary, and the percentage of the standard this concentration represented for the chemicals of concern for this study.

Table 17-1. Air Pollution Standards and Concentrations Predicted by Air Dispersion Modeling at the SRS boundary, in 1993, for Air Toxics and Criteria Pollutants[a]

Chemical	Maximum allowable concentration set by SCDHEC ($\mu g\ m^{-3}$)	Concentration predicted at the Site boundary ($\mu g\ m^{-3}$)	Percent of the standard
Air toxics			
Chlorine	75.0	7.63	10.17
Nitric acid	125.0	50.97	40.77
Trichloroethylene	6750.0	6.43	0.10
Hydrogen sulfide	140.0	0.20	0.14
Tetrachloroethylene	3350.0	2.0	0.06
Aldicarb	6.0	.007	0.12
Benzene	150.0	31.71	21.14
Cadmium	0.25	0.00028	0.11
Hydrazine	0.50	0.0018	0.36
Manganese	25.0	0.82	3.29
Mercury	0.25	0.01	5.57
Nickel	0.50	0.27	54.21
1,1,1-trichloroethane	9550.00	80.83	0.85
Criteria pollutants (standard)			
Sulfur dioxide (3 hour)	1300	2319.06	178.39
Sulfur dioxide (24 hour)	365	1039.10	284.69
Sulfur dioxide (1 year)	80	75.21	94.02
Nitrogen dioxide (annual)	100.0	125.41	125.42
Lead (quarterly mean)	1.50	0.0015	0.10

[a] Source: Dukes (1993).

The modeling results predicted that the 3 and 24-hour standards for sulfur dioxide and the annual standard for nitrogen dioxide could be exceeded. The criteria pollutant with the largest potential offsite impact was sulfur dioxide, modeled to be 289.69% of the maximum 24-hour average Site boundary concentration at maximum operations.

Plans Applicable to Chemical Releases

The Best Management Practices Plan was required by the State of South Carolina, which administers the National Pollutant Discharge Elimination System (NPDES) program in South Carolina, and regulatory requirements of the Federal Clean Water Act. The plan was required to "identify and control the discharge of hazardous and toxic substances listed in 40 CFR Part 122"

(Westinghouse 1997a). The plan has been maintained by the Environmental Protection Department in 742-A. It contained potential spill sources for each area and listed the chemical, department, tank, building, outfall, and equipment to which it is related. It also described the quantity and secondary containment that was in place (Westinghouse 1997a).

A Spill Prevention Control and Countermeasures Plan was also required for identification and pollution prevention measures for oil facilities at the Site. This document characterizes polychlorinated biphenyl (PCB) oils in transformers onsite, as well as non-PCB oils. It lists the underground and aboveground fuel and oil tanks, tank trucks, and pipelines that store oils, fuels, and solvents. It also describes liners, basins, concrete pads, and other secondary containment measures in use. Outfalls are listed and drawings of the surface water flow, basins, and facilities were included for some of the areas. The Spill Prevention Control and Countermeasures Plans for both 1987 and 1997 (Graham et al. 1987; Westinghouse 1997b) were reviewed and entered into the Phase II document database.

From these plans, the total amount of chemicals, the total number of tanks, and volume of a chemical could be compiled. The plans are also a relatively condensed source of information about which areas, processes, and facilities are associated with which NPDES outfalls. Data on the storage of toxic chemicals could also be derived from inventories, such as those taken for the SARA Title III reports, which we used to select chemicals of concern using methods described in Chapter 16.

Toxic Release Inventory

From 1987 to 1995, the TRI reported to the EPA and SCDHEC included the pounds of benzene, lead, manganese compounds, nitric acid, and 1,1,1-trichloroethane released per year from the SRS (Westinghouse 1996b). It is likely that in years with no amount reported some amount below the reporting limit was released. Release estimates reported in the TRI are summarized in the sections on each chemical that follow.

CHEMICALS RELEASED TO AIR

Ammonia

Ammonia was used onsite but not in sufficient quantities to result in a screening ratio greater than 1. Like sulfur dioxide and the oxides of nitrogen, ammonia was a product of the dissolving processes at the canyons, TNX operations, and Fuel Production Facility processes and was released from process stacks. Aluminum dissolution in sodium hydroxide can produce hydrogen gas, a serious explosion hazard, so sodium nitrate was added to the reagents producing ammonia and nitrate rather than hydrogen. About 0.167 kg of ammonia was produced per kilogram of aluminum dissolved. A large percentage of the ammonia (50–80%) could remain in solution or condense before the gas was exhausted, depending on the temperature of the off-gas system. The total ammonia released was estimated to be about 0.050 kg NH_3 kg^{-1} of aluminum dissolved (Allender 1985). Ammonia is irritating but is relatively nontoxic and would not be expected to have been a concern offsite.

Ammonium Nitrate

Ammonium nitrate flakes or spalls were released to the air from the stacks in F-Area. These were of concern because they caused radioactive contamination of sidewalks and other surfaces in F-Area. Sodium hydroxide was used in F-Area to dejacket (remove the cladding) from slugs. This reaction gave off ammonia (NH_3), which could combine with nitric acid fumes from other parts of the process and result in a precipitate of ammonium nitrate (NH_4NO_3). This precipitate adhered to the inside of the stack and was jarred out periodically to result in the 'spalls' on the sidewalk. The precipitate was water-soluble, so washing the stack with water from time to time helped remedy the problem. A 1957 monthly report says that solid particles discharged from the F- Area stack during August and September were principally ammonium nitrate and mortar, carrying ruthenium and plutonium activities and that flushing the stack with water removed essentially all of the ammonium nitrate (Du Pont 1957a). The wash water was probably transferred to a sump. Sometime after 1962, the ammonia and dissolving effluent was separated by the addition of two small stacks that run along the main stack. The ammonia was discharged out the small stacks and the rest of the dissolving/nitric acid process fumes were exhausted up the large stack (Pickett 1996). Ammonium nitrate was also periodically removed from the hot and warm canyon process vessel vent filters. A monthly report from 1976 described the removal of ammonium nitrate canyon process vessel vent filters after a 28-month operating period. A total of 4900 kg of ammonium nitrate was removed during two flushes of each filter. The authors expressed concern that ammonia in waste tanks from these flushes might reach explosive limits (Du Pont 1976). The primary concern with the ammonia nitrate flakes that came out of the stack was their radioactivity. This is addressed in Chapter 4.2, in the discussion about releases of beta emitters.

Benzene

Gasoline and volatile solvents, like xylene and toluene, contain benzene. Benzene was released from gasoline tanks, gasoline transfer equipment and tanks, and equipment for other solvents and fuels used at the SRS.

Most of the emissions for benzene in the AIRS database were for the DWPF, which is not being considered as a part of this study because it began operations in 1990. Research and development for the DWPF was conducted at TNX through the 1980s, and this testing also resulted in the release of benzene, which was included in our estimates. The Standard 8 modeling results submitted to SCDHEC in 1993 stated that, in 1991, benzene was released from sources in all of the areas at the SRS. The maximum 24-hour average Site boundary concentration was calculated to be 31.7 $\mu g\ m^{-3}$, well below the ambient air standard of 150 $\mu g\ m^{-3}$ (Westinghouse 1993a).

Emission estimates for benzene in the AIRS database included those from 10 waste storage tanks, each emitting less than 10^{-6} ton y^{-1}. Many gasoline tanks, diesel fuel storage tanks, and underground fuel tanks were listed with emissions ranging from less than 10^{-6} to 3.8×10^{-3}. Benzene emissions were also calculated for gasoline generators, diesel generators and emergency generators (Faugl 1996b). Some of the larger emissions estimates are listed in Table 17-2.

Some of the additional emissions noted in 1990 were for operations at the vitrification plant. Numerous organic liquid storage tanks were listed with small emissions. Emission estimates for

A-Area waste tanks were less than 10-6 ton y^{-1}. Waste storage tank purges were listed but were blank except for one. Waste storage tank number 48 in H-Area had a maximum emission estimate for tank purges of 2.65 lb h^{-1}. No ton per year values were given and how often the tank was purged is unknown. If we assume that the tank was continuously purged, as much as 11.6 ton y^{-1} may have been released from this tank. The highest benzene emissions for 1985 were from the two paraffin tanks in the F-Canyon building. H-Canyon did not report such tanks. The next highest emission was for the F-Area seepage basin, followed by the diesel generators in the generator house in H-Area, Building 254-05 with actual emission estimates of 9.45×10^{-2} ton y^{-1} and 9.36×10^{-2} ton y^{-1} (Faugl 1996b).

Benzene emissions were calculated for 18 waste storage tanks; 31 gasoline, diesel, and other fuel tanks; 2 paraffin tanks; 48 generators 2 diesel pumps; 5 painting and related activities; and 2 tanker truck loading stations (Faugl 1996b). If we assume that gasoline, diesel fuel, paraffin, and organic solvent use in 1987 was similar to uses in years past, we could apply the 1987 totals to the entire time period and estimate that 2.3 ton y^{-1} actual and 17.8 ton y^{-1} maximum of benzene may have been released. This provides an estimate of 87 ton actual and 676 ton maximum of benzene emissions from 1952 to 1989. We would expect that more vehicles would have been in use in 1987 than in earlier years and that using the 1987 values would tend to overpredict the fuel use and resulting emissions. It may be that use in the 1950s and 1960s was more careless and more care to prevent spills, worker inhalation, and transfer errors was taken in the 1970s and 1980s. Fuel efficiency may also have been important for consumption during the energy crisis in the 1970s. More information on fuel use can be found in the section about gasoline in this chapter.

The Part 70 Operating Permit Application contained emission estimates for almost all of the diesel and gasoline fueling stations as well as storage tanks thought to emit volatile organic compounds (VOCs). The air quality permit gave example calculations for gasoline tanks and gasoline and fuel-dispensing stations, which were generally considered exempt because of insignificant activity, based on emission levels. A maximum emission rate for a dispensing station with four pumps was reported to be 0.0166 ton y^{-1} for benzene. Maximum emissions estimates for a 5000-gal underground gasoline fuel tank was 0.0215 ton y^{-1} for benzene (Westinghouse 1996a).

Two identical aboveground gasoline tanks at 715-6A, with a capacity of 10,000 gal each, are used to store gasoline for the entire Site. These tanks have been used to fill tanks at the gasoline station and to fill Site gasoline trucks. Gasoline vapors are continuously released from the tank vents. Because of the large volume of the tanks, the maximum uncontrolled emissions estimates for the transfer pump are high and would exceed air toxics limits. However, the actual throughput was about 2000 gal of gasoline per year, which corresponds to what the air quality permit terms as “insignificant air emissions of all components.” The actual emissions estimate for benzene from both tanks totaled 4.13×10^{-2} ton y^{-1} (Westinghouse 1996a). We can multiply this by 38 years for the years 1952–1989 for a total estimate of 1.6 ton for the entire time period.

Table 17-2. AIRS Database Emissions Estimates for Benzene for 1985, 1987 and 1990[a]

Year Source Description	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985 Total	**1.16×10^{1}**	**1.50**
F-221 Canyon, N-Paraffin Tank 21	4.0×10^{-1}	4.0×10^{-1}
F-221 Canyon, N-Paraffin Tank 22	4.0×10^{-1}	4.0×10^{-1}
F-Area Tank Farm degreaser	2.50×10^{-3}	2.50×10^{-3}
G F-Area Seepage Basin	2.14×10^{-1}	2.14×10^{-1}
G Old Sanitary Landfill	1.21×10^{-2}	1.21×10^{-2}
S Area Organic Waste Storage Tank Building 430	3.00×10^{-1}	0
T-Area Building 672, DWPF Semiworks Building Process tank	5.0	2.70×10^{-3}
T-Area 678 Chemical Semiworks Building, Organic Storage Tank A-3	1.00×10^{-3}	1.00×10^{-3}
T-Area 678 Chemical Semiworks Building, Organic Storage Tank	1.00×10^{-3}	1.00×10^{-3}
E 643007 burial ground, 643-7E buried waste	1.0×10^{-6}	1.0×10^{-6}
T Pilot Plant building incinerator	1.86×10^{-4}	2.33×10^{-7}
1987 Total	**1.78×10^{1}**	**2.29**
F-221 Canyon, N-Paraffin Tank 21	4.0×10^{-1}	4.0×10^{-1}
F-221 Canyon, N-Paraffin Tank 22	4.0×10^{-1}	4.0×10^{-1}
F-Area Tank Farm degreaser	2.50×10^{-3}	2.50×10^{-3}
G F-Area Seepage Basin	2.14×10^{-1}	2.14×10^{-1}
G Old Sanitary Landfill	1.21×10^{-2}	1.21×10^{-2}
S Area Organic Waste Storage Tank Building 430	3.00×10^{-1}	0
T-Area Building 672, DWPF Semiworks Building Process Tank	5.0	2.70×10^{-3}
T-Area 678 Chemical Semiworks Building, Organic Storage Tank A-3	1.00×10^{-3}	1.00×10^{-3}
T-Area 678 Chemical Semiworks Building, Organic Storage Tank	1.00×10^{-3}	1.00×10^{-3}
E 643007 burial ground, 643-7E buried waste	1.0×10^{-6}	1.0×10^{-6}
T Pilot Plant building incinerator Building 667	1.86×10^{-4}	1.79×10^{-6}
Naval Fuels Glove Boxes, Building 247	1.50×10^{-1}	1.50×10^{-1}
1990 Total	**1.64×10^{1}**	**2.06**
Open Burning Fire Training Pit #1, in D-Area, fire fighting simulator	8.92×10^{-4}	1.25×10^{-4}
F-221 Canyon, N-Paraffin Tank 21	4.0×10^{-1}	9.0×10^{-2}
F-221 Canyon, N-Paraffin Tank 22	4.0×10^{-1}	9.0×10^{-2}
F-Area Tank Farm degreaser	2.50×10^{-3}	2.50×10^{-3}
G F-Area Seepage Basin	2.14×10^{-1}	4.22×10^{-3}
G Old Sanitary Landfill	1.21×10^{-2}	1.21×10^{-2}
S Area Organic Waste Storage Tank Building 430	3.00×10^{-1}	0
H-Area Seepage Basin	1.85×10^{-10}	5.51×10^{-12}
T-Area Building 672, DWPF Semiworks Building Process tank	5.0	8.20×10^{-3}
T-Area 678 Chemical Semiworks Building, Organic Storage Tank A-3	1.00×10^{-3}	1.00×10^{-3}
T-Area 678 Chemical Semiworks Building, Organic Storage Tank	1.00×10^{-3}	1.00×10^{-3}
T Pilot Plant building incinerator	1.86×10^{-4}	1.79×10^{-6}

[a] Source: Faugl (1996b).

[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Purges from waste tank 22, a 1,300,000-gal tank installed in 1962, resulted in the release of benzene. Although some measurements were said to have been taken, they were not included in the worksheets and no report or reference to them could be found. The maximum emission rate for the tank purge was calculated to be 0.044 ton y^{-1}. The tank was permitted to release an annual average of 0.01 lb h^{-1} of benzene. It is unclear from the air permit forms whether other waste tank purges also result in benzene releases. The total VOCs released from the tanks was compiled for the air emissions inventory, and this value may include benzene (Westinghouse 1996a; Faugl 1996b). We can estimate that at a rate of 0.044 ton y^{-1} for the 28 years from 1962–1989, the total benzene emissions from regular purges of this tank would be a maximum of 1.2 ton.

The 760-2G diesel fuel dispensing station was included in the permit application. Fugitive emissions of benzene had estimated emissions rate of 1.19×10^{-2} ton y^{-1}. Estimates for the 620-G diesel fuel station fugitive emissions were 1.44×10^{-2} ton y^{-1} for benzene. Emission estimates for xylenes and toluene were similar. The estimates involved worse case assumptions of continuous emissions from seals, valves, and flanges. Benzene was assumed to be 6% of the total VOCs in diesel fuel and 7% of the total in gasoline. Pumps were assumed to operate at maximum capacity, and lines were assumed to be filled with fuel at all times. Emissions for the gasoline refueling station were 1.90×10^{-2} ton y^{-1} for benzene for each of the gasoline dispensing stations 715-1G and 715-2G (Westinghouse 1996a).

Benzene emissions from process-related operations in 1985 and 1987 included 0.4 ton y^{-1} from the F-Canyon building, 2.50×10^{-3} ton y^{-1} from the F-Area tank farm, 0.214 ton y^{-1} from the F-Area seepage basins, and 0.012 ton y^{-1} from the sanitary landfill (Westinghouse 1996a). These are relatively small amounts compared to the amount probably released from gasoline and fuel and stations.

The actual emissions estimate for the 200-H emergency power generator, assuming 2080 hours of operation each year, was 6.46×10^{-5} ton y^{-1} for benzene (Westinghouse 1996a). Information in the K-Area Air Emission Inventory Calculation Procedures Notebook, prepared by Radian in 1992 for the Air Emissions Inventory, included a computer printout of a speciation report for VOCs emitted from the 184-K powerhouse boilers (Radian 1992b). It is not clear if releases of the compounds were measured or estimated but no concentration data were provided. The design maximum emission for benzene was calculated to have been 0.17 ton y^{-1}, and the actual emission was 0.075 ton y^{-1} in 1988 based on the amount of coal burned (Radian 1992b). The air quality permit application estimated that the two 784-A coal-fired stoker boilers burned about 8500 ton of coal per year each and released a maximum total of 2.27×10^{-2} ton y^{-1} of benzene (Westinghouse 1996a). Estimates for benzene from coal burning were not included in the AIRS database information. If the air permit calculation for A-Area boilers is applied to coal burning Site-wide, then an estimate of 0.68 ton y^{-1} benzene corresponds to burning 500,000 ton of coal per year, which was the amount reportedly burned in the early and mid- 1970s. The emissions sources reported in the AIRS database for F-Area and H-Area should be similar, but F-Area included the canyons, seepage basin, and paraffin tanks, while H-Area included generators and the seepage basin. The F-Area emissions totaled about 2.04 ton y^{-1} maximum, while H-Area emissions totaled about 6.5×10^{-5} ton y^{-1}. The emissions reported for the F-Area seepage basin were 9 orders of magnitude greater than those estimated for the H-Area seepage basins. If we assume that all of the sources in H-Area were also in F-Area, then maximum emissions of about 2.04 ton y^{-1} should apply to both areas. Fuel facilities tank emissions, including purges and waste

areas such as the sanitary landfill, totaled about 0.14 ton y^{-1}. Totaling the individual estimates for the largest sources reported by the AIRS database in 1985, 1987, or 1990 totals 4.2 ton y^{-1}.

From 1987 to 1995, the TRI that was reported to the EPA and SCDHEC included estimates of the pounds per year of benzene released from the SRS (see Table 17-3).

Table 17-3. Benzene Release from the SRS (1989–1995)

Year	Air emissions (lb y^{-1})	Ton y^{-1}
1989	1590	0.79
1990	2850	1.42
1994	5878	2.94
1995	3000	1.50

It is likely that in years with no amount reported, some amount below the reporting limit was released (Westinghouse 1996b). It is important to recognize that automobile and truck traffic, refueling, refinery operations, and many industrial operations also release benzene in similar quantities. The benzene released from the SRS historically has not been the result of a special process or large-scale use. Most has come from fueling and engine use.

In summary, the AIRS database actual emissions estimates seem to range from 1.5 to 17.8 ton y^{-1}; the TRI estimates range from 0.79 to 2.94 ton y^{-1}. Emissions from coal burning were probably less than 0.68 ton y^{-1}. Taken together, the total maximum benzene emissions for the entire Site in the late 1980s from the sources described above were likely to have ranged from 1.8 to about 18 ton y^{-1}. If we assume that benzene releases from 1952–1989 were similar to the values estimated for 1985–1990, then a total benzene release for SRS operations from 1952–1989 might be estimated between 68 and 684 ton. The highest maximum release total would correspond to 684 ton for the entire period. The central value is more likely to be between 60 and 200 ton for the period from 1952–1989.

Although there was more than one available estimate for benzene released from the Site, the range of 68 to 684 ton over the 38-year operating period spans only one order of magnitude and is probably quite reasonable given the available information. Uncertainty calculations would not offer any more detailed information on benzene, and it is difficult to measure uncertainty in estimating historical releases from current data. For these reasons, uncertainty calculations for benzene were not made.

Cadmium

Inhalation of cadmium can cause lung cancer. Cadmium was not used in the F-Area, H-Area, A-Area or M-Area processes. However, cadmium was found to be elevated at the Four Mile Creek seepline and in the sediment of the M-Area settling basin. The source is unknown. Evidence of cadmium release to the air from plant processes was not found.

Cadmium has been released from the combustion of fuel and coal. The AIRS database contained emission estimates for cadmium from 41 emergency and other diesel generators and pumps and a variable number of welding and brazing operations. Cadmium emissions from the coal storage piles in H-Area and K-Area were also calculated for the AIRS database (Faugl 1996c). Table 17-4 contains the total cadmium emissions reported in the AIRS database.

Table 17-4. Total Cadmium Emissions Reported in the AIRS Database

Year	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1985	5.83×10^{-3}	4.97×10^{-4}
1987	5.96×10^{-3}	4.71×10^{-4}
1990	6.38×10^{-3}	3.48×10^{-4}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Emissions estimates for individual sources were provided in Table 17-5. The estimates were the same for the three years examined. The estimates for H-Area and K-Area were calculated using conservative assumptions.

Table 17-5. Cadmium Emission Rates for 1985, 1987, and 1990

Source description	Maximum (ton y^{-1})	Actual[a] tons (y^{-1})
H-Area powerhouse Building 284; coal storage pile	1.70×10^{-4}	1.0×10^{-5}
H-Area powerhouse ash sluice sump	1.45×10^{-5}	3.16×10^{-6}
K-Area coal pile	5.40×10^{-6}	5.40×10^{-6}
K-Area coal storage runoff basin	5.40×10^{-6}	5.40×10^{-6}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

The highest release estimated for cadmium in 1985, 1987, and 1990 was 1.35×10^{-4} actual ton y^{-1} from the H-Area diesel house diesel generator, followed by 2.0×10^{-5} for each of eight diesel generators in K-Area engine house 108001 and 108002 (Faugl 1996c). Emissions from the powerhouse from coal combustion were not given, and emissions from D-Area powerhouse coal and ash handling and burning were not included. We assume that emissions from D-Area coal pile and ash basin would have been higher than for H-Area or K-Area because more coal was stored and burned and more ash was created and disposed of in D-Area.

Actual emissions estimates in the operating permit application for metals from the fuel oil-fired package boilers in K-Area included cadmium with, 2.04×10^{-4} ton y^{-1} (Westinghouse 1996a). The coal crushing operation at 784-A was also evaluated for the air quality permit. No data about the cadmium content of the coal burned were found. The air quality permit application, using AP-42 values, estimated that the two coal-fired stoker boilers in 784-A burned 8500 ton y^{-1} of coal each and released a total of 6.25×10^{-3} ton y^{-1} of cadmium (Westinghouse 1996a). If 6.25×10^{-3} ton of cadmium was produced from burning 17,000 ton of coal, then burning 500,000 ton Site-wide may have produced 0.184 ton (367 lb or 167 kg) of cadmium each year. Releases from coal burning dominate the emissions.

If we assume combustion engines were used the same amount in past and recently, then the average of the 3 years AIRS database totals about 6.05×10^{-3} ton y^{-1} maximum and 4.38×10^{-3} ton y^{-1} actual. When we add the 0.184 ton y^{-1} cadmium produced by coal burning during the

maximum coal burning year (1972), we estimate a total of approximately 0.19 ton y^{-1} (380 lb or 172 kg) of cadmium were released each year. The uncertainty in this estimate is very large. We do not know how the coal burned in A-Area in 1994 relates to the coal burned throughout the Site in earlier years. We do not know how much coal was burned before 1972 or the cadmium content of the coal. We do not know how many generators and other small engines were used in the past compared to their use in 1985, 1987 and 1990. The estimates in the permit and the AIRS database, on which this estimate is based, are conservative so our estimate likely overestimates the release. The available release estimates, however, are all point values. Calculating uncertainty from these values would not be useful, and we have little other information to support ranges of releases. Therefore, uncertainty was not calculated for cadmium. Cadmium releases from the SRS to surface water from coal and ash seem to be more worthy of concern than cadmium releases to air. Releases to surface water are discussed in Chapter 18.

Chlorinated Solvents

Three solvents were used in large quantities at M-Area and in moderate amounts at other facilities at the SRS and are evaluated in this phase of the study: tetrachloroethylene, trichloroethylene, and 1,1,1-trichloroethane. Tetrachloroethylene is also called perchloroethylene, Perc, Perclene® and PCE. Trichloroethylene is also called Trike, Triclene®, and ethylene trichloride and is often abbreviated as TCE. Trichloroethane is abbreviated TCA and is also called methyl chloroform. Abbreviations for the solvents have varied over time and were different in different Site reports. Care must be taken in interpreting tables where TCE has been used to refer to both trichloroethylene and trichloroethane. To avoid any confusion in the text of this report, these solvents will not be abbreviated.

Trichloroethylene was used from startup in 1952 until 1962 in Building 313-M and until 1970 in Buildings 320-M and 321-M. Tetrachloroethylene was used from 1962 in Building 313-M and from 1970 in Buildings 320-M and 321-M. In 1979, tetrachloroethylene was no longer used and was replaced with 1,1,1-trichloroethane (Gordon 1982; Christensen and Gordon 1983).

Many of the reports characterizing groundwater contamination in M-Area and documents characterizing liquid effluents for planning the effluent treatment facility have estimated the amount of chlorinated solvents that were discharged to the process sewers, seepage basins, and Tim's Branch. Often, the same estimates seem to be perpetuated in subsequent reports, and the basis for the original estimates is not always clear.

This section describes the use and disposal of solvents in M-Area, discharges to Tim's Branch and the M-Area settling basin, evaporation of solvents from M-Area operations and surface water, the air strippers being used to remediate M-Area groundwater, and more recent air quality permit and air emissions inventory estimates of trichloroethane releases from M-Area. From all of this information, we estimated the releases of trichloroethylene, tetrachloroethylene, and trichloroethane to the air. Although releases to surface waters were notable, most of the solvents released would have evaporated into the air before reaching people offsite. When these chlorinated solvents have been released or spilled to surface waters, the primary removal process is evaporation, with half of the solvent volatilizing within minutes, days, or up to several weeks depending on the conditions (Howard 1990). Almost all of the solvents in Site streams probably evaporated or were degraded long before they reached the Savannah River.

Chlorinated Solvents in Liquid Effluents Discharged from M-Area

M-Area wastewater drained to two process sewers. One discharged to Tim's Branch, which flowed into Steed Pond (also called Steed's Pond or Forrest Oakely Pond) then into Upper Three Runs and the Savannah River. The other emptied into the settling basin, which overflowed forming a small stream (often called the seep area) that seeped into the ground adjacent to Lost Lake, described as an upland depression or Carolina Bay (Christensen and Gordon 1983; Merz 1982).

The history of liquid effluent discharges in M-Area is important for characterizing releases. From 1952 (production started in 1954) until 1958, all effluents were discharged directly to Tim's Branch. The canning process effluents discharged from Building 321-M contained uranium. Because of the uranium in the effluent, a seepage basin was constructed and put in service in 1958 (Christensen and Brendell 1981). Several documents suggest the seepage basin was first used in 1973 (Specht 1991; Pickett 1990). Colven et al. (1985) suggests that 313-M effluents first went to the seepage basin in 1960. In their discussion of the solvents released to the M-Area sewers, Christensen and Brendell (1981) indicate that solvents had been released to sewers leading to the seepage basins since 1958. We believe that 1958 is the correct year, but more effluent was diverted to the seepage basin with time and some effluents may not have gone to the seepage basin until 1973.

In 1970, a program to decrease the amount of liquid waste discharged from 300-M Area was initiated. It involved repairing the Steed Pond Dam, recovering waste tetrachloroethylene (Du Pont 1972b), neutralizing caustics, and monitoring uranium oxide releases (Du Pont 1970). In 1970, a memo (Hardt 1970) explained that the process wastes from Buildings 313-M and 320-M were discharged through a process sewer through a uranium oxide sampler to the Tim's Branch. Tim's Branch emptied into Steed's Pond, located about 1.5 mi from M-Area. The dam partially washed away in 1966, reducing the size of the pond from 10 acres to about 2 acres. The dam was repaired in December 1970, restoring the pond to its original size. The larger pond facilitated settling of particulate material (Du Pont 1970). The overflow from the pond ran into Upper Three Runs and then the Savannah River. About 5×10^6 gal of water per week (or about 2.6×10^8 gal y^{-1}) was discharged from the Raw Materials Area via this route in 1970 (Hardt 1970).

In 1972, a new sewer line was constructed to discharge 313-M process wastes into the 321-M settling basin instead of into Tim's Branch. In 1973, all discharges except laboratory drains were routed to the settling basin. In 1979, the laboratory drain discharges were diverted to settling basin. In May 1982, discharges of process effluent to the Tim's Branch, which totaled about 370,000 gal d^{-1}, or about 1.35×10^8 gal y^{-1} were stopped and diverted to the basin. In November 1982, most of the cooling water and noncontact process effluent was directed back into Tim's Branch (Gordon 1982; Colven et al. 1985). In July 1985, the M-Area Liquid Effluent Treatment Facility (LETF) was completed and all effluents were treated and discharged to Tim's Branch (Specht 1991; Zeigler et al. 1986).

The process sewer line to the basin was described as a 76-cm diameter underground vitrified clay sewer line. Each process building had leader sewer lines 15–30 cm in diameter that intersected the 76-cm line. The process sewer line to the settling basin was about 715 m long with a slope of about 0.03%. Many cracks and misalignments in the sewer pipe were discovered in 1981, when the sources of groundwater contamination were being investigated. The sewer lines were lined with a 12-in. PVC liner in 1983 (Christensen and Gordon 1983). Wastes from 321-M

and 322-M flowed through the process sewer to the setting basin, which overflowed to Lost Lake, a Carolina Bay about 2–3 acres in size. About 5×10^5 gal wk^{-1} or 2.6×10^7 gal y^{-1} of wastewater was discharged to the settling basin in 1970 (Hardt 1970).

The first comprehensive attempt to estimate the amounts of chlorinated solvents used and released from M-Area seems to have been summarized in a report by Christensen and Brendell (1981) published the same year the groundwater contamination was discovered. The total solvent use and percentage thought to have leaked or have been discharged to the process sewer was estimated for each year. Christensen and Brendell (1981) acknowledge that estimating these quantities was "difficult, since no measurements of solvent loss to the process sewers or annual use in M-Area were ever made. The solvent use and loss estimates are derived from past solvent purchase orders, past operational events and M-Area personnel experience."

Separating out the solvents discharged for each time period, based on the solvent reported to have been used at the time and calculating the amount discharged from the percentage discharged and use estimates, resulted in estimates for each solvent for each year summarized in Table 17-6.

Potential understatement of the use from 1952–1970 was acknowledged by Christensen and Brendell (1981) on whose data many subsequent Site evaluations and our estimates are largely based. Because their estimates of use and release were the best data available and are the basis of our source term estimates for the early years, the solvent releases will be addressed for three time periods: (1) from startup until 1981, (2) after 1981, and (3) after 1984 when the air emissions inventory and air permit application calculations were done.

Chlorinated Solvents Use and Release from 1952–1981

An inventory of the number of degreasers and their volumes was found in the memo written by Christensen and Brendell (1981). Building 313-M had three 200-gal degreasers; Building 320-M had one 1000-gal and one 200-gallon degreaser; and Building 321-M had two 1000-gal degreasers and one 200-gal degreaser in 1981 (Christensen and Brendell 1981).

Degreasers are large vats partitioned in halves that contained heated and cooled solvent. Reactor components were cleaned by passing them through hot solvent vapor. Some of the vapor was condensed by water coils around the top of the vat. Some of the degreasers also had refrigerated coils that improved recovery. Periodically, as the oil and grease removed from the parts accumulated in the solvent, the vats were emptied and the solvent was replaced with fresh. In the early years, the dirty solvent was drained directly to the process sewers. At some point, some of it was funneled into holding tanks until it could be distilled for reuse. Occasionally, during the 1970s the still bottoms, degreaser sludge, and dirty solvent were drummed and stored until distillation recovery. When storage became a problem or drums began to rust, their contents were often emptied into the seepage basin process sewer. Most of the solvent used in these degreasers eventually evaporated. It seems that all of the solvent that did not evaporate was discharged to the process sewer between 1952 and 1979. Beginning in 1979, waste solvent and sludges were drummed and stored in the Hazardous Waste Interim Storage Facility, Building 710-U (Christensen and Brendell 1981).

From 1952 to 1958, trichloroethylene was used as a degreasing agent in Buildings 313-M and 320-M. The degreasers each had a still and a hold tank. By 1958, the stills and hold tanks had corroded and replacements had not been installed. The degreasers had also began to leak. Operations began in Building 321-M in 1958, with three new degreasers. Process liquid effluent

from 321-M went to the new M-Area seepage basin. The basin was intended to keep uranium from reaching surface waters (DOE 1987). By 1961, the basin began to overflow. The overflow traveled along an engineered ditch to Lost Lake. In 1962, the process in 313-M changed and tetrachloroethylene was used in the place of trichloroethylene. The tetrachloroethylene waste was released into Tim's Branch. Leakage from the degreasers continued. In 1971, 320-M and 321-M processes substituted tetrachloroethylene for trichloroethylene. In 1973, about one-half of the solvent discharged to Tim's Branch from 313-M was diverted to the seepage basin. In 1976, the remainder of the 313-M solvent discharged was going to the seepage basin. The leaking degreasers in 313-M were replaced in 1974. The degreasers in 320-M and 321-M continued to leak. Spot welding, installation of stainless steel liners, and other repair efforts were said to have been unsuccessful. In 1977, one of the three original degreasers in 321-M was replaced, but the new unit was not put into use until 1979. In 1978, the 320-M degreaser was replaced with a cold solvent dip tank. In 1979, concern over the potential carcinogenicity of tetrachloroethylene was raised and an effort to replace this solvent with trichloroethane was made. Another one of the old degreasers in 321-M was removed and a new degreaser, with refrigerated cooling coils, was installed. In 1979, the sewer line from 313-M to the seepage basin became blocked and discharges were routed to Tim's Branch. The solvent residues and sludge were being barreled, but some trichloroethane, although small amounts compared to discharges in earlier decades, were still being routed to Tim's Branch. The cold solvent dip tank in 320-M was replaced with a new degreaser in June 1981 (Christensen and Brendell 1981).

Although solvent consumption was said to have been estimated from former purchase records, Christensen and Brendell (1981) states that "area triclene records were not available and use-estimates are derived from M Area personnel judgment." The M-Area cost charging ratios suggested that solvents were allocated so that 20% went to 313-M, 25% went to 320-M, and 55% went to 321-M. Each 105 building in the reactor areas obtained one or two barrels of solvent from M-Area stores. The 105 degreasers were 1000 gal each (the same size as the degreasers in 320-M and 321-M). Degreaser solvents used in 773-A were also taken from the M-Area stocks. Allocations to other areas from M-Area were estimated to be from 25,000 to 50,000 lb each year. This was taken into account in estimates of M-Area consumption.

The leakage of solvent to the process sewers from the older, corroded degreasers was thought to have been proportional to solvent use. Christensen and Brendell (1981) estimated that 20–50% of the tetrachloroethylene used was released to the process sewers, higher than the 15–20% released for trichloroethylene and 3–5% for trichloroethane. Christensen and Brendell (1981) reported that site personnel felt that by the time tetrachloroethylene was in use, in about 1971, the degreasers in 313-M and 320-M were about 19 years old and those in 321-M were 13 years old. Corrosion and leaking increased during the 1970s. The increase in the amount of solvent purchased during this time was thought to reflect the deterioration and leakage problems and resulting losses. Tetrachloroethylene is also less volatile that trichloroethylene or trichloroethane. More tetrachloroethylene would have been expected to reach the process sewers if less evaporated (Christensen and Brendell 1981).

Christensen and Brendell concluded that since 1952, M-Area has used about 13 million lb (6,000,000 kg) of chlorinated solvents as degreasers and cleaners. They believed that from 50–95% of the solvents evaporated during degreasing operations, and the rest went to the M-Area process sewer systems. They estimated that about 2 million lb (901,100 kg) of solvents had been released to sewers leading to the seepage basins since 1958 and about 1.5 million lb (682,020 kg)

of solvent had been released to sewers going to Tim's Branch since 1952. The total discharges for the time period they evaluated are given in Table 17-6.

Table 17-6. Discharge Estimates for Trichloroethylene, Tetrachloroethylene, and Trichloroethane from M-Area Based on Christensen and Brendell (1981) Solvent Use and Process Sewer Discharge Estimates for M-Area Solvents[a]

Year	Estimated trichloro-ethylene use (ton y^{-1})	Estimated tetrachloro-ethylene use (ton y^{-1})	Estimated tri-chloro-ethane use (ton y^{-1})	% to sewers from 321-M	% to sewers from 320-M	% to sewers from 313-M	Trichloro-ethylene to the settling basin (ton y^{-1})	Trichloro-ethylene to Tim's Branch (ton y^{-1})	Tetra-chloro-ethylene to the settling basin (ton y^{-1})	Tetra-chloro-ethylene to Tim's Branch (ton y^{-1})	Trichloro-ethane to the settling basin (ton y^{-1})	Trichloro-ethane to Tim's Branch (ton y^{-1})
1952	76.5				15	15		11.5				
1953	76.5				15	15		11.5				
1954	76.5				15	15		11.5				
1955	76.5				15	15		11.5				
1956	76.5				15	15		11.5				
1957	76.5				15	15		11.5				
1958	76.5			20	15	15	11.5	12.5				
1959	140			20	15	15	11.5	12.5				
1960	140			20	15	15	11.5	12.5				
1961	140			20	15	15	11.5	12.5				
1962	89	54		20	25	25	12.5	7.5		13.5		
1963	89	54		20	25	25	12.5	7.5		13.5		
1964	89	54		20	25	25	12.5	7.5		13.5		
1965	89	54		20	25	25	12.5	7.5		13.5		
1966	89	54		20	25	25	12.5	7.5		13.5		
1967	89	54		20	25	25	12.5	7.5		13.5		
1968	89	54		20	25	25	12.5	7.5		13.5		
1969	89	54		20	25	25	12.5	7.5		13.5		
1970	89	54		20	25	25	12.5	7.5		13.5		
1971		185		20	25	25			25	24.5		
1972		315		25	30	30			51.5	49.5		
1973		415		35	35	40			96	53		
1974		335		35	35	20			70.5	42.5		
1975		575		45	45	20			153.5	76		
1976		500		45	45	20			143.5	56.5		

Table 17-6. Discharge Estimates for Trichloroethylene, Tetrachloroethylene, and Trichloroethane from M-Area Based on Christensen and Brendell (1981) Solvent Use and Process Sewer Discharge Estimates for M-Area Solvents[a]

Year	Estimated trichloro-ethylene use (ton y^{-1})	Estimated tetrachloro-ethylene use (ton y^{-1})	Estimated tri-chloro-ethane use (ton y^{-1})	% to sewers from 321-M	% to sewers from 320-M	% to sewers from 313-M	Trichloro-ethylene to the settling basin (ton y^{-1})	Trichloro-ethylene to Tim's Branch (ton y^{-1})	Tetra-chloro-ethylene to the settling basin (ton y^{-1})	Tetra-chloro-ethylene to Tim's Branch (ton y^{-1})	Trichloro-ethane to the settling basin (ton y^{-1})	Trichloro-ethane to Tim's Branch (ton y^{-1})
1977		560		45	45	20			161	63		
1978		412		45	20	20			130	20.5		
1979–		412		25	20	20			73.5	20.5		
–1979			85	5	5	5					2.5	3
1980			150	5	5	5					4	3.5
1981			100	3	3	3					3	1
Totals from 1952–1981							158.5 (25,000 gal)	191.5 (30,000 gal)	900 (133,000 gal)	500 (77,000 gal)	9.5 (14,000 gal)	6 (8850 gal)

[a] Solvent releases to the process sewers in tons per year (1 ton = 2000 pounds) for trichloroethylene, tetrachloroethylene, and trichloroethane estimated by Christensen and Brendell (1981). The 1981 total includes an accidental spill of 300 gal of trichloroethane. Discharges from the three M-Area facilities (313-M, 320-M, and 321-M) were combined.

Table 17-7. Estimates of the Chlorinated Solvents Used and Released in M-Area[a]

Solvents used and released	Solvent and years of use: Trichloroethylene 1952–1970	Tetrachloroethylene 1971–1979	1,1,1-Trichloroethane 1979–1982	Totals
Total used	3,700,000 lb	8,700,000 lb	670,000 lb	13,070,000 lb
	1,680,000 kg	3,950,000 kg	305,000 kg	5,941,000 kg
Released to the	317,000 lb	1,800,000 lb	19,000 lb	2,136,000 lb
Settling Basin	144,100 kg	820,000 kg	8,600 kg	971,000 kg
Released to Tim's	383,000 lb	1,000,000 lb	12,000 lb	1,395,000 lb
Branch	175,000 kg	450,000 kg	5,500 kg	634,090 kg

[a] Source: Christensen and Brendell (1981).

Both the draft (Colven et al. 1985) and final (Pickett et al. 1987) versions of the Environmental Information Document relevant to the M-Area settling basin (which had a different order of authors and much revised text but the same Site document number) reported the same numbers as Christensen and Brendell (1981). Slight differences, with the exception of one obvious typographical error, seemed to be due to differences in rounding amounts or rounding kilogram values converted from pounds.

The values reported by Merz (1982) are summarized in Table 17-8 in a format similar to Table 17-7. Merz does not reference the source of his estimates, but they were likely to have been based largely on Christensen and Brendell (1981).

Table 17-8. Estimates of the Chlorinated Solvents Releases to the M-Area Process Sewers[a]

Solvents used and released	Solvent and years of use: Trichloroethylene 1952–1971	Tetrachloroethylene 1971–1979	1,1,1-Trichloroethane 1979–1981	Total solvent released 1952–1981
Released to the	320,000 lb	1,700,000 lb	17,000 lb	2,037,000 lb
Settling Basin	145,450 kg	772,730 kg	7,730 kg	925,910 kg
Released to Tim's	383,000 lb	1,100,000 lb	21,000 lb	1,504,000 lb
Branch	175,000 kg	500,000 kg	9,550 kg	683,640 kg
Total released	703,000 lb	2,800,000 lb	38,000 lb	3,541,000 lb
	319,550 kg	1,272,730 kg	17,300 kg	1,609,550 kg

[a] Source: Merz (1982).

Other estimates of releases seem to have been based on those of Christensen and Brendell (1981) and were consistent with their conclusions. The estimates in Christensen and Brendell (1981) average to 118,303 lb y^{-1} or 53,650 kg y^{-1} discharged to surface water from M-Area. Another report from 1970 suggested that about 90,000 lb (40,900 kg y^{-1}) of tetrachloroethylene had been discharged annually to the plant streams (Du Pont 1970).

In summary, Christensen and Brendell (1981) estimated that about 6 million kg of solvents was used in M-Area, 1 million kg was released to the settling basin, and 0.6 million kg was released to Tim's Branch from 1951 to 1981. The remaining 4.4 million kg may have evaporated. Certainly, much of the 1.6 million kg discharged in liquid effluent also evaporated, although some seeped into the groundwater and some was degraded.

Perhaps Christensen and Brendell's estimates are far better than any estimates we can make because they interviewed Site personnel in 1981. These personnel had far more institutional memory and understanding of historical practices than we would expect to find in 1996 and 1997. We attempted to verify their arithmetic and observe whether the percentage of usage amount estimated to have been discharged to the sewer correlated with process changes involving solvent use (such as replacement of old degreasing units and changes in drumming of solvents) described above. The process and equipment changes described above appear to agree with those described in the *Savannah River Plant History for the Raw Materials Area for July 1954 through December 1972* (Du Pont 1972b). This report is a likely source for some of the historical information compiled by Christensen and Brendell (1981) about process changes and installation of new degreasers. The estimates seem to correlate with the practices described for each time period. It is not clear how the percentages of solvent going to Tim's Branch and the settling basin were determined to vary from 15–40% in different years. The percentages assigned to each year appear to have changed as the degreasers aged and presumably corroded and leaked more often. It is difficult to improve on the approach and estimates of Christensen and Brendell (1981) because of a lack of knowledge and information.

An attempt to further characterize the M-Area solvent releases was published in a report, in a draft document (Colven et al. 1985) and then in a final version (Pickett et al. 1987). These documents suggested that M-Area processes began in 1954 rather than 1952. Other records (Christensen and Brendell 1981) suggest that processing in 313-M and 320-M began in 1952 and processing in 320-M, which resulted in releases of uranium to the liquid effluent from the canning process, began in 1954. Other than this, discrepancies between the 1981 analysis and later reports are not evident and no new information on solvent discharges was presented.

Chlorinated Solvent Use and Release After 1981

In May 1982, process sewer discharges to Tim's Branch were stopped and all effluents went to the settling basin. In November 1982, waste considered nonradioactive went back into Tim's Branch (Pickett et al. 1987).

The Environmental Survey (DOE 1987), conducted in the late 1980s, described vapor degreaser operations in Buildings 313-M, 320-M, and 320-M in the 1980s. Used solvent was recycled using a solvent still. Evaporation of 1,1,1-trichloroethane from the degreasers was limited by refrigerated cold traps, condensers, and degreaser tank covers. Local ventilation of the areas was required for worker safety. Vapors from the degreasers were vented to the outside air through hoods. Ventilation of the vapor degreasers was important for worker protection and appears to have been sufficient in the late 1980s; however, the survey team found that one cold trap was out of service and covers were not always in place (DOE 1987). One of the key findings of the Environmental Survey was that emissions of 1,1,1-trichloroethane to the air from the 300-Area degreasing operations were large and may have been exceeding 200 ton y^{-1} (DOE 1987) for an undetermined number of years.

Monitoring data of use to help verify release estimates for chlorinated solvents are not available. The available surface water and sediment monitoring data, most of which was collected to characterize M-Area effluent and settling basin sludge in preparation for the Effluent Treatment Facility, were reviewed and are summarized here.

In 1982, less than 5 lb d^{-1} (2.3 kg d^{-1}), or less than 829 kg y^{-1} of solvent was said to have been discharged in M-Area effluents. Samples taken during "routine operations" indicated about 0.2 mg L^{-1} 1,1,1-trichloroethane in the sewers with "occasional surges to about 10 mg L^{-1} (ppm) when cleaning tanks are being drained"(Merz 1982).

Concentrations of 1,1,1-trichloroethane measured in a 24-hour composite sample of sewer effluent sampled in December 1981 when the plant was operating were 0.47 mg L^{-1} in sewer effluent going to the settling basin and 0.09 mg L^{-1} in sewer effluent going to Tim's Branch (Merz 1982). Colven et al. (1985) implied that peak process discharges to the Tim's Branch in 1982 were 1.35×10^{8} gal y^{-1} or 5.1×10^{-8} L y^{-1}. Using volume data from Colven et al. (1985) and concentrations reported by Merz (1982), we can estimate that a total of 286 kg y^{-1} released to surface water in the 1980s. Of this, about 240 kg may have gone into the settling basin and 46 kg into Tim's Branch each year.

Chlorinated Solvents Released to Tim's Branch

In 1968, an organic compound, discovered to be tetrachloroethylene, was observed in a Tim's Branch water sample. The memo describing this discovery said that, "discussions with M-Area personnel indicated that 313-M is the only building using large quantities of tetrachloroethylene and that they do routinely dispose of this material into the sewer system" (Johnson 1968).

Hardt (1970) described releases to Tim's Branch and predicted the release of the same materials after initiation of proposed waste reduction measures, which included recovery of waste tetrachloroethylene by distillation.

Volumes and concentrations of waste discharged to the Tim's Branch, 300-Area effluent, and to the 321-M settling basin corresponding to production data from November 1968 to February 1969 were estimated in Monier (1970). Monier (1970) estimated the amount of solvents in the in 300-Area liquid effluent based on an analysis of 4 months of production data from November 1968 to February 1969. He estimated that 6000 gal (29,809 kg) of trichloroethylene and 13,000 gal (64,586 kg) of tetrachloroethylene (all were 100% solutions) had been discharged to Tim's Branch in 1 year, and that about 5000 gal (24,840 kg) of trichloroethylene were discharged to the 321-M settling basin in a year. References for the estimates and for the data from which they were determined were not included, and it was not clear how the estimates were determined (Monier 1970). If we assume a conversion of 10.93 lb gal^{-1} and 2.2 lb kg^{-1}, then 29,809 kg and 24,840 kg of trichloroethylene were discharged that year to the Tim's Branch and the settling basin and 60,816 kg of tetrachloroethylene was discharged to surface water in that year (Monier 1970).

In a study of waste reduction methods, Hardt (1970) estimated that each year about 91,000 lb (41,364 kg) of tetrachloroethylene, and 12,000 lb (5455 kg) of trichloroethylene were being released to Tim's Branch. These amounts represented 100% solutions, calculated from larger amounts of more dilute solutions actually discharged. At that time, tetrachloroethylene from Building 313 and trichloroethylene from Building 320 were discharged to the process sewer. The site was said to be planning to convert from trichloroethylene to tetrachloroethylene in 1971 and to distill waste tetrachloroethylene. The authors predicted that in the future all but 1% of it would be recovered, and the 1% in the heel could be barreled and buried (Hardt 1970).

In a handwritten note or logbook entry about a meeting with Raw Materials and Health Physics personnel, Johnson (1978) said that tetrachloroethylene waste from 321-M was collected in 560-gal tanks and released to the seepage basin every 2 weeks. The potential for low-level uranium release from this practice was of concern. Samples of the 321-M 'cleaning solution' were to be analyzed for uranium, and the possibility of installing a trebler sampler at the seepage basin was discussed.

In 1985 and 1986, a study was done to determine any adverse effects of Outfall A-014 effluent, which received M-Area effluents, on the Tim's Branch and Upper Three Runs Creek. The study was required as a part of the NPDES permit modification for the M-Area Liquid Treatment Facility. Chemicals detected in Tim's Branch at the outfall at concentrations higher than upstream locations included nitrate, zinc, uranium, and trichloroethylene (Specht et al. 1987).

In January 1985, 75 gal of trichloroethylene was spilled onto the ground in M-Area and the soil was removed and taken to the M-Settling Basin (Jewell 1990). We have no information on spills that occurred before 1980. It is likely that spills occurring before about 1985 would have been allowed to evaporate or would have been routed to the sewer or seepage basin, where most evaporated.

The solvents reaching the basin or Tim's Branch either evaporated, seeped into the ground and eventually into groundwater, accumulated in basin sludge and sediments, or were biodegraded.

Evaporation of Chlorinated Solvents from Surface Water

Evaporation of chemicals with a high vapor pressure (volatile chemicals) and low solubility from settling ponds and seepage basins can be important for evaluating releases to the air. Looney et al. (1987) used a simple mass balance model to determine the fraction of tritium and volatile organic compounds that evaporated rather than entered the soil. Equations incorporating volatility, solubility, inflow, outflow, seepage rate, and other parameters were used for each surface impoundment or seepage basin examined. The goal seemed to be to determine the fraction of chlorinated organics that entered the groundwater and identify which materials were of concern for groundwater contamination at each waste site. Appendixes in Looney et al. (1987) include data tables with an estimated discharge mass for each site, which were developed from analysis of groundwater and soil data as well as process knowledge. A fraction to convert the mobile mass (moving to groundwater) to the total disposal mass was developed for common contaminants. The disposal mass estimates were calculated from groundwater concentrations and seemed very uncertain. Soil concentrations and groundwater concentrations were compared to multiples of drinking water standards and other criteria to select contaminants of concern for each disposal site. Background concentrations of chemicals in groundwater from SRS wells were also compiled.

The data tables in Looney et al. (1987) for M-Area do not include estimates for the amount of solvents that may have evaporated, even though these were said to have been calculated and accounted for in the estimates of releases to groundwater. The total disposal mass was calculated to have been 84,000 kg of tetrachloroethylene, 15,000 kg of trichloroethylene, and 1000 kg of trichloroethane for 1971–1985. The soil core inventory estimated in 1985 was 3600 kg for tetrachloroethylene, 170 kg for trichloroethylene, and 140 kg for trichloroethane. The maximum

groundwater concentration measured was 427,000 μg L^{-1} tetrachloroethylene, 161,000 μg L^{-1} for trichloroethylene and 203 μg L^{-1} for trichloroethane from well MSB-3A (Looney et al. 1987). The total amount of chlorinated solvents in the groundwater was not estimated. These data are not sufficient to allow us to use a mass balance approach for estimating the amount of solvents that evaporated.

Trichloroethane Use in the 1980s and 1990s

Another potentially helpful handwritten ledger called *the 300-Area Essential Materials Inventory Control* covered the receipts of some of the process chemicals, including 1,1,1-trichloroethane (Westinghouse 1986b, Westinghouse 1989). The ledger for 1,1,1-trichloroethane was a handwritten log that listed the railroad cars that delivered 1,1,1-trichloroethane, the balance of the purchase order, and the amount "consumed" by building from July 1, 1979, to June 1, 1986. There are very few entries for 320-M, and some of the values under 313-M and 321-M appear to have been corrected. It is not clear whether the distribution to the facilities was a cost accounting or the actual amount delivered. There are many handwritten corrections and a few illegible entries, but most of the values are legible. However, notes on the lack of any delivery correspond to a consumption entry left blank, and some of the entries are out of sequence. A note is written on the top of the page, "20%-313M, 15%-320M and 65%-321M," which appears to be the formula by which the total amount used was partitioned between the three buildings. This is most likely a cost accounting breakdown, but it was useful in estimating values that were illegible.

From February 1981 to August 1982, and again from January 1983 to December 1983, three values were entered into the consumed column. These were added together to calculate a number that presumably represented the total consumption for all buildings. Most of the values are positive, except for several Decembers when consumption numbers are negative, presumably to allow the totals to match the year-end balance. To avoid implying a certainty that is lacking, 3-month totals were compiled rather than monthly totals. The approximately quarterly totals are shown in Table 17-9. Monthly averages and annual totals are shown in Table 17-10. The ledger contained entries of both gallons and/or pounds and stated that a conversion of 10.926 lb gal^{-1} was used to convert the gallons to pounds. The values were converted to kilograms using 10.93 lb gal^{-1} and 2.2 lb kg^{-1}.

Table 17-9. Quarterly 1,1,1-Trichloroethane Consumption for 1979-1986 from Handwritten 300-Area Essential Materials Inventory Control Ledgers

Time period	kg
July, Aug, Sept. 1979	3.5×10^4
Oct., Nov., Dec. 1979	7.8×10^4
Total for the last 6 months of 1979 (× 2)	2.3×10^5 kg y^{-1}
Monthly average	1.9×10^4 kg mo^{-1}
Jan., Feb., March 1980	3.2×10^4
April, May, June 1980	4.3×10^4
July, Aug., Sept. 1980	2.7×10^4
Oct., Nov., Dec. 1980	2.9×10^4
Total for 1980	1.3×10^5 kg y^{-1}
Monthly average	1.1×10^4 kg mo^{-1}
Jan., Feb., March 1981	4.1×10^4
April, May, June 1981	3.2×10^4
July, Aug., Sept. 1981	4.9×10^4
Oct., Nov., Dec. 1981	5.3×10^5
Total for 1981	1.8×10^5 kg y^{-1}
Monthly average	1.5×10^4 kg mo^{-1}
Jan., Feb., March 1982	5.4×10^4
April, May, June 1982	7.1×10^4
July, Aug., Sept. 1982	6.8×10^4
Oct., Nov., Dec. 1982	5.5×10^4
Total for 1982	2.5×10^5 kg y^{-1}
Monthly average	2.1×10^4 kg mo^{-1}
Jan., Feb., March 1983	3.3×10^4
April, May, June 1983	4.9×10^4
July, Aug., Sept. 1983	1.2×10^5
Oct., Nov., Dec. 1983	7.4×10^4
Total for 1983	2.8×10^5 kg y^{-1}
Monthly average	2.3×10^4 kg mo^{-1}
Jan., Feb., March 1984	3.7×10^4
April, May, June 1984	1.1×10^5
July, Aug., Sept. 1984	9.6×10^4
Oct., Nov., Dec. 1984	3.9×10^4
Total for 1984	2.8×10^5 kg y^{-1}
Monthly average	2.3×10^4 kg mo^{-1}
Jan., Feb., March 1985	6.4×10^4
April, May, June 1985	7.3×10^4
July, Aug., Sept. 1985	1.4×10^4
Oct., Nov., Dec. 1985	8.9×10^4
Total for 1985	2.4×10^5 kg y^{-1}
Monthly average	2.0×10^4 kg mo^{-1}
Jan., Feb., March 1986	5.3×10^4
April, May, June 1986	5.8×10^4
Total for the first 6 months of 1986 (× 2)	2.2×10^5 kg y^{-1}
Monthly average	1.8×10^4 kg mo^{-1}

Table 17-10. Approximate Monthly and Annual Amounts of Solvent Used Based On the Handwritten 300-Area Essential Materials Ledgers

Year	Monthly average (kg)	Total for each year (kg)	Ton y^{-1}
1979	1.9×10^4	2.3×10^5	253
1980	1.1×10^4	1.3×10^5	143
1981	1.5×10^4	1.8×10^5	198
1982	2.1×10^4	2.5×10^5	275
1983	2.3×10^4	2.8×10^5	308
1984	2.3×10^4	2.8×10^5	308
1985	2.0×10^4	2.4×10^5	264
1986	1.9×10^4	2.2×10^5	242
Total 1979–1986	1.5×10^5	1.8×10^6	1,980
Average	$1.5 \times 10^5 \div 8\ y = 1.9 \times 10^4$	$1.8 \times 10^6 \div 8\ y = 2.3 \times 10^5$	248

Source: Westinghouse 1986b, Westinghouse 1989.

Essential materials records from M-Area for 1984, 1985, and January through April 1986 were found in Phase I of the dose reconstruction study (Westinghouse 1983, 1984, 1985, 1986a, 1987a). These are computerized (as opposed to the handwritten ledgers just described) cost accounting records that included monthly inventories of the amount of process chemicals consumed in gallons. Three values for 1,1,1-trichloroethane are printed for each month, which correspond to the amount delivered to each of the three process buildings, each designated by a charge code. The monthly values do not seem to be accurate. The quantities were apparently overestimated for some months and then given negative values for the following month. It seemed best to average values over a longer time period, at least 1 year. Annual averages are presented in Table 7-11. The monthly values vary but generally range between 2,000 and 12,000 gal mo^{-1}. The values printed for October 1984 totaled 61,248 gal. What appears to be a handwritten correction of 7743 gal is written over the values. The values reported for November 1984 are unusually large, totaling 83,866 gal, then the values for December total –6786 gal. The values for November are about 10 times the monthly average, which suggests a decimal place error occurred, but the negative numbers in October and December may have been an attempt at correcting the balances. If the numbers in the printout are taken at face value, and the corrected value for October is assumed to be accurate, the total consumption for 1984 is 149,700 gal (7.5×10^5 kg) averaging 12,474 gal mo^{-1} (6.2×10^4 kg mo^{-1}). If we disregard the unusual monthly values for October, November, and December, the total for January through September 1984 is 64,875 gal or 7208 gal mo^{-1}. The consumption for 1985 totaled 29,108 gal (1.4×10^5 kg), which averages out to be 2,425 gal mo^{-1} (1.2×10^4 kg mo^{-1}). A total of 24,478 gal was recorded as consumed from January 1, 1986, to April 30, 1986; an average of 6120 gal mo^{-1}; and a projected average for the year of 73,434 gal y^{-1} (3.6×10^5 kg y^{-1}) (Westinghouse 1984, 1985, 1987a). These records suggest that the consumption of 1,1,1-trichloroethane was very inconsistent from month to month and may have ranged from about 2500 to 12,500 gal mo^{-1} during peak periods of production.

Table 17-11. Summary of the Average Amount of Trichloroethane Used in M-Area for Three Years Based on Computerized Essential Materials Ledgers

Year	Average (kg mo^{-1})	Average (kg y^{-1})	Ton y^{-1}
1984	6.2×10^4	7.5×10^5	825
1985	1.2×10^4	1.4×10^5	154
1986	3.0×10^4	3.6×10^5	396
Average	3.5×10^4	4.2×10^5	462

The annual use estimates derived from averaging the values in the essential materials ledgers differ from estimates derived from the Inventory Control ledgers for 1984–1986. Using the highest total estimated for each year from either source, we can estimate that as much as 2.4×10^6 kg or 2662 ton of trichloroethane was used from 1979–1986.

Chlorinated Solvents in M-Area Groundwater

Although most of the solvent released in liquid effluent evaporated, some entered the groundwater because of (a) seepage through the basin and from basin overflow areas through cracks in the pipelines to the basins and (b) leaks and spills in M-Area (Bradley 1981).

Groundwater under M-Area was found to be contaminated with metal degreasing solvents in June 1981 (Zeigler et al. 1985). Groundwater samples from four monitoring wells found that trichloroethylene and tetrachloroethylene were approaching the parts-per-thousand (g L^{-1}) range (Christensen and Brendall 1981). At that time, Du Pont estimated that 60,000 lb of chlorinated solvents had contaminated 330 million gal of groundwater in a plume that had traveled a distance of about 2200 ft (Zeigler et al. 1985). A 1982 fact sheet on M-Area solvent contamination and a Technical Data Summary prepared by Gordon (1982) both said 59,000 lb of solvents had entered the groundwater. Gordon (1982), Du Pont (1982b), and Bradley (1981) used a value of 60,000 lb in a preliminary scoping documents, fact sheets, and evaluations prepared for planning groundwater cleanup. Test well samples in 1982 were said to have identified a 330-million gal plume of groundwater contaminated with about 60,000 lb of chlorinated organic solvent (Merz 1982). Additional groundwater monitoring wells were drilled and the contamination was studied over the next several years. By 1985, the plume of contaminated groundwater in M-Area had been defined by more than 700 samples and an additional 200 monitoring wells. In 1987, the inventory of solvents in the groundwater was estimated to have been between 260,000 and 450,000 lb, with concentrations as high as 300 mg L^{-1}. About 70% of the solvent was thought to be trichloroethylene (Colven et al. 1987). Bebbington (1990) reported that 450,000 lb of chlorinated solvents had seeped or leaked into the groundwater.

No chlorocarbons have been detected in offsite drinking water in the vicinity of the 300/700-Area (Zeigler et al.1986). Groundwater studies led Site researchers to predict that the plume of solvent-contaminated water beneath M-Area might reach the Site boundary by the year 2005 (DOE 1988; Gordon 1982). Although the groundwater does not represent a complete exposure pathway for people offsite, the groundwater has been and is still being remediated. This has resulted in solvents being aerated into the air.

M-Area Air Strippers and Soil Vacuum Extraction Unit Emissions. Air strippers have been and are still being used to remove volatile chemicals from groundwater under M-Area. Groundwater is pumped through the stripper where the water is aerated and the solvents are released to the air. Stripped water is returned to the groundwater. The M-Area Groundwater Remedial Action Program began in 1983. Additional recovery wells and a pilot air stripper began operating in 1984. A full-scale recovery system with 11 recovery wells and a 400-gal min^{-1} air stripper was put in place in September 1985, and it removed an estimated 53,000 lb (24,100 kg) of solvent in the first year it operated. The remediation plan was to remove and treat groundwater for about 30 years (Colven et al. 1987). The goal of the groundwater treatment systems was to reduce the concentrations in groundwater from the parts per million to the parts per billion range (Bradley 1981).

Detailed descriptions of the air stripper can be found in several Site documents (Looney et al. 1991; Gordon 1982). The air stripper removed solvents from the groundwater and discharged them through a stack into the air. The groundwater was pumped to the top of the air stripper's column and allowed to trickle down over packing. Volatile organics evaporated into the air, which was blown into the bottom of the column and exited out the top (Gordon 1982). It was recognized that concentrations of solvents in the air exiting the stripper might be in excess permissible occupational exposure limits, but ground concentrations were predicted to be well within the threshold limit values (Gordon 1982).

A full-scale test of the air stripper near at 300-M Area was described by Looney et al. in 1991. During the test, from 100 to 140 lb (45 to 63 kg) of volatile organic chemicals was extracted each day or 16,000 lb (7272 kg) over 139 days. The air containing the chemicals was recovered by vacuum extraction. The concentration of the contaminated vapors extracted from the horizontal vacuum extraction well was measured approximately three times each day. Concentrations after the process first started were as high as 5000 ppm. The concentrations stabilized to about 300 ppm after several days. The vacuum extraction process removed 109 lb d^{-1} (49.5 kg d^{-1}) and the air stripping component removed an additional 20 lb (9.1 kg). Groundwater samples were taken daily (Looney et al. 1991). If this removal rate would have been sustained, up to 565 ton y^{-1} or 3.6 kg h^{-1} would have been released from the vacuum extraction and groundwater stripping operation. To address the question about potential air pollution, Site engineers also modeled the transport of solvents released to the air from the air stripper and attempted to calculate redeposition and expected concentrations in rainfall. Using an atmospheric concentration of 10 μg m^{-3}, they estimated that less than 0.002% of the trichloroethylene would be redeposited. The remainder would be diluted, transported, and photodegraded. The predicted maximum rainfall concentrations were 25 μg m^{-3} (Looney 1984). Air quality effects were also examined by Colven et al. (1987). Air emission testing was required for the air stripper's air emissions operating permit. In October 1985, stack emissions were tested for trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane. Based on the test results, an average emission rate of 7.87 lb h^{-1} (3.6 kg h^{-1}) was predicted, just in compliance with the permit emission limit of 7.9 lb of volatile compounds per hour. An adsorbent sampling train monitoring method approved by the EPA and SCDHEC was used. The error of the method used was estimated to be as high as ±50%. Effluent water samples were also tested for solvents. The total chlorocarbon removal rate varied from about 3.5 to 10 lb h^{-1}. Water samples analyzed by the laboratory in 321-M was used to determine an average air emission rate of 6.50 lb h^{-1} (2.95 kg h^{-1}). In addition, modeling studies were conducted to predict the dispersion of organic compounds in the air and to estimate

concentrations at several locations. Dispersion calculations using EPA's Industrial Source Complex model were made and included as a part of the materials accompanying the permit application. Meteorological data for 1976, which were thought to produce the highest predicted concentrations, were used. Modeling for trichloroethylene was done and downwind concentrations for tetrachloroethylene and 1,1,1-trichloroethane were predicted using the ratio of these compounds to trichloroethylene in the stack. The maximum trichloroethylene concentrations predicted for the plant property line were predicted to be less than 0.013% of the threshold limit value (occupational exposure limit). Values for 1,1,1-trichloroethane and tetrachloroethylene were less. The authors of this report concluded that "predicted values for downwind organic concentrations are judged to be insignificant and below the sensitivity of the most sophisticated measurement techniques" (Colven et al. 1987).

Another report described the air stripper that began operating in 1985 as having a capacity of 400 gal min^{-1} and emitting about 7.9 lb h^{-1} (3.6 kg h^{-1}) of chlorinated solvents into the air, roughly equivalent to 35 ton y^{-1}. Groundwater inlet and treated water outlet analyses, said to be more accurate than exhaust air measurements, were used to estimate solvent emissions (DOE 1987).

By the second quarter of 1988, cumulative throughput of groundwater through the stripper was estimated to have been 532 million gal, with 130,300 lb (59,000 kg) of solvent removed since startup in September 1985. A total of 164,500 lb (75,000 kg) was calculated to have been removed, including all of the other experimental removal programs, up to 1988. The influent concentrations to the air stripper ranged from about 22,800 to 23,978 μg L^{-1} (DOE 1988).

The system was upgraded in 1990. In 1992, it was estimated that 285,000 lb (129,550 kg) of volatile organics had been removed from 1.5 billion gal of groundwater (Arnett et al. 1993).

For the air emissions inventory, trichloroethylene and tetrachloroethylene emissions from the air stripper used to treat groundwater (shown in Table 17-12) were estimated from the difference in inlet and outlet concentrations and information about treatment system flow rates (Radian 1992a).

Table 17-12. Estimates of the Amount of Chlorinated Solvents Removed by the 323-M Air Stripper, Reported in an Operating and Performance Summary Published in 1992 by Radian for the Building 323-M Air Stripper

Year	Total VOC removed (lb)	Operating time (h)	Emission rate (lb hr^{-1})	Trichloroethylene emissions (ton y^{-1})	Tetrachloroethylene emissions (ton y^{-1})
1985	19,523	2339	8.34	6.74	3.03
1986	48,756	8419	5.79	16.58	7.80
1987	44,346	8388	5.29	15.96	6.21
1988	36,790	8632	4.26	12.51	5.89
1989	26,024	8194	3.18	9.11	3.90
1990	28,323	8313	3.41	9.77	4.39
Total	203,762			70.67	31.22

Release of trichloroethylene is a concern for ozone depletion. In recent years, the air stripper and the vapor extraction units are connected to catalytic oxidation (Catox) equipment that

converts most of the chlorinated solvents to hydrogen chloride (hydrochloric acid) which is also a regulated air pollutant (Faugl 1996a).

The air stripper contribution to surface water releases seems to have been negligible. Trichloroethylene did not exceed the permit limits at the air stripper outfall, M-005 (Specht et al.1987).

Other Air Strippers and Soil Vacuum Extraction Units. The A-1 groundwater air stripper, installed in 1990, was described in the Part 70 Operating Permit Application. Releases for trichloroethylene, tetrachloroethylene, and hydrochloric acid from the unit were modeled for compliance with Standard 8 regulations. The limits required by the State Bureau of Air Quality Control to be in compliance with Standard 8 was 5.34 lb h^{-1} for hydrochloric acid and 6.4 lb h^{-1} for the solvents. The emission estimate for volatile compounds was 0.267 ton y^{-1}. The maximum design capacity emissions estimates were 9.55×10^{-3} ton y^{-1} for tetrachloroethylene and 2.94×10^{-3} ton y^{-1} for trichloroethylene. These were based on 1994 estimates that the unit operated for 7705 hours, removing a total of 517.3 lb of trichloroethylene and 16.8 lb of tetrachloroethylene.

In 1994, six soil vapor extraction units (SVEUs) were operating. These were somewhat like large vacuums used to remove solvents from soil. The emissions from all of these units totaled about $1/10^{th}$ of the emissions estimated for the M-Area air stripper in 1994 (Faugl 1996m). The Savannah River Technology Center (SRTC) soil vacuum extraction unit, used for field demonstrations of pollutant treatment systems, was also described in the operating permit. The unit was used to extract contaminated vapors from the soil and send the contaminants through whatever technology was being demonstrated. The unit exhausted through a 15-ft stack. Using engineering calculations, operators estimated that the actual emissions of volatile compounds were 4.87×10^{-3} ton y^{-1}. Most of this, 1.01×10^{-3} ton y^{-1}, was trichloroethylene. 1,1,1-Trichloroethane emissions were estimated to be 4.80×10^{-5} ton y^{-1}, and the estimate for tetrachloroethylene was 1.01×10^{-3} ton y^{-1} (Westinghouse 1996a).

Estimates for a rate of discharge of trichloroethane from M-Area operations and also for trichloroethylene and tetrachloroethylene to the air from the air stripping operation were made as a part of the air emissions inventory (Radian 1992a).

Emissions in the AIRS database for trichloroethylene and tetrachloroethylene from air strippers, soil vacuum extraction units, basins, and tanks in 1985, 1987, and 1995 are summarized in Table 17-13.

Table 17-13. Emissions in the AIRS Database for Trichloroethylene and Tetrachloroethylene from Air Strippers, Soil Vacuum Extraction Units, Basins, and Tanks in 1985, 1987, and 1995

Emission source	Year	Actual[a] emission estimate (ton y^{-1})
Trichloroethylene		
H-Area tank farm	1985	0.0003
	1987	0.0003
M-Area air stripper M-1	1985	6.74
	1987	16.0
	1995	3.31
321-M SVEU	1995	0.054
Tetrachloroethylene		
F-Area seepage basins	1985	0.0214
	1987	0.0214
M-Area settling basin	1985	0.205
	1987	0.154
M-Area air stripper M-1	1985	3.03
	1987	6.21
	1995	2.15
5-SVEU in M-Area (totaled)	1995	0.697
321-SVEU	1995	0.425

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

About three times as many emissions points were listed for trichloroethylene in 1994 than in 1985. In 1994, more estimates for the tank farm and SVEUs in M-Area were listed. Table 17-14 presents the 1994 sources listed in the AIRS database. Table 17-15 provides the totals for trichloroethylene emissions.

The total actual trichloroethylene emissions for 1994 in the AIRS database were 5.65 ton y^{-1}. These emissions included releases from the burial ground solvent tanks; solvent tank trailer; tank farm painting; small degreasers in separations areas; tanks and vessels in H-Area; M-Area SVEUs and air strippers; and equipment used after 1990 like the ICF Tank farm, mobile experimental bioreactor, and demo waste incinerator. About one-half as many of the emission points were listed in 1992 than in 1994. The 1992 actual emissions totaled 8.66 ton y^{-1}. The actual emissions for 1990 totaled 9.78 ton y^{-1}. As expected, the air stripper in M-Area dominated the estimates, followed by the A-1 air stripper in 1992 and 1994. For all years, almost all of the trichloroethylene emissions were from the M-1 air stripper. About 95% of the total was from the M-1 air stripper in 1994. The next largest source was the A-1 air stripper, accounting for 0.05%.

In 1990, the M-1 air stripper accounted for 99.9% of the total. The highest annual emissions totaled 16 ton y^{-1} in 1987, with almost 100% coming from the M-1 air stripper. Trichloroethylene emissions from M-Area degreasers, sewers, and liquid effluent occurred long before the air emissions inventory was being done.

Table 17-14. Trichloroethylene Emission Sources for 1994 in the AIRS Database[a]

Source description	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
F-Area tank farm degreaser and miscellaneous uses	2.3×10^{-2}	3.0×10^{-4}
Air stripper G-Area A1	2.9×10^{-1}	2.6×10^{-1}
H-Area tank farm	1.84×10^{-2}	2.40×10^{-4}
Consolidated Incinerator (CIF) tank farm emissions total	6.6×10^{-2}	1.1×10^{-5}
SVEU For M-Area process sewers	1.05	0
SVEU For M-Area seepage basin	1.05	0
IOU-SVEU 782-7M	4.4×10^{-2}	2.3×10^{-2}
SVEU for A014 Outfall	1.05	0
SVEU	1.05	0
Air stripper M1	5.63	5.35
321-M SVEU	1.05	0
Groundwater air stripper	2.19×10^{-1}	blank

[a] Source: Faugl (1996l).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Table 17-15. Total Trichloroethylene Emissions from the AIRS Database[a]

Year	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985	11.5	2.64
1987	25.	16.0
1990	25.2	9.78
1992	34.6	8.66
1994	12.9	5.65

[a] Source: Faugl (1996l).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Tetrachloroethylene emissions in 1985 included waste handling and tanks, burial ground, laboratories, F-Area, H-Area and M-Area seepage basins, landfill and tank farm emissions, Pilot Plant equipment, painting, and the air stripper. The actual total emissions were 3.26 ton y^{-1}, with 3.03 ton y^{-1} from the M-1 air stripper. The next highest release was from the M-Area settling

basin with an estimate of 0.205 ton y^{-1}. In 1987, the total actual emissions were 6.39 ton y^{-1}, with 6.21 ton y^{-1} from the M-1 air stripper. The 1990 total was 4.4 ton, with 4.39 ton from the M-1 air stripper. The M-Area settling basin was not listed for 1990. Actual emissions in 1992 totaled 4.35 ton y^{-1}, with 99.5% from the M-1 air stripper (Faugl 1996m).

The AIRS database also contained emissions estimated for tetrachloroethylene from waste storage tanks, incinerators seepage basins, disposal and landfills, painting and printing operations, and laboratories (Faugl 1996l) (see Table 17-16). Table 17-17 provides the totals for tetrachloroethylene emissions from the AIRS database.

Table 17-16. Emissions in the AIRS Database for Tetrachloroethylene from Waste Storage Tanks, Incinerators Seepage Basins, Disposal and Landfills, Painting and Printing Operations, and Laboratories[a]

Year Source description	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985		
A-Area waste storage tanks (each)	3.63×10^{-7}	1.82×10^{-7}
F-Area seepage basin	2.14×10^{-2}	2.14×10^{-2}
H-Area seepage basins	1.47×10^{-10}	1.47×10^{-10}
723-A Met Lab basin	1.10×10^{-5}	1.10×10^{-5}
Landfill 740-G	2.20×10^{-3}	2.20×10^{-3}
H-Area tank farm, use for maintenance	2.40×10^{-4}	2.40×10^{-4}
M-Area settling basin	2.05×10^{-1}	2.05×10^{-1}
M-Area air stripper M1	1.13×10^{1}	3.03
M-Area use for maintenance	3.70×10^{-3}	3.70×10^{-3}
Pilot Plant incinerator	3.74×10^{-6}	4.69×10^{-9}
Burial Ground 643	1.4×10^{-8}	1.4×10^{-8}
1987 was the same as 1985 except for the addition of the		
M-Area air stripper M1	1.13×10^{1}	6.21
The same emissions estimates were given in 1990 except for		
H-Area seepage basins	1.85×10^{-10}	1.85×10^{-10}
M-Area air stripper M1	1.13×10^{1}	4.39

[a] Source: Faugl (1996l).

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Table 17-17. Total Tetrachloroethylene Emissions from the AIRS Database

Year	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1994	13.6	3.55
1992	20.7	4.35
1990	11.3	4.40
1987	11.5	6.39
1985	11.5	3.26

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Operating Permit and Air Emissions Inventory Information about M-Area Operations

M-Area emissions estimates for the permit application included volatile solvents emitted from degreasers and operations of the cap/can and plating lines. For the solvents, a mass transfer coefficient was calculated assuming an equilibrium from liquid to vapor taking into account mixing and aeration. For calculating trichloroethane emissions from the cap/can line, the process rate was determined from knowing the number of caps and cans per shift or per hour and the number of gallons in each bath. The cap/can line cleaned the aluminum caps and cans used in slug production. The line involved nitric acid etch tanks, phosphoric acid etch tanks, degreaser, aluminux etch, and a number of hot and cold water rinses. A capacity of 165 gal of 1,1,1-trichloroethane per bath was assumed. Degreasing emissions were estimated using the average and maximum production rate, the tank volumes, and approximate amount of raw materials in each tank. Solvent emissions were assumed proportional to the surface area of the tanks. Solvent dragout onto parts and fugitive losses from holding tanks and drips were included. The standing losses because of the tanks ‘breathing’ and working losses because of vapor displacement during filling were also added to the emissions. These loses are most important for the aboveground tanks that were not insulated and expanded and contracted daily because of temperature changes.

The 1,1,1-trichlroethane used in 321-M and 313-M was recycled by a solvent distillation unit in each building in 1985. Trichloroethane was heated to its boiling point; evaporated solvent rose to the top of the still and then was condensed by cooling coils. The condensate went through a water separator and into a solvent cleaning tank. The oils and grease were removed as sludge by heating the solution. The still was considered a closed loop system.

Emission estimates for equipment were not made because the degreaser emissions were estimated using the difference of the use and disposal information. The estimates also accounted for fugitive emissions from the distillation units or hold tanks and losses to sumps (Radian 1992a).

Use of 1,1,1-trichloroethane in M-Area seemed to be a function of the production of caps and cans. The cores were plated then put inside a can, so there was a one to one correspondence between the number of caps and cans cleaned and the number of parts plated. Degreasers were completely changed out from one to four times each year. Engineers calculating the emissions for

1996 permit plotted the trichloroethane use as a function of production for each month from November 1986 to August 1987 and found that the use and production were correlated as expected. In 1992, Radian tried to correlate the use of trichloroethane reported in degreaser and solvent disposal logs to production from November 1986 to August 1987. After accounting for tank cleaning and changeout of degreasers and the number of parts from storage or recovery, which inflated the number of caps and cans actually cleaned, a correlation was found (Radian 1992a) (see Table 17-18).

Table 17-18. Estimates of the Production and Use of Trichloroethane Cleaning Solvent from November 1986 To August 1987[a]

Month and year	Number of parts produced	Gallons of 1,1,1- trichloroethane used
11/86	11881	170
12/86	15795 [a]	258
01/87	11743	255
02/87	7744	163
03/87	12427	532
04/87	12739	113 (278)[b]
05/87	5887	256 (91)[b]
06/87	2507	72
07/87	5468	338
08/87	713	129

[a] In December 1986, 32,652 parts were produced, but 16,857 parts were thought to have come from storage or recovery and were not reflective of the number actually cleaned that month.

[b] Degreaser records for April 1987 suggested than only 113 gal of trichloroethane were added for 12,739 parts plated. The tank was cleaned on May 7. Radian attributed the cleanout volume to April and subtracted the amount for May, averaging the two points. Adjusted values are in parenthesis.

Source: (Radian 1992a).

Emissions from the cap/can line were listed for 61 sources. A maximum production rate of 110 cans h^{-1} and an average rate of 528 caps and 528 cans per shift was used for production of all types of caps and cans. The degreasers held 165 gal of trichloroethane each, and evaporation and dragout emissions were exhausted out one of several hoods along the line (Radian 1992a).

The calculations given in the notebook were for documentation of general methods and do not describe how emissions for each source were calculated. It seems that the methods required more detailed information than we have been able to collect for the dose reconstruction. The methods also seem to be conservative. The estimates are probably less uncertain than any we could calculate based on information available to us now. In their 1992 recommendations for improving the emissions estimates, Radian suggested that better use data, tank throughput data, waste generation and solvent charge data records should have been kept, which suggested that these records were incomplete or inadequate. Used solvent was shipped to offsite solvent recovery, and although the shipping records were not compiled in an areawide useful format, it appears that Radian used these types of records to estimate solvent disposal.

The disposal rate was used to determine the production in comparison to other years. Radian reported that interviewees indicated that the tool degreaser operated about 4 hours per day and was covered when not in use. Because the use and disposal data for this equipment were not available, Radian (1992a) used the production for caps/cans and assumed that emissions were a function of the production rate.

Radian (1992a) estimated actual emissions for 1985–1990 using use and disposal logbook data obtained during interviews. Fugitive emissions (dragout, recycling still losses, holding tanks, floor sumps, etc.) were calculated as the difference between use and disposal volumes. As *RAC* has also found, these data were not available for much of the time period. However, data on trichloroethane use from November 1986 to August 1987 were plotted against production through 313-M (see Table 17-18). After making corrections for cleaning out the tanks and adding stored parts into the production, the two correlated well. Therefore, the use data for this 1 year, where it seemed most complete, was scaled based on production for other years. Although the degreasers have cooling coils that might be considered a pollution reduction device, no other abatement equipment was in place and all emissions were assumed to have been uncontrolled. The operating procedures (DPSOL313-230) specified that the heat was to be turned off and the degreaser cover was to be kept closed when the degreaser was not in use. If this was done, the downtime releases should have been minimal. The tool degreaser was assumed to have been used 4 hours each day and was covered when not in use. The cap/can degreaser operated 24 hours each day in 1986. The ultrasonic cleaners in 321-M used Freon, so they were not included.

Peak production for Building 313-M was said to have been in 1985 and 1986, 'ramping down' in 1987, and stopping in 1988. The emissions rate, based on maximum solvent use during this peak production period for the degreaser, was reported to have been about 96 ton y^{-1} in 1985 and 1986. Degreaser emissions for 1987 totaled 43.3 ton (Westinghouse 1996a).

For 1985, 1986, and 1987, a materials balance approach was also used, calculating the amount emitted as the difference between the amount used and the amount reported to have been disposed. The use and disposal data for 1986–1987 were scaled to production for other years and provided the basis for the annual actual estimates for 1985–1990.

Emissions for 1987 and 1988 were calculated by comparing production rates for 1986 with years for which log information was missing. The production in 1987 was said to be 200,000 parts, resulting in 19 ton y^{-1} of degreaser solvent from a Freon degreaser. Production in 1988 was said to have been 175,000 parts, corresponding to 16.6 ton y^{-1} based on the 1987 degreaser log data.

Calculations of trichloroethane release from degreasers involved using a measured emissions rate for a Freon degreaser bath, then applying this value to other degreasers by relating the surface areas and vapor pressures of other solvents in various tanks and baths. The design annual emission rate was obtained by converting pounds per hour to pounds per year, assuming 8760 h y^{-1}.

Emissions test data from 321-M for Freon were applied to the degreasers in 313-M by assuming that solvent releases were proportional to the tank surface area. Because the monitoring data were for Freon, Radian (1992a) used the ratio of the vapor pressure of trichloroethane to Freon to estimate trichloroethane emissions.

For example, the 321-M degreaser for which stack test data was available was 10,080 in^2 and used Freon. The 313-M cap/can degreaser of interest was 2520 in^2 and used trichloroethane.

$$65.4\,\text{lb h}^{-1} \times \frac{263\,\text{mmHg vapor pressure trichloroethane}}{602\,\text{mmHg vapor pressure Freon}} \times \frac{2520\,\text{in}^2}{10080\,\text{in}^2} = 7.14\,\text{lb in}^{-2}\ \text{trichloroethane}$$

$$7.14\,\text{lb h}^{-1} \times 8760\,\text{h y}^{-1} = 62{,}546\,\text{lb y}^{-1} = 31.3\,\text{ton y}^{-1}\ \text{trichloroethane maximum design emissions}$$

This kind of calculation for maximum design emissions was done for all of the degreasers in M-Area.

The degreaser in 313-M was not used in 1988, 1989, or 1990, so the actual emissions estimates were zero. Emissions estimates for the specific degreasers were obtained from the worksheets and are summarized in Table 17-19.

Table 17-19. Estimates of Solvent Emissions from M-Area Degreasers for Selected Years Between 1985 and 1990[a]

Equipment	Years	Pounds per year design maximum	Pounds per year actual based on (use – disposal)	Comments
313-M cap/can degreaser	1985	62,546	40,874 (47408 – 6534)	1985, 90% production
	1986		45,413 (52673 – 7260)	1986, 100% production
	1987		13,624 (15802 – 2178)	1987, 30% production
	1988	62,546	0	degreaser not in use,
	1989		0	degreaser empty
	1990		0	
Tool degreaser	1985–1990	62,546	7569	scaled by 4 hrs/24 hrs
320-M solvent degreaser	1985	250,300	145770	actual based onsite
	1986		145770	interviews
	1987		72920	
	1988–1990	250,300	0	degreaser not in use, degreaser empty
321-M tube cleaning degreaser	1985	250,300		
	1986			
	1987			
	1988–1990		0	used Freon
321-M component cleaning degreaser	1985	85,664	5214	based on production,
	1986			related to 1986
	1987			
	1988–1990	85,664	0	degreaser not used, degreaser empty

[a] These estimates were developed by Radian (1992a) for the air emissions inventory.

Degreaser releases in Table 17-19 totaled 99.7 ton in 1985, 99.3 ton in 1986, and 47 ton in 1987. Working losses from the trichloroethane tanks were also calculated. The large tank had an

economizer vent to minimize breathing losses. Working losses for the tank were 116.4 lb y^{-1} from 1985 to 1988 and zero in 1988 and 1989 when tank was not used (Radian 1992a).

From 1987 to 1995, the TRI, reported to the EPA and SCDHEC, included estimates of the pounds per year of 1,1,1-trichloroethane released from the SRS (Westinghouse 1996b) (Table 17-20). The estimate for 1987 is much larger than the air permit application estimates (Westinghouse 1996a).

Table 17-20. Estimates of 1,1,1-Trichloroethane Released from the SRS

Year	Air emissions(lb y^{-1})	Ton y^{-1}
1987	429,800	215
1988	10,400	5.2
1989	21,300	10.6
1990	18,290	9.2

[a] Source: Westinghouse (1996b).

Summary

This section has presented many pieces of information on the use and release of chlorinated solvents from M-Area. Several approaches could be used to estimate releases of chlorinated solvents to the atmosphere based on the information collected from historical reports and the more recent air emissions inventory information. It is difficult to know which data to use and how to weight information according to its reliability or applicability to developing a source term. Data from the mid to late 1980s are most complete, but they might not apply to the 1960s when the older, leaking degreasers were in use.

We believe that almost all of the chlorinated solvents used were discharged to surface water until 1979 and most of this evaporated. In other studies of this kind, where information on site-specific environmental fate and transport are lacking, researchers have estimated that 95–100% of the chlorinated solvent was released to surface water or soil evaporates (McGavran et al. 1996; ChemRisk 1994). Unfortunately, inventory amounts did not always reflect use and are not available for all facilities or all time periods. Christensen and Brendell (1981) attempted to base their release estimates on solvent consumption estimates, which were based on purchase records. However, they found that the records for trichloroethylene were not available, and their use estimates had to be derived from “M Area personnel judgment.”

Christensen and Brendell (1981) estimated that solvent use from 1952 to 1979 totaled about 13 million lb or about 6500 ton. They estimated approximately 1850 ton of trichloroethylene, 4350 ton of tetrachloroethylene, and 335 ton of trichloroethane were used during that time period. For 1970, Christensen and Brendell (1981) estimated 89 ton of trichloroethylene and 54 ton of tetrachloroethylene were used. Monier (1970) estimated the gallons of 100% solvent released to Tim’s Branch and the settling basin, which corresponded to 58.5 ton of trichloroethylene and 66.9 ton of tetrachloroethylene, using a 10.9 lb gal^{-1} conversion. Monier (1970), in a 1-page memo, presents values for tetrachloroethylene discharged that are about 20% greater than Christensen and Brendell (1981) estimates for use. However, the Monier (1970) estimate for trichloroethylene is about 30% of the Christensen and Brendell (1981) use estimate. The Monier (1970) estimates were said to have been based on production levels, but how the estimates were made is unknown. Hardt (1970) estimated that 6 ton of trichloroethylene and 45.5 ton of tetrachloroethylene were

released to Tim's Branch in 1 year. Looney et al. (1987) estimated that 16.5 ton of trichloroethylene and 92.4 ton of tetrachloroethylene were discharged to the settling basin from 1971–1985, which averages to about 1.1 ton y^{-1} of trichloroethylene and about 6.2 ton y^{-1} for tetrachloroethylene over the 15-year period. The variability of the estimates is large, but the estimates of Christensen and Brendell seem larger than most. Their estimates seem to be the most defensible because they explained the methods used to calculate their estimates.

Essential Materials Ledgers suggest that about 2.4×10^6 kg or 2662 ton of trichloroethane was used from 1979–1986 (Westinghouse 1984, 1985, 1987a). The 1979 Essential Materials Reports suggest that 253 ton was used that year, an estimate nearly 3 fold larger than the 85-ton estimate reported in Christensen and Brendell (1981).

The largest shipments of chemicals were received by M-Area between August 1984 and September 1986 (Gary 1996). The permit application and Site workers stated that production for Building 313-M was greatest in 1985 and 1986, began ramping down in 1987, and stopped in 1988 (Westinghouse 1996a; Gary 1996). Radian determined that peak production was in 1986. They called this 100% and assumed that 1985 production was 90% and 1987 production was 30% of the production in 1986 (Radian 1992a). Radian (1992a) actual emissions estimates implied that five degreasers were operating in 1985, but only three were operating in 1986. The essential materials ledgers suggest that more trichloroethane was used in 1985 than in 1986 (Westinghouse 1987a). Based on production information compiled for the permit application (Westinghouse 1996a), we assumed that the 1987 amounts were 30%, the 1988 amounts were 26% of the 1986 amounts, and that there was no production in 1989.

If we subtract the amount of solvent estimated by Christensen and Brendell (1981), shown in Table 17-6, to have gone to the Tim's Branch and settling basin from the total amount used for the different time periods, then from 77–85% of the solvent remains. This amount might have evaporated during routine use in M-Area. If 95% of what was released to the sewers and then to the Tim's Branch or the settling basin in turn evaporated, then the total amount evaporated would be the amount evaporating during use plus 95% of what was discharged. For the values derived by Christensen and Brendell, this seems an unnecessarily complex analysis given the uncertainty of the values. As demonstrated in Table 17-21 (for trichloroethylene and the first 8 years of tetrachloroethylene use), the total amount evaporated from use and discharge to surface waters equals about 99% of the amount used. From 0.9–1.2% may have remained in groundwater.

If we assume that 95–99% of the solvent used before 1980 evaporated into the air (eventually as it was used in degreasers or after being released into liquid effluent), then we might estimate that the range of amounts given in Table 17-22 might have evaporated into the air. All of the estimates in the second and third columns of Table Table 17-22 are from Christensen and Brendell (1981).

Table 17-21. Trichloroethylene and Tetrachloroethylene Evaporated during Use and Surface Water Discharge[a]

Time period	Tons used per year minus release to sewers	Tons remaining	% remaining per year	95% released to sewers	Total tons release to air each year
Trichloroethylene					
1952–1985	76.5 – 11.5	65	85	11	76
1959–1961	140 – (12.5 + 11.5)	116	83	23	139
1962–1970	89 – (12.5 + 7.5)	69	77	19	88
Tetrachloroethylene					
1962–1970	54 – (12.5 + 7.5)	34	63	19	53

[a] The amount of solvent used, minus the amount discharged to the sewers, plus the amount evaporated from sewers, equals the amount evaporated during use and surface water discharge.

Table 17-22. Use Amounts Estimated by Christensen and Brendell (1981) and 95% and 99% of These Amounts

Time period	Amount used per year	Total = amount used per year × number of years	95% of the amount used	99% of the amount used
Trichloroethylene				
1952–1958	76.5	535.5	72.7	75.7
1959–1961	140	420	133	138.6
1962–1970	89	801	84.5	88.1
1952–1970 total		1756.5	1668.7	1738.9
Tetrachloroethylene				
1962–1970	54	486	51.3	53.5
1971	185	185	175.7	183.2
1972	315	315	175.8	311.8
1973	415	415	394.2	410.8
1974	335	335	318.2	332
1975	575	575	546.2	569.2
1976	500	500	475	495
1977	560	560	532	554.4
1978	412	412	391.4	407.8
1979	412	412	391.4	407.8
1962–1979 total		4195	3985.2	4153
Trichloroethane				
1979	85	85	80.75	84.2
1980	150	150	142.5	148.5
1981	100	100	95	99
1979–1981 total		335	318.2	331.7

After 1979, trichloroethylene and tetrachloroethylene were not being used. Most of the solvent was recycled and waste solvent was barreled and buried. Eliminating most of the surface water discharges greatly reduced the amount evaporating from surface water, but trichloroethane in the degreasers continued to evaporate into the air during use and leakage of equipment or spills. After 1985, the air stripper emissions also contributed to releases to air.

The estimates in Table 17-23 are derived from the values reported in the M-Area essential materials and inventory control ledgers (Westinghouse 1984, 1985, 1987a), except for 1988, which was calculated to be 26% of the 1986 production levels according to the values compiled for the permit application (Westinghouse 1996a). We believe the 1987 ledger total of 825 ton is in error. It is more than twice a value that would be consistent with the other ledger entry totals. The handwritten 1987 entries were difficult to read and had been corrected several times. In addition, several different sources insist that production and use in 1987 was less than in 1986 or 1985 (Gary 1996; Westinghouse 1996a; Lorenz 1998). With the exception of this one entry, the largest value for each year was used. The estimate for 1987 was derived from the TRI submitted to the EPA (Westinghouse 1996b). The air permit application suggested production in 1987 was 30% of 1986, which led to an estimate of 119 ton of trichloroethane used in 1987. The TRI estimate of trichloroethane releases from the Site is 215 ton, almost twice the permit's estimate of the amount used. There are no other large sources of trichloroethane at the SRS as far as we know to account for the difference. The TRI is certainly a conservative estimate, but 119 ton may be an underestimate.

Christensen and Brendell (1981) estimates for trichloroethane in Table 17-22 were much less than those in Table 17-23 and were not used to derive totals. After 1979, when waste solvent was barreled and more care was taken to limit releases, we assume that 75–95% of the solvent used eventually evaporated from the process, resulting in the estimates in Table 17-23.

Table 17-23. Amount of 1,1,1-Trichloroethane Used, Estimated from the Essential Materials Ledgers and Operating Permit Application, and 75% and 95% of These Amounts

Time period	Amount used	75% of the amount used	95% of the amount used
1979	253	189.7	240.4
1980	143	107.2	135.8
1981	198	148.5	188.1
1982	275	206.2	261.2
1983	308	231	292.6
1984	308	231	292.6
1985	264	198	250.8
1986	396	297	376.2
1987	215	161.2	204.2
1988	103	77.2	97.8
1979–1988 total	2463	1847.2	2339.8

These estimates are larger than the air permit applications estimates for the M-Area degreasers, which total about 100, 99, and 47 ton in 1985, 1986, and 1987, respectively.

The DOE Environmental Survey team thought that 200 ton y^{-1} of trichloroethane may have been released into the air from M-Area. The survey report mentioned that 1,1,1-trichloroethane released from the M-Area was derived from measured release data (DOE 1987). However, no records or personnel recollecting any monitoring of solvents in M-Area have been found during

our study. The monitoring data from which their estimate was derived were not summarized in their report. It is interesting that the average of 75% of the use amount for 1979–1988 is 187 ton y^{-1} and for 95% it is 243 ton. The average of 75% of the use estimates for 1984–1987, when the survey was being conducted, is about 220 ton y^{-1}.

After 1985, the air strippers released trichloroethylene and tetrachloroethylene to the air. The catox unit reduction of emissions seemed to be obvious after 1989. The accuracy of estimates in the annual reports, compared to the operating permit, compared to the AIRS database, is unknown. Because they are the largest, most conservative estimates, we used the estimates in the calculations made to estimate the AIRS database emissions estimates (Radian 1992a). The estimates in the calculations notebook appear to be higher than the AIRS database estimates for the M-Area air stripper in 1985–1987, but they are lower by as much as a factor of 2.5 for 1988–1990. For the estimates in Table 17-24, we used the highest value given for 1985–1990. We assumed that 70% of the solvent released was trichloroethylene and 30% was tetrachloroethylene based on the assessment by Colven et al. (1987).

Table 17-24. Estimates of Trichloroethylene and Tetrachloroethylene Released from Air Strippers and Soil Vacuum Extraction Units

Year	Total emissions from the air strippers in tons	Trichloroethylene	Tetrachloroethylene
1985	9.8	6.8	3.0
1986	24.4	17.1	7.3
1987	22.1	15.5	6.6
1988	18.4	12.8	5.6
1989	14.2	9.9	4.2
1990	4.4	3.1	1.3
1992	8.6	6.0	2.6
1985–1992 total	102	71.3	30.6

We might refine this estimate by subtracting what was known to have contaminated groundwater, been barreled for disposal, or retained in the soil. We know that much of the tetrachloroethylene was recycled by distillation, beginning in about 1971, but eventually most of this would have evaporated. We know some of the solvent released to soil and surface water was degraded and some remained complexed in the soil. However, environmental fate and transport studies on lakes and streams suggest this was probably a small percentage of the total. We know an amount of solvent worthy of remediation has seeped into the groundwater below M-Area. We have little basis for a reasonably certain estimate of how much solvent traveled to the groundwater below M-Area. We might also assume that a large percentage of the solvents in the groundwater will eventually be removed and released to the air through the remedial air stripping program. Some of the information available about these quantities, generated by the Site for all three solvents are summarized in Table 17-25.

Table 17-25. Summary of the Use and Release and Inventory Estimates for Chlorinated Solvents in M-Area for Various Time Periods (amounts are in tons)

Inventory	Time period	Trichloro-ethylene	Tetrachloro-ethylene	Trichloro-ethane	Reference
Settling basin soil inventory	1971–1985	0.18	3.96	0.15	Looney et al. (1987)
Total amount in the groundwater below M-Area, total solvent reported, 70% reported to be trichloroethylene	1987	121	51.7		Colven et al. (1987)
In the groundwater, 70% assumed to be trichloroethylene	1992	99	42.7		Arnett et al. (1993)

Similar kinds of amounts were reported for all three chlorinated solvents combined. From 1952 to 1970, we can assume that no trichloroethane was used, but it is hard to estimate what percentage of the total is trichloroethylene compared to tetrachloroethylene. Table 17-26 summarizes the various total inventory amounts in groundwater and estimates of the amount removed from groundwater using the air strippers taken from various reports.

Table 17-26. Total Chlorinated Solvent Estimated Inventories from Various Reports

Inventory	Time period	Amount of solvent (in kg)	Reference
Total amount of solvents in groundwater in 1990	1989	225 ton	Bebbington (1990)
Amount estimated to have been removed from groundwater as of 1992	1992	143 ton	Arnett et al. (1993)
M-Area air stripper	1985–1990	176 ton for 5 years	Westinghouse (1996a)
M-Area air stripper	1985–1990	102 ton for 6 years	Radian (1992a)
M-Area and A-Area air stripper	1985–1994	121 ton for 10 years	Faugl (1996l, 1996m)
M-Area air stripper	1987	35 ton for year	DOE (1987)

An estimate of releases of all three solvents to the air could be made more accurate by subtracting the amount thought to have been retained in the settling basin soil and the amount thought to have traveled to the groundwater, then adding back the air stripper releases. However, the estimates we have for the amount in groundwater and soil are very uncertain and very small relative to the total amounts released. We added the air stripper releases because they occurred from 1985 to the present time, were based on monitoring data, and seemed fairly reliable.

Estimates of the amount of solvent in groundwater or removed from groundwater since 1985 vary from about 100 ton to more than 200 ton as shown in Tables 17-25 and 17-26. This is 2–3%

of the total amount of trichloroethylene and tetrachloroethylene that we estimate may have been used. Given the wide range of uncertainty associated with these estimates, the subtraction of the relatively small amount lost to groundwater would make little difference to the totals. These solvents are fairly soluble in water and would not be expected to be retained in settling basin soil. Looney et al. (1987) estimates of the total solvent inventory in basin soil are less than 0.07% of the total amount of the two solvents used. Subtracting these values would make the total estimates less conservative. For these reasons, subtracting the amounts did not seem justified.

We might also try to refine the estimate using what we know about the volatility of the solvents and the history of operations in M-Area. Although tetrachloroethylene is less volatile than trichloroethylene, it was used during a time when the degreasers were older, more corroded, and leaking. In 1979, we know that new degreasers were put in place, tetrachloroethylene was replaced with trichloroethane, and solvent residues and sludge were being barreled for disposal. Much less trichloroethane was discharged to the process sewers and Tim's Branch after 1979. Before waste solvents were barreled and buried in 1979, almost all of the solvent used eventually evaporated. Assuming that 95–99% of what was used eventually evaporated seems to be a reasonable but cautious assumption.

Based on the assumption that 95–99% of what was used before 1980 and 75–95% of what was used after 1980 was released to the air, the ranges total

- 1740–1810 ton of trichloroethylene: 1669–1739 ton from M-Area operations from 1952–1970 and 71 ton from the air strippers from 1985–1992
- 4016–4184 ton of tetrachloroethylene: 3985–4153 ton from M-Area operations from 1962–1979 and 31 ton from the from the air strippers from 1985–1992
- 1847–2340 ton of 1,1,1-trichloroethane from M-Area operations from 1979–1988.

The total for all three solvents is 7603–8334 ton. These ranges represent the assumption of 95–99% for 1952–1979 and 75–95% for 1980–1992. These ranges do not represent propagated uncertainty values.

These estimates are probably greater than a central value because of the conservative assumptions made for the air emissions inventory and permit application and our cautious assumption that 95–99% of what was used from 1952–1979 and 75–95% of what was used from 1979–1988 eventually evaporated. We do not know whether the estimates used for 1952–1985 overestimate or underestimate the true releases. Some people may think that because the degreasers are covered when not in use, used solvent was distilled and recycled and still bottoms were barreled after 1979, estimating 75–99% of the solvent used volatilized is an overestimate. However, we have little information on the condition of the degreasers or about leaks and spills before 1985 and studies of other degreasing operations have shown that assuming 75–99% evaporation is not unreasonable.

The uncertainty in the estimates is large. Various estimates of usage from different sources suggest that use estimates may vary by as much as a factor of 3, especially for those derived from monthly ledgers. The amount evaporated may have varied from 75–99% of what was used, depending on the retention of the material, migration in groundwater, degradation, and other parameters for which we have little or no site-specific information.

Based on a factor of three uncertainty in usage and using likely usage quantities described previously, and also utilizing ranges of percent released from volatilization, uncertainty was calculated for chlorinated solvents. Triangular distributions were assigned to the usage estimates,

with the preferred value being the most likely estimate. Uncertainty in percent volatilized was represented by uniform distributions. Total releases for the periods during which each solvent was used were estimated for comparison with the above totals.

For trichloroethylene, usage during the years 1952–1970 resulted in total releases from M-Area operations that are lognormally distributed with a geometric mean of 1700 ton and a geometric standard deviation of 1.07. This distribution increases the range of releases between the 5^{th} and 95^{th} percentiles to 1530–1900 ton. This 5^{th}–95^{th} percentile range is used to describe all subsequent uncertainty ranges. Releases from the air strippers for this solvent from 1985–1992 are also lognormally distributed with a geometric mean of 70 ton and a geometric standard deviation of 1.14. The range on these releases is from 57–87 ton.

Tetrachloroethylene releases total 4055 ton with a GSD = 1.09 for the years 1962–1979, with a range from 3520–4675 ton. For the air strippers, this solvent was released over the period from 1985–1992 in the quantity of 30 ton with a GSD = 1.2. The air stripper releases ranged from 22–40 ton.

A variety of trichloroethane release estimates were made from 1979–1988. Factor of three uncertainty bounds were placed on releases that did not have estimates with a range this great, but even larger bounds were used if the estimates of release exceeded a factor of three. Uncertainty calculations for releases of this solvent were lognormally distributed with a GM=2200 ton and a GSD=1.14, with releases ranging from 1780–2710 ton.

The Standard 8 results submitted to SCDHEC said that in 1991, trichloroethylene was emitted by 24 sources in A-Area, E-Area, F-Area, G-Area, H-Area, L-Area, and M-Area. The ambient standard was 6750 μg m^{-3}, and the maximum 24-hour average Site boundary concentration was calculated to be 4.77 μg m^{-3}. The Standard 8 results submitted to SCDHEC said that in 1991, tetrachloroethylene was released from 22 sources in A-Area, E-Area, F-Area, G-Area, H-Area, M-Area, and N-Area. The maximum 24-hour average Site boundary concentration was calculated to be 2.0 μg m^{-3}. The ambient air standard was 3350 μg m^{-3}. Since M-Area operations have stopped, tetrachloroethylene and trichloroethane releases seem to be from many different sources that use small amounts for cleaning, degreasing, or laboratory work.

Chlorinated Solvent Releases from the Reactor Areas

Chlorinated degreasing solvents were also used in the reactor areas, as a cleaner in the tritium facilities, and probably in the canyons as well.

In an analysis of M-Area use of solvents, Christensen and Brendell (1981) reported that each of the reactor areas (C, K, L, P, and R) had 1000-gal degreasers. They also noted that the 105 Buildings in the reactor areas obtained one or two barrels of solvent from M-Area storage each year (Christensen and Brendell 1981). We have been unable to find records that characterize the use of the degreasers in the 100-Areas. It is likely that each was used as long as each reactor was operating. Documentation on the rate of solvent use and how dirty solvents were disposed of has not been found. Emissions of chlorinated solvents from the reactor areas were not included in the AIRS database emissions estimates.

Trichloroethylene is also mentioned in several reports as having been a quality assurance concern in the reactor areas. A Works Technical Monthly Report from February 1953 says that a "difficulty with trichloroethylene in the 305 reactor had been substantially eliminated" (Du Pont 1953). Reactivity had been nearly restored to its initial level. However, there were still traces of

trichloroethylene in the effluent gas that was being recirculated through a purification system. They expected it to take months to remove all traces. Meanwhile, the reactor was back in normal operation. Efforts to avoid any similar problem in the 100-Areas were intensified. The Reactor Technology Section of the report for this same month reports that a means for detecting small quantities of triclene in the reactor complex and in fuel column assemblies was investigated. The GE leak detector was being used for this purpose in 305 Building, and this appeared to be a satisfactory method.

The Metallurgy Section Report added that trichloroethylene was being removed in a 3-week air purge at a rate of about 2 g h^{-1}. Helium was being discharged from the pile, purified of trichloroethylene, and recirculated through the pile (Du Pont 1953). Mention of this problem does not occur in subsequent years. Although the nature of the problem is not completely clear, it did not appear to involve environmental releases or large quantities of solvent and does not seem to be of concern for dose reconstruction. It seems that trace amounts of trichloroethylene on fuel, and perhaps other reactor components, led to trichloroethylene vapors in the blanket gas.

Chromium

Chromium is a carcinogenic metal. Hexavalent chromium (VI) is more toxic than the predominant form in the environment, trivalent chromium (III). Chromium (VI) is corrosive and causes ulcerations, liver and kidney damage, and a wide range of respiratory effects. Hexavalent chromium causes lung, nasal, gastric, and other cancers in humans, and high levels cause birth defects in laboratory animals.

Chromium may have been released to the air as a contaminant of ash from coal burning. Particulates from coal-fired power plants have been shown to contain chromium in the range of 2.3–31 ppm, reduced to 0.19–6.6 ppm by fly ash collectors (EPA1988).

Emission factors for drift losses from cooling towers described in AP-42 could be used to calculate chromium emitted as drift from the towers as water cycles through and aerosolization from cooling towers. These calculations would be based on the assumption that dissolved salts and suspended solids become concentrated in the liquid phase as a result of evaporation. However, data on the throughput through cooling towers is not readily available. Although chromium concentrations in some of the cooling and process water spills (summarized in Chapter 18) were estimated, we do not know the concentration of chromium in cooling water, nor the time periods for which chromium was used for water treatment in different areas. Lacking this information, we can not estimate chromium releases to the air from cooling water with acceptable uncertainty. A screening calculation based on information about how much cooling and process water was treated with chromium and how much of this water was run through some sort of cooling tower where it may have be subject to aerosolization might be useful. Based on chromium concentrations and throughput data, 37 kg of chromium was the maximum amount calculated to have drifted from reactor cooling water at Argonne National Laboratory-West in 1972, under worst-case conditions when the throughput was an estimated 1.8×10^7 gal y^{-1} (Argonne National Laboratory-West 1973). Although worst-case, this amount was below levels of industrial hygiene concern for workers working under the towers. SRS progress reports contain information on discharges of water to surface streams and seepage basins. From this, a maximum of 2.1×10^{11} gal y^{-1} was discharged from the reactor areas and separations areas. If all of this water was heavily treated with chromium, like the water used at the Argonne Cooling Towers,

then as much as 475 ton of chromium may have been aerosolized, for the worst case. Generally, drift from cooling towers and aerosolization of chromium-treated water from other uses may be of concern for worker exposure, but they are not of concern for offsite exposures. Emissions estimates for chromium were extracted from the AIRS database. Chromium sources for 1985 included 56 welders, 3 diesel fire protection pumps, 16 diesel generators, 21 emergency diesel generators, and 12 grinders. In 1987, chromium emissions were reported from 31 welders, 3 diesel pumps, 18 diesel generators, 21 emergency diesel generators, 5 grinders, and 1 blaster. In 1991, chromium releases were estimated for 8 grinders; 54 welding units (listed as welding exhaust, arc welders, welding machines, plasma arcs, arc torches, welding tables, pack welders, seam welders, tank welders, and other welding operations); 3 pumps; 21 diesel generators; 22 emergency diesel generators; and 1 blaster. These sources were calculated to emit less than 10^{-3} ton y^{-1} actual in 1985 and most of these emissions estimates were less than 10^{-6} ton y^{-1}.

Table 17-27. Chromium Releases of Most Concern

Year and source description	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1985		
Coal Storage pile in H-Area	1.5×10^{-3}	9.0×10^{-5}
H-Area Powerhouse, ash sluice sump	2.2×10^{-4}	4.4×10^{-5}
H-Area Manufacturing Building 232 radiological equipment repair	7.8×10^{-3}	1.3×10^{-4}
H-Area Manufacturing Building 234 finishing operations	1.34×10^{-4}	1.43×10^{-4}
H-Area Manufacturing Building 234 inert finishing operations	1.73×10^{-5}	1.73×10^{-5}
H-Area Manufacturing Building 234 fabricated metals machining	2.60×10^{-1}	8.69×10^{-2}
H-Area Reclamation Building 238 Milling and machining hood	1.17×10^{-3}	1.70×10^{-4}
H-Area Reclamation Building 238 lathe hood, Room 1	2.35×10^{-2}	2.59×10^{-4}
H-Area, Building 241058 Maintenance and E&I shops grinding		
There are four of these:		
1. Aluminum grinder	3.13×10^{-2}	1.30×10^{-3}
2. Vertical drill press	3.13×10^{-2}	3.91×10^{-3}
3. Band saw	3.13×10^{-2}	1.30×10^{-3}
4. Abrasive Belt Grinder	3.13×10^{-2}	1.30×10^{-3}
K-Area coal pile	4.9×10^{-5}	4.9×10^{-5}
K-Area coal storage run-off containment basin	4.9×10^{-5}	4.9×10^{-5}
1987 emissions were the same as 1985, with the addition of:		
H-Area Building 232 Hood metallurgy	4.50×10^{-2}	1.08×10^{-3}
H-Area Building 232 Hood cutting	2.85×10^{-2}	1.34×10^{-3}
H-Area Manufacturing Building 232 radiological equipment repair	7.8×10^{-3}	1.3×10^{-4}
H-Area Manufacturing Building 234 finishing operations	1.56×10^{-4}	1.56×10^{-4}
H-Area Manufacturing Building 234 inert finishing operations	3.19×10^{-5}	3.19×10^{-5}
H-Area Manufacturing Building 234 fabricated metals machining	2.60×10^{-1}	8.69×10^{-2}

Year and source description	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
H-Area Reclamation Building 238 milling and machining hood	1.17×10^{-3}	1.64×10^{-4}
H-Area Reclamation Building 238 lathe hood, Room 1	2.35×10^{-2}	3.29×10^{-5}
H-Area, Building 241058 Maintenance and E&I shops Grinding included four sources:		
1. Aluminum grinder	3.13×10^{-2}	1.30×10^{-3}
2. Vertical drill press	3.13×10^{-2}	3.91×10^{-3}
3. Band saw	3.13×10^{-2}	7.14×10^{-3}
4. Abrasive belt grinder	3.13×10^{-2}	1.30×10^{-3}
K-Area coal pile	4.9×10^{-5}	4.9×10^{-5}
K-Area coal storage run-off containment basin	4.9×10^{-5}	4.9×10^{-5}
1990		
H-Area Building 232 hood metallurgy	4.50×10^{-2}	1.08×10^{-3}
H-Area Building 232 hood cutting	2.85×10^{-2}	1.34×10^{-3}
H-Area Manufacturing Building 232 radiological equipment repair	7.8×10^{-3}	6.50×10^{-5}
H-Area Manufacturing Building 234 finishing operations	1.55×10^{-4}	1.56×10^{-4}
H-Area Manufacturing Building 234 inert finishing operations	3.19×10^{-5}	1.43×10^{-5}
H-Area Manufacturing Building 234 fabricated metals machining	2.60×10^{-1}	8.69×10^{-2}
H-Area Reclamation Building 238 milling and machining hood	1.17×10^{-3}	1.57×10^{-4}
H-Area Reclamation Building 238 lathe hood, Room 1	2.35×10^{-2}	3.77×10^{-5}
K-Area coal pile	4.9×10^{-5}	4.9×10^{-5}
K-Area coal storage run-off containment basin	4.9×10^{-5}	4.9×10^{-5}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Table 17-28 presents the total emissions for years 1985, 1987, 1990, and 1992.

Table 17-28. Total Chromium Emissions for 1985, 1987, 1990, and 1992

Year	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1985	4.51×10^{-1}	9.92×10^{-2}
1987	4.85×10^{-1}	1.02×10^{-1}
1990	4.89×10^{-1}	1.01×10^{-1}
1992	4.14×10^{-1}	5.37×10^{-2}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

About 125 emissions points were listed for chromium each year. The largest air emissions for chromium reported were from machining in 234-H, followed by the maintenance shops grinding and drilling operations in H-Area (Faugl 1996d). The total actual release estimate in the AIRS database was about 0.1 ton y^{-1} or 200 lb y^{-1} in the late 1980s and 1990s. The maximum release estimate in the AIRS was about 0.46 ton y^{-1}. It is likely that metal fabrication and welding operations may have been greater in the early years when many facilities were being constructed. Generator use is probably greater today than in the early years of operations. Chromium releases probably totaled from 0.1 to 0.5 ton y^{-1} for most years. There was not enough information available to do useful uncertainty calculations for the chromium release estimates. There is insufficient information available to estimate chromium releases from its use as a corrosion inhibitor in cooling and process water with reasonable certainty.

Coal

Much of the electric power distributed at the SRS was generated onsite at the power plants. These plants also provided steam for the Site. Historically, electricity and steam at the SRS has been generated by burning coal. The coal was generally moderately to low sulfur coal, which was received by rail, sprayed with water, and stored in open piles. Coal piles originally existed in A-Area, C-Area, D-Area, F-Area, K-Area, H-Area, L-Area, P-Area, and R-Area. The coal pile in R-Area was removed in 1964, the L-Area coal pile was removed in 1968, and the coal piles in C-Area and F-Area were removed in 1985. In 1991, the K-Area coal pile was removed down to a 2-in. base and 75% of the P-Area coal pile was also removed (Arnett et al. 1993).

The power facilities usually kept at least a 90-day supply of coal, which was not rotated; therefore, the coal was subjected to long-term exposure, weathering, and release to the environment. Oxidation of sulfur compounds in coal piles during weathering can result in the formation of sulfuric acid, and the acid and metals can contaminate rainwater runoff and leachate from coal piles. Releases to surface water from coal and ash are discussed in Chapter 18.

There were seven coal-fired steam plants onsite: 484-D, which has four pulverized coal-fired boilers; 784-A, 184-C, 184-K, and 184-P, which all have two boilers; 284-F with four boilers; and 284-H with three boilers (DOE 1987). The SRS power plants have been in operation since 1952. They have perhaps lasted longer than most commercial coal power plants due, in part, to the fact that only two or three of the four boilers in D-Area and one or two of the two or three boilers in the other areas operated at any one time (Faugl 1996a). The L-Area powerhouse was put out of service in about 1964, R-Area stopped operating in about 1978, and C-Area and F-Area

powerhouses were shutdown between 1985 and 1988. In 1987, the D-Area to F-Area steam line was installed. The K-Area powerhouse has burned oil since 1994 and the P-Area powerhouse has burned oil since about 1987 (Willis 1997). The powerhouses appear to have been operated independently from other facilities in each area. Mention of their operations was rarely made in the monthly progress reports. Very few historical records about the operations of the power plants were located in Phase I. Most of the information on the powerhouses came from interviews with current and former employees of the Power Department, from the recent Title V Part 70 Air Permit (Westinghouse 1996a), or the Site annual environmental reports.

Coal Consumption and Composition

The amount of coal burned before 1972 is unknown. The annual environmental reports summarized the status of power plants onsite and reported the amount of coal burned and the approximate sulfur content of the coal. Beginning in 1972, the reports gave estimates of the power plant emissions of sulfur dioxide, nitrogen dioxide, and fly ash particulates in the early and mid-1970s and carbon monoxide, and volatile organic compounds (VOCs) in recent years, for each year. The site did not conduct analyses to estimate the content other metals, such as cadmium, chromium, lead, manganese, mercury and nickel, in the coal burned. Attempts to locate more primary data on sulfur analysis of coal and coal receipt, inventory, or storage information were not successful. Records of this type were not found in the Phase I document search. Essential materials ledgers for D-Area and the other powerhouses were not located. The Bureau of Mines did much of the coal analysis in earlier years. The regional office recommended we contact the office in Washington, D.C. Neither office had an idea where we might find records of coal analysis for the SRS. In 1996, Tom Thome, Stan Smith, and H.S. (Sid) Willis, with the Power Department; Robert Garvin and Mal Schroeder, who worked in D-Area; and retired workers Henry Main, Ray Fleming, Leo Shelton, Peter Gray, W.B. Holt, and Jim King were interviewed about power plant operations, essential materials records, coal inventory and analysis records, and potential releases of chemicals to the environment.

Many of the people interviewed indicated that dispersion of coal into the air from the coal pile was not considered to have been a problem. It seems that suspension of reject coal and dust from the coal storage piles were not of concern because the moisture content of the coal was very high. At some times during the year, the piles may have been dry, but dust emissions were probably not of concern for offsite exposures. Dust pollution from the piles would probably have been much less than boiler stack releases of ash and other pollutants. Any estimates of fugitive dust emissions would be very uncertain and require a modeling effort that is probably not justified given the low magnitude of the release and the distance from the coal piles to offsite populations.

Emissions of oxides of nitrogen, sulfur dioxide, metals and particulates from the powerhouses because of coal combustion were evaluated for this study. The annual environmental reports provided data on the amount of coal burned; the coal's sulfur content; estimates of the amount of sulfur dioxide, fly ash, and oxides of nitrogen emitted; and how the emissions compared to South Carolina Emission Standards effective at the time. This information and information from other reports about the coal burned and the ash and particulate matter (PM) released was compiled and is summarized in this section. Later in this chapter, nitrogen dioxide

and sulfur dioxide emissions from coal are characterized, along with nitrogen dioxide and sulfur dioxide emissions from other sources. We also assessed the metals contained in coal and in ash emissions and address them individually in this chapter.

Powerhouses

D-Area Powerhouse. The largest power plant was in D-Area. The D-Area power plant has four units or boilers with a total capacity of 396×10^6 BTU h^{-1} (Evans and Giesey 1978). The plant was described in Savannah River Ecology Laboratory (SREL) documents published in the early and mid-1970s as a 83-MW pulverized coal-fired plant with four 38-m stacks that had been in operation since 1952 and burned approximately 2.6×10^5 metric ton of coal each year. The coal and ash disposal and runoff systems used in D-Area are described in Chapter 18.

H-Area Powerhouse. The 284-H powerhouse was southwest of the H-Canyon. The H-Area coal piles were located near the powerhouse. A coal pile runoff basin, with a maximum runoff reported to be approximately 219,400 ft^3, had an overflow pipe that drained water to an NPDES outfall. The basin was reported to be wet most of the time, and fugitive dust emissions were said to be negligible (Radian 1993). A description of the three stoker-fired steam generators at the H-Area powerhouse said that coal, received by rail in hopper-bottom cars, was dumped into a track hopper, conveyed by belt to a crusher, then to a bucket elevator, then to the silo for consumption or to the storage yard. From the silo, the coal was fed into hoppers above each boiler by conveyer. The crusher sized the coal to about ¾-in. Ash generated from this facility was said to go from cinder hoppers by water jets to a jet pump. Dust collectors removed fly ash from gases leaving the boilers. Fly ash was removed from the dust collector hoppers and the stack by a hydroveyor. The ashes were mixed in the hydroveyor with water, discharged to an air separator and then to a jet pump, which discharged to an ash basin about 1500 ft south of the boiler house (Fisk and Durant 1987). Bottom and fly ash collected from the coal-fired boilers were transported to the ash disposal basin via a wet sluice. When the ash slurry reached the basin, the suspended ash settled to the bottom and the supernatant was decanted to an NPDES outfall (Radian 1993).

K-Area Powerhouse. In 1992, two stoker boilers operated in Building 184-K. Cyclonic precipitators were used to control particulate emissions, but sulfur dioxide and nitrogen dioxide emissions were not controlled. Radian (1992b) calculated emissions from the K-Area powerhouse and from coal storage, transport, disposal, and runoff systems. Coal from rail cars was stored in piles and delivered to the crusher by conveyor. Bottom ash and fly ash were transported by wet sluice to an ash disposal (evaporation) pond.

Ash and Particulate Matter

Burning coal produces ash. Ash typically contains arsenic, cadmium, chromium, lead, mercury, and selenium. Ash is of concern as an air pollutant, contributing to particulates, and as a surface water contaminant because of contamination of runoff precipitation from ash disposal piles and leaching of toxic compounds from piles and disposal basins. The effects of ash effluents released to surface water are discussed in Chapter 18, which describes the release of chemicals to surface water.

The annual reports estimated an annual fly ash emission of 2.75 lb/10^6 BTU heat input for 1972 to 1975. It is reasonable to assume that the emissions before 1972 were similar. From 1972

to 1975, fly ash releases were said to have been within standards with the exception of fly ash in D-Area, which was reported as 2.75 lb/10^6 BTU heat input for all 4 years. The fly ash standard reported in the 1974 annual report was 0.6 lb/10^6 BTU heat input (Ashley and Zeigler 1975). In 1972, funding for equipment to reduce fly ash emissions had been obtained (Du Pont 1973a) and construction of fly ash emission control equipment was said to be underway in 1974 (Du Pont 1975). In 1973 and 1974, according to the annual reports (Du Pont 1974a, 1975), 400-D Area powerhouse was discovered to be releasing more fly ash than was then permitted from commercial electrical generating plants, so electrostatic precipitators were installed (Bebbington 1990). A 1973 report of environmental activities at the SRP compiled for press day stated that electrostatic precipitators were being installed on each of the four pulverized coal fired boilers and the major powerhouse to help comply with particulate emission regulations (Rusche 1973). In 1975, all of the standards were met except for fly ash. However, emissions from the largest source, the D-Area power plant (which burned about 65% of the coal burned at the SRS during that time), were for the first time in compliance with the standard. Electrostatic precipitators, put into operation in November 1975, were said to have reduced emissions from 2.75 lb to less than 0.03 lb/10^6 BTU heat input (Du Pont 1976). Fly ash emissions exceeded standards at the other power plants in 1976. Dust collectors were being installed at the A-Area plants, and installation was planned for plants in the other areas depending on the performance in A-Area (Du Pont 1977a). Fly ash emission estimates were reported as within standards in 1977 and 1978 (Du Pont 1978). By 1978, two-stage mechanical dust collectors had been installed on 11 of the 15 stoker-fed boilers and the remaining four were to be installed by July 1979 (Du Pont 1979). The emissions reported for 1979 were similar to 1978 estimates (Du Pont 1980). Mechanical cyclone collectors were used on all of the other boilers after 1979. In 1985, the A-Area boilers failed the test for particulate emissions. The steam input was reduced and the boilers overhauled during the next summer. They then passed State compliance tests for particulates (Ziegler et al. 1986). In 1986, the total suspended particulate standards were still set at 0.6 lb/10^6 BTU heat input (Ziegler et al. 1987). The total suspended particulates from the power plants were within applicable standards in 1987, 1988, and 1989 (Mikol et al. 1988; Davis et al. 1989; Cummins et al. 1990).

Analysis of fly ash for ^{226}Ra was an interest in 1964 after an article in the journal *Science* reported that conventional fossil fuel plants discharge relatively greater amounts of naturally occurring radionuclides into the air than nuclear powered plants of similar size (Eisenbud and Petrow 1964). The amount of ^{226}Ra in the D-Area powerhouse ash samples was measured. Coal used at the Site was said to have averaged about 9% ash. The fly ash collectors in the powerhouse were judged to be about 80% efficient, but not all of the ash formed reached the collectors. The memo stated, “The amount of fly ash discharged per ton of coal was obtained from a study made here within the past ten years by Combustion Engineering Company, acting as consultants.” This study, which was not found among the Site documents reviewed, was said to have reported 40 lb of ash per ton of coal for the D-Area Powerhouse, 10 lb ton^{-1} for F-Area and H-Area, 4 lb ton^{-1} for P-Area, 11 lb ton^{-1} for C-Area, and 11 lb ton^{-1} in the 300/700-Area (Brogdon 1964). No mention of the amount of coal burned during this time period is given. The amount of fly ash discharged appears to mean the amount discharged to the air. The amount collected by the fly ash collectors used at the time and sent to the ash basins would have likely been larger than the amounts reported. Why P-Area emissions are lower than the other areas and D-Area is so much larger was not explained (Brogdon 1964). If we weight percentages to account for the fact that most of the coal was burned in D-Area, an average of about 33 lb ton^{-1} results. The ash calculated

to have been released by applying this average estimate to the amount of coal reported to have been burned in the annual reports for the 1970s is given in the fifth column of Table 17-29.

In an effort to estimate the amount of mercury released from coal combustion, Kvartek et al. (1994) reported the amount of coal burned at the SRS each year for 1980–1993. The values are reproduced in the fourth column of Table 17-29. The source of these values or how they were derived was not explained. It is interesting that the values derived by Kvartek nearly match the annual report values, implying that perhaps they came from the same records that led to the annual report numbers.

Vendor analysis in the 1990s suggest that the coal averages about 12,180 BTU lb^{-1} or 2.43×10^7 BTU ton^{-1} (Faugl 1996a). The fly ash emissions through the 1970s were estimated to have been 2.75 lb/ BTU which corresponds to 67.1 lb ton^{-1} of fly ash.

The operating permit application implied that 2757 lb of PM were produced from coal burned in 1986. According to the annual reports, 455,000 ton of coal was burned in 1986 (Westinghouse 1996a). If we use this same relationship between coal burned and PM produced, the values in the last column of Table 17-29 result.

Table 17-29. Estimates of the Amount of Fly Ash and PM Generated Based on Estimates of the Average Amount of Coal Burned. Derived from Data in Brogdon (1964), Kvartek et al. (1994), and the Site Annual Environmental Reports

Year	Amount of coal burned reported in annual reports (ton)	Amount of coal burned reported in annual reports (kg)	Coal burned at the SRS each year estimated by Kvartek (1994) (kg)	Pounds of fly ash released per year based on Brodgen (1964) and annual reports (based on 33 lb ton^{-1})	Pounds of fly ash released per year (based on 65 lb ton^{-1})	PM emissions
1952–1971						
1972	500,000	4.5×10^8		1.65×10^7	3.2×10^7	3030
1973	500,000	4.5×10^8		1.65×10^7	3.2×10^7	3030
1974	500,000	4.5×10^8		1.65×10^7	3.2×10^7	3030
1975	500,000	4.5×10^8		1.65×10^7	3.2×10^7	3030
1976	500,000	4.5×10^8		1.65×10^7	3.2×10^7	3030
1977	500,000	4.5×10^8		1.65×10^7	3.2×10^7	3030
1978	500,000	4.5×10^8		1.65×10^7	3.2×10^7	3030
1979	500,000	4.5×10^8		1.65×10^7	3.2×10^7	3030
1980	500,000	4.5×10^8	4.0×10^8	1.65×10^7	3.2×10^7	3030
1981	500,000	4.5×10^8	4.3×10^8	1.65×10^7	3.2×10^7	3030
1982	500,000	4.5×10^8	3.9×10^8	1.65×10^7	3.2×10^7	3030
1983	460,000	4.2×10^8	4.2×10^8	1.51×10^7	3.0×10^7	2787
1984	460,000	4.2×10^8	4.1×10^8	1.51×10^7	3.0×10^7	2787
1985	455,000	4.1×10^8	4.1×10^8	1.50×10^7	3.0×10^7	2757
1986	455,000	4.1×10^8	4.0×10^8	1.50×10^7	3.0×10^7	2757
1987	453,000	4.1×10^8	4.1×10^8	1.49×10^7	2.9×10^7	2745
1988	374,000	3.4×10^8	3.4×10^8	1.23×10^7	6.3×10^7	2766
1989	227,000	2.1×10^8	2.1×10^8	7.5×10^6	1.5×10^7	1375

It is interesting to note the amounts of coal burned by the D-Area power plant reported in some of the reports on ash basin ecology. In 1975, 333,500 ton of coal, averaging 1.39% sulfur, were burned. In 1975, the ash content of the coal was said to have been 11.9%, which had increased from 9% in earlier operations (Evans and Giesey 1978). In 1978, the D-Area plant burned 451,940 metric ton of coal annually, producing 32,650 metric ton of ash, which was sluiced into a settling basin by approximately 4.5 billion L of water (Rodgurs et al. 1978).

Before 1976, or for 24 years between 1952 and 1975, fly ash was removed by mechanical cyclone separators that had a maximum efficiency of about 75%, which implied that as much as 75% of the fly ash was collected by mechanical cyclone collectors. About 40% of the ash generated was bottom ash. The electrostatic precipitators installed on each of the four stacks of the D-Area powerhouse in 1975 and 1976 were estimated to be about 99% efficient in removing fly ash from stack emissions (Weiner 1979; Evans and Giesey 1978).

Several SREL studies on the effects of ash and coal pile and basin runoff on the swamp ecosystem evaluated the deposition of ash released to the air from the D-Area power plant. Weiner (1979) noted that submicron fly ash particles can be transported considerable distances in the air and can contain many trace elements. Researchers studied 29 trace elements in soils in relation to distance from the 484-D power plant and found elevated levels of barium, beryllium, copper, mercury, manganese, selenium, and strontium near the stacks. Levels of cadmium were below the detection limit. Lead levels were not thought to be impacted by the stack emissions. Data collected in 1976 were used by Weiner (1979) and later by Evans et al. (1980) to estimate annual inputs of cadmium, copper, manganese, and lead in bulk precipitation at Skinface Pond. A total of 130.7 cm of rainfall was reported at the pond during 1976. Approximately 87% of this was sampled and analyzed. The deposition values were 0.68 mg m^{-2} for cadmium, 3.0 mg m^{-2} for copper, 3.0 mg m^{-2} for manganese, and 8.4 mg m^{-2} for lead. These levels were said to be similar to inputs reported for other rural sites, such as Lake Superior, Walker Branch in Tennessee, and a lake in Nebraska; however, proximity of these waters to power plants was not noted (Weiner 1979).

A study conducted in 1979 on bulk aerial deposition of trace elements supported a prediction of limited impact of fly ash on aerial inputs of trace metals at a distance from the power plant (Weiner 1979). The cadmium, copper, manganese, and lead levels in bulk precipitations were analyzed for this study. At a distance of 5.5 km, little of the copper, manganese, or lead deposited from air could be directly attributed to ash deposition. Researchers found no significant changes in mean concentrations after installation of electrostatic precipitators on the stacks of the power plant (previously equipped with mechanical cyclone collectors for the removal of fly ash). This led Weiner to conclude that fly ash was not a major source of airborne metals for Skinface Pond, located near Jackson, South Carolina, about 5.5 km northwest of 484-D power plant. Because the total concentration of cadmium in soil was less than the detection limit of the analytical method used, it was not determined whether the concentrations of cadmium in soil were influenced by the power plant emissions (Weiner 1979).

A similar assessment, published several years later, used the same data as Weiner (1979) and reported the aerial deposition of cadmium, copper, lead, and manganese at Skinface Pond measured for 21 months in bulk precipitation (Evans et al. 1980). The authors had already developed a model to predict cumulative deposition of fly ash as a function of distance from the power plant. They calculated a correlation coefficient of the log of the concentrations of elements in the surface soil and the log of the distance from the power plant. The soil data supported their model because it found a negative correlation between ash content and distance from the plant, but levels were very low (0.035 μg g^{-1} for mercury, 10.5 μg g^{-1} for lead, and 1.1 μg g^{-1} for arsenic). The authors concluded that based on the soil measurements and precipitation measurements, the D-Area power plant was a minor contributor of cadmium, copper, lead, and manganese to the pond. The inputs to the pond were similar or less than those measured for Lake Superior. The model had predicted that detectable elevations in metal concentrations in soils would occur only within a few kilometers of the plant. They observed a negative correlation for strontium, mercury, arsenic, and copper, which were most enriched in ash relative to background soils (Evans et al. 1980).

Evans et al. (1980) found that basin disposal was a more serious metal contamination threat to the terrestrial and aquatic ecology of the swamp near D-Area than deposition of ash released from the stacks. The deposition of copper, cadmium, lead, and manganese within 3 km of the

plant was similar to other rural areas, which suggested to Evans et al. (1980) that little of the deposition was from fly ash.

This research showed no significant changes in the concentrations of metals after installation of the new electrostatic precipitators on all four stacks of the power plant, which had previously been equipped with mechanical cyclone collectors for removal of fly ash. Evans et al. concluded that fly ash from the stack emissions was not a major source of metals to the ponds.

Ash emissions to the air from ash piles were not estimated in any of the reports because by 1985, most of the ash disposal involved water slurries and disposal basins. Dry ash piles were not mentioned as an environmental or occupational health concern in the documents we reviewed.

Taken together, the monitoring data suggest that the ash released to the air did not influence the area surrounding the D-Area power plant. Ash and coal dust release from coal and ash piles were probably not a concern for offsite exposures. Emissions of ash before 1973 were on the order of 3.3×10^7 lb y^{-1} for the entire site. After 1973, much of the ash release was controlled by precipitators. How much respirable PM was released from the power plants is difficult to estimate, but a release of about 3000 lb or 1.5 ton y^{-1} during maximum operations seems reasonable.

These estimates are quite uncertain. The D-Area power plant annual release estimates were used to predict coal burning for the entire site. This assumption introduces a non-quantifiable amount of uncertainty, which may be as large as an order of magnitude, since the D-Area power plant appears to have burned more coal than any other plant on Site.

The uncertainty that can be quantified for coal burning and therefore fly ash releases relates to the amount of ash released per ton of coal burned. The study that analyzed fly ash releases for radium predicted fly ash releases for each powerplant, with a weighted average of 33 lb ton^{-1} and a median estimate of approximately 10 lb ton^{-1}. The vendor analysis predicted fly ash releases on the order of 65 lb ton^{-1}. Because 33 lb ton^{-1} represents an actual weighted average of Site fly ash releases, this estimate for fly ash released per ton of coal burned was used as the most likely estimate for the distribution of these values ranging from 10 to 65 lb ton^{-1}, distributed triangularly.

All fly ash was assumed to be released to the environment before 1972. After 1972, the fly ash releases were assumed to be captured by pollution control equipment, which were somewhere between 75 and 99% effective at removing fly ash from the effluent stream. This distribution was assumed to be uniform.

The fly ash release estimates were calculated for each year between 1952 and 1989, based on values for amount of coal burned, estimates of fly ash released per ton of coal burned, and information about the reduction in fly ash emissions after 1972. The estimates for coal burned before 1972 were inferred from reactor production values, and estimates for coal burned from 1972–1989 were obtained from annual reports, as noted in Table 17-29. Annual estimates are shown in Figure 17-1.

Figure 17-1 shows the releases of fly ash depicted annually, along with the total amount of coal burned. It is important to note the differences in the scales for coal burned (on the right-hand side of the figure) and fly ash (on the left-hand side of the figure). With the exception of the first few years, coal use remained relatively constant over the period of study. Fly ash releases, however, decreased dramatically after 1972, when emission controls were put into place to reduce emissions from 75–99%. This had the effect of reducing the total release values, as compared to

the values in Table 17-29. The range of values represented by the 5th and 95th percentile levels reflects the uncertainty in the total amount of fly ash released per ton of coal burned.

Using these annual release estimates to calculate total fly ash releases and annual average release of fly ash over the entire period of study yields lognormal distributions. The distribution of total fly ash released from 1952–1989 had a geometric mean of 1.5×10^5 ton and a geometric standard deviation of 1.42. The average release per year had a GM of 4.2×10^3 ton y^{-1} and a GSD of 1.42. Although many of the years of operation had median fly ash releases over 8.0×10^3 ton y^{-1}, averaging all of the annual releases drops the annual average estimate to a lower level because of the inclusion of the years after 1972.

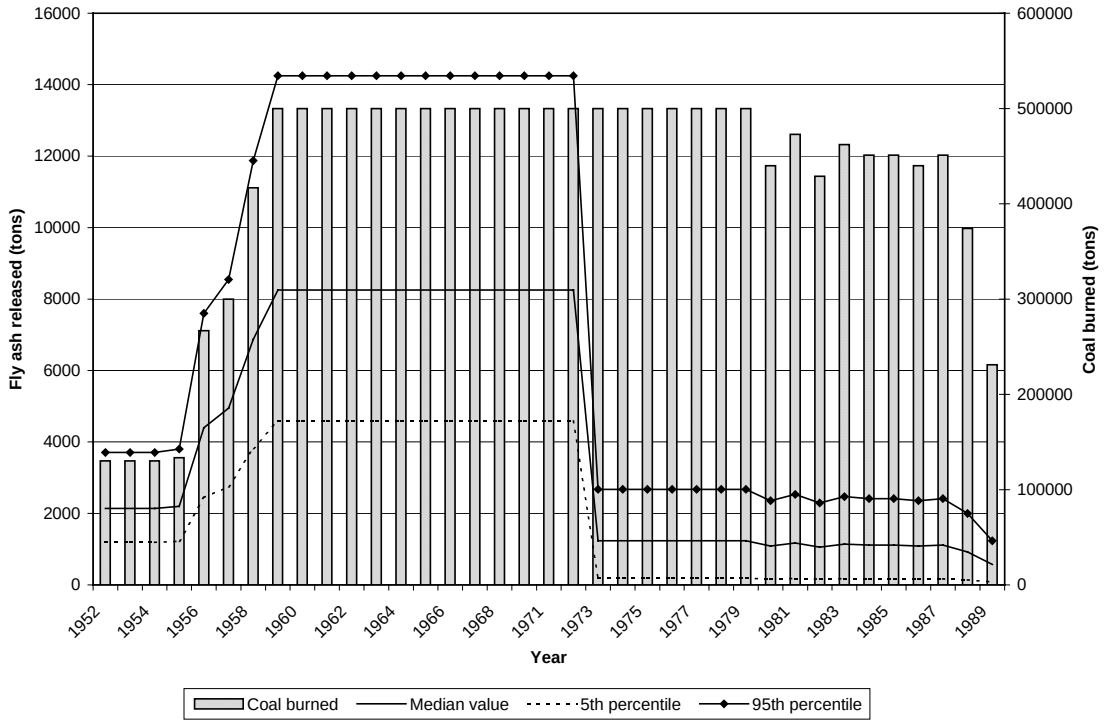

Figure 17-1. Coal burned and fly ash released calculated annually from 1952–1989. The bars in the figure represent coal burned each year in tons, with the scale on the right hand side of the figure. The lines represent the median, 5th and 95th percentile values for estimates of fly ash released annually in tons, with the scale on the left hand side of the figure.

Gasoline and Fuel Oils

Automotive gasoline typically contains more than 150 chemicals, including small amounts of benzene, xylene, toluene, and sometimes lead. Much of the health concern about gasoline has centered around the hazard from breathing vapors while filling fuel tanks. There is no evidence that exposure to gasoline causes cancer in humans, but gasoline does contain small amounts of carcinogens, like benzene and contained lead, especially before the late 1970s. Benzene is the

primary concern for gasoline emissions. Estimates of benzene releases, including those from gasoline tanks and transfer stations, are included in this chapter in the section about benzene.

The concern for this dose reconstruction study is chemicals in gasoline that might enter groundwater, surface water, or the air after being spilled or leaked from transfer tanks or storage tanks. When gasoline is spilled on soil or surface water, most of it will evaporate.

Fuels oils are petroleum mixtures used for fuel and as solvents. Examples of fuel oils are kerosene, diesel fuel, heating oil, and range oil. Fuel oil can contain varying amounts of many different hydrocarbons and additives depending on its use. Fuel oils can contain carcinogens, but for most normal uses, they do not present a carcinogenic hazard. The Occupational Safety and Health Administration (OSHA) standard for petroleum distillates is 400 ppm in air (ATSDR 1996).

Much of the gasoline and diesel fuel at the SRS has been stored in underground tanks. Leaks, spills, and transfer errors resulting in the release of gasoline, diesel, or fuel oil to surface water is discussed in the section on surface water discharges. Emissions of gasoline from storage tanks can be made using AP-42 values and methods developed by the American Petroleum Institute, involving conservative assumptions, estimates of tank throughput, and characteristics of the tanks. The vapor space is generally assumed to be 25% of the tank volume. Working losses are derived from data on fill rate. Benzene emissions from gasoline use and storage were estimated and are described in the previous section on benzene.

Diesel-powered Generators

Generators have been and are still some of the largest contributors of air pollutants from the SRS. Diesel exhaust is a pollutant that exists everywhere. It is a highly complex mixture of gases, vapors, and particulates that are mutagenic to bacteria and have irritant effects. Diesel exhaust would be important to consider for emissions of benzene and sulfur dioxides (Mauderly 1995). Diesel exhaust has been included in the AIRS database emission estimates. Many SRS facilities have diesel engines and generators for use in the field or during a power failure. These are periodically run as a part of testing and maintenance. The highest release for cadmium in 1985, 1987, and 1990 was 1.35×10^{-4} actual ton per year from the H-Area diesel house diesel generator. Followed by 2.0×10^{-5} for each of eight diesel generators in K-Area engine house 108001 and 108002. Diesel exhaust also accounts for much of the oxides of nitrogen, sulfur dioxide, and other toxic metals released from the Site.

For example, the 200-H emergency power generator is a 600-kW generator used for emergency power. Testing is performed routinely on the generator. The engine is permitted for 2080 hours of operation each year. Actual emissions calculated were 2.82×10^{-6} ton y^{-1} for lead, 1.47×10^{-1} ton y^{-1} for oxides of nitrogen, 2.93×10^{-3} ton y^{-1} for oxides of sulfur, 6.46×10^{-5} ton y^{-1} for benzene, 5.43×10^{-7} ton y^{-1} for arsenic, 6.70×10^{-7} ton y^{-1} for mercury, 1.05×10^{-6} ton y^{-1} for manganese, and 1.32×10^{-6} ton y^{-1} for nickel (Westinghouse 1996a). Emissions from most of the diesel engines at the SRS are included in the AIRS database estimates for each chemical. Uncertainty was not calculated for these emissions.

Hydrazine Mononitrate

Hydrazine compounds and ferrous sulfamate were used in the separations process for reducing plutonium to Pu (III). Hydrazine mononitrate was also used in the frames process that produced ^{238}Pu (Pickett 1996). Most of the concern about hydrazine and formation of azides and hydrazoic acids were about explosion hazard, rather than health hazard (Thompson and Hale 1972).

In 1975, the Energy Research and Development Administration (now the U.S. Department of Energy) formed a Toxic Materials Advisory Committee to advise them on the use of toxic materials in the weapons complex. The SRS requested that the committee investigate the current status of hydrazine, which had just been classified by OSHA as a carcinogen. It was noted in the Industrial Hygiene Summary report for 1975 that this request had been made and that hydrazine mononitrate was used extensively in the SRS separations areas (Harper and Croley 1976).

Hydrazine was handled as the 30% mononitrate solution in 200-F and 200-H Areas and as hydrazine hydrate (85%) solution and hydrazine sulfate (100%) powder in Building 773-A. Industrial hygiene surveys indicated the highest air concentrations that might affect workers were in the drum handling area in Building 223-F. Air samples were taken by a gas scrubber technique using a Drager multigas detector with hydrazine detector tubes. A maximum concentration of 0.5 ppm was detected in the hydrazine drum handling area in Building 223-F. The hydrazine stored at 221-H was supplied from the 223-F handling area (Harper and Croley 1976).

A computerized essential materials ledger for the Separations Department from April 1982 listed a beginning inventory for hydrazine mononitrate of 25,650 lb and an ending inventory of 24,400 lb, so presumably 1250 lb had been used that month (Du Pont 1982a). Hydrazine was not noted on other ledgers found in central records.

A 1984 document characterizing wastes, lists hydrazine as a part of the waste from the FB Line, HB Line, and the canyons, all of which went to the waste tanks (Smithwick 1984). Hydrazine was also listed as a component of the Savannah River Laboratory (SRL) liquid wastes. A memo on the SRL seepage basins said that in over 28 years of use, less than 3 lb of hydrazine had been discharged to the SRL seepage basins (Lower 1983).

A memo written in 1985 on workplace monitoring, reports that hydrazine mononitrate was no longer used in the canyon process after 1985 (Karoly 1985). A search of the AIRS database for both hydrazine and hydrazine mononitrate found no emissions estimates for H-Area or F-Area from 1985 or after. Five emissions were reported in 1985 for A-Area (700-Area) totaling less than 2×10^{-5} ton y^{-1} maximum design emissions and less than 9.0×10^{-6} ton y^{-1} actual emissions, or about 8.18×10^{-3} kg y^{-1} (Faugl 1996a). However, a set of handwritten essential materials control sheets, labeled “total for the 200-Area, 222-F, 221-H, and B-Line” (in H-Area) list hydrazine mononitrate (EM Code 107), with the monthly consumption amounts shown in Table 17-30 (Westinghouse 1987b). The amounts reported were probably in pounds. The amounts were extremely variable and represent bookkeeping rather than actual use amounts, as evident by the large negative inventories at the end of several 6-month periods. Based on these sheets, the average monthly consumption during the time period was about 1816 lb mo^{-1} (Westinghouse 1987b).

Table 17-30. Monthly Consumption of Hydrazine Mononitrate in H-Area (1986 and 1987)[a]

Month and year	Total (lb)	222-F (lb)	221-H (lb)	B-Line (lb)
Jan 1986	0	0	0	
Feb 1986	0	0	0	
March 1986	2700	0	2700	
April 1986	1800	0	1800	
May 1986	2700	0	2250	
June 1986	6032	3150	3150	
July 1986	318	0	250	68
Aug 1986	950	0	950	0
Sept 1986	2400	0	2400	0
Oct 1986	197	0	0	197
Nov 1986	3613	0	3600	13
Dec 1986	–2560	0	–2700	140
Jan 1987	1820		1800	20
Feb 1987	1350		1350	0
March 1987	2475		2475	
April 1987	2475		2475	0
May 1987	900		900	0
June 1987	5530		5250	280
July 1987		0	–1200	
Aug 1987		0	1800	
Sept 1987		0	0	
Oct 1987		0	0	
Nov 1987		0	450	
Dec 1987		0	1350	

[a] Source: Westinghouse (1987b).

A table of bulk chemical consumption in H-Area that was part of a file on waste reduction studies kept by a chemical engineer in H-Area, listed the number of pounds of hydrazine mononitrate consumed per month from July 1987 through September 1988 (Pickett 1997). The values are presented in Table 17-31.

The total is given as 4200 lb or 1909 kg, which averages about 280 lb or 127.2 kg mo^{-1} or 1526 kg y^{-1} (Pickett 1997). These same notes list components of the high activity and low activity waste and contained no information to suggest that the hydrazine was not completely reacted in the process.

The operating permit application described the frame waste recovery system in H-Area, which purified and concentrated ^{238}Pu solutions and used hydrazine. A solution of 30% hydrazine mononitrate ($N_2H_5NO_3$) was added to the solution to stabilize plutonium at the lower valence state. It acted as a reductant and also helped scavenge ions that affect column adsorption. The permit application said that the frames waste recovery received plutonium and neptunium solutions from the HB-Line. The solutions were treated with aluminum nitrate to complex any fluorides, nitric acid to form nitrates, then hydrazine mononitrate and ferrous sulfamate to reduce the plutonium or neptunium in preparation for heat kill and anion exchange steps. Heat kill involved heating the solutions to enhance the reduction to a valence state for anion exchange. The

anion exchange columns absorbed the plutonium and neptunium ions, which were removed from the column with weak nitric acid and transferred back to the HB-Line. The permit application suggests that the reaction of hydrazine mononitrate and nitric acid produced nitrogen, nitrous oxide, and water.

Table 17-31. Estimates of the Monthly Consumption of Hydrazine Mononitrate in a Waste Reduction Study[a]

Month and year	Pounds consumed per month in H-Area
July 1987	–1200
Aug 1987	1800
Sept 1987	0
Oct 1987	0
Nov 1987	450
Dec 1987	1350
Jan 1988	900
Feb 1988	900
March 1988	9000
April 1988	–300
May 1988	150
June 1988	–8850
July 1988	0
Aug 1988	0
Sept 1988	0
Total	4200

[a] Source: Pickett (1997).

Clearly, hydrazine used in the canyon solvent extraction, frames, and B-Line processes would have reacted to form gaseous products, primarily oxide of nitrogen. All of hydrazine was probably converted to nitrogen compounds and water. What was left may have remained in liquid waste; however, canyon wastes were neutralized with caustic, and the sodium nitrate should have reacted with any excess hydrazine. We have found no evidence of any spills or releases of hydrazine to the soil, seepage basin, or air. Although we can reconstruct the amount of hydrazine that may have been used in the process from the 1982 inventory, we do not know and lack the information necessary to estimate how much of what was used may have been released to the environment. Current and former employees with knowledge of separations area processes were asked about the use and release of hydrazine and they thought that any hydrazine used would have been consumed by the process.

Hydrogen Sulfide

Hydrogen sulfide is a very toxic gas. Exposure to hydrogen sulfide is not associated with long-term, chronic effects like cancer. The workplace standard (OSHA Permissible Exposure Limit) is 10 ppm. A concentration of 500 ppm in air is lethal to most people.

Hydrogen sulfide was used in large quantities to make heavy water in D-Area from 1952 to 1982. The heavy water production process, called the GS process, involved continuous countercurrent contacting of water with hydrogen sulfide, through first a cold tower then a hot

tower (much like distillation towers). This operation used large quantities of pressurized hydrogen sulfide gas. Leaks were a constant concern for worker safety. Alarmed monitoring instruments were placed in the operating areas, and personnel carried hydrogen sulfide-sensitive paper. There were a number of releases of hydrogen sulfide, none of which was reported to cause injuries to employees (Bebbington 1990).

In 1954, Clark discussed the impact of a hypothetical hydrogen sulfide or firestorm situation from burning large amount of hydrogen sulfide (Clark 1954). SRS researchers thought that an accident in the 400-Area would have most likely affected the Georgia Bank of the Savannah River at the point closest to the 400-Area. Hypothetical problems such as a fire, large leak of gas that did not burn, an attack on the facility, a hurricane or tornado, and an earthquake were discussed. This memo also described the safety measures taken in construction of the towers and operation and maintenance of the plant (Clark 1954). In a letter written to the Atomic Energy Commission in 1957, Site personnel stated that the probabilities of personnel offsite receiving a serious overdose of hydrogen sulfide were calculated to be about 10^{-6}. At that time, the Site had operated safely for the previous 3 years and they felt there was no need for an offsite warning system (Cole 1957).

Routine purges of hydrogen sulfide from the heavy water facility and minor leaks were routed to a 400-ft flare tower, where the carried hydrogen sulfide was burned (forming sulfur dioxide) (Rusche 1973). Reinig et al. (1973) described a 320-ft flare tower for controlled process venting of carried hydrogen sulfide from the extraction plant. The amount of sulfur dioxide released was said to be very small compared to the amount emitted from the powerhouse operation in 484-D (Reinig et al. 1973).

Reinig et al.. (1973) estimated that 42 ton of hydrogen sulfide per year were released from the GS process via the high and low pressure lines of the 320-ft flare tower. Some of this was burned to sulfur dioxide. The flow and hydrogen sulfide concentration in the stream vented to the flare tower was being measured on a grab-sample basis in 1973. Reinig et al. (1973) estimated that a total of about 150 ton y^{-1} was released from D-Area processes, including releases to the flare tower. Reinig et al.. (1973) recommended ambient air monitoring be conducted offsite in Georgia for sulfur dioxide and hydrogen sulfide. As far as we can determine, monitoring for hydrogen sulfide was not routinely performed until a special program to monitor for hydrogen sulfide and sulfur dioxide using monitoring equipment in mobile trailers was started in 1977. Hydrogen sulfide and sulfur dioxide were detected in ambient air most frequently at stations near D-Area. The maximum hydrogen sulfide level detected was 0.10 ppm at the D-Area 3G pumphouse. The average hydrogen sulfide concentration at all sites was about 0.004 ppm. Georgia and South Carolina had no standards for hydrogen sulfide at that time (Du Pont 1979). The worker health and safety standard, National Institute of Occupational Safety and Health's ceiling limit, is 10 ppm or 15 mg m^{-3} (NIOSH 1994).

Several accidental releases of hydrogen sulfide have been reported in Site reports and local newspapers. On March 19, 1960, a hydrogen sulfide gas release and fire occurred in GS Unit 22. The gas was released from a pipe connection at the bottom of a condenser, which pulled apart because of insufficient thread engagement. The pipe joint, 16 in. in size, opened several inches allowing about 40 ton of hydrogen sulfide to be rapidly released. The gas immediately caught fire. The area was evacuated. According to the incident report, the fire burned for 46 minutes and the force of the pressurized gas release was felt throughout the 400-Area. Five "very minor

injuries" were sustained by maintenance personnel in the area. After this incident, all of the 16-in. screwed flanged connections were replaced with welded connections (Ellett 1960).

Another leak occurred over May 19–30, 1980. This incident involved a tank at Building 402-D. Hydrogen sulfide leaked from a crack in a weld of the bottom flange of storage tank 22. Another tank, 8B, was empty and undergoing a bolt inspection. This tank was filled with nitrogen in preparation for hydrogen sulfide transfer from the leaking tank 22 to tank 8B. The first transfer attempt May 20 failed because a hydrate plug had formed in the leaking line. As the crack length and leak rate increased, the 400 and CNX and TNX Areas were evacuated. Rather than transfer the hydrogen sulfide as a liquid, the hydrogen sulfide was transferred as a vapor to a shutdown extraction unit and then into Tank 8B. It took until May 29 to vaporize and transfer all of the hydrogen sulfide. About 900 lb of gas remained in the tank. This was flared and the tank was purged by steam. The hydrogen sulfide release was said to have been minimized by a hydrate that formed and sealed the crack from the inside. Ice that formed on the outside of the line may also have helped contain the leak. Nonessential personnel returned to work in the 400-Area and the roads were reopened on May 30. Smudge pots (flambeaus) were lighted and placed on the ground north and south of the tank just outside the dike to ignite any large release of hydrogen sulfide that might have occurred. The concentration of hydrogen sulfide 0.5 m from the leak was less than 1 ppm between May 21 and May 29, with the exception of a 100-ppm level on May 21 when the leak first started and several levels of 2.0 and one of 10 ppm when the last of the hydrogen sulfide was purged from the tank (Haywood 1980). A Public Affairs report and numerous newspaper articles on this incident were also found in the Phase I document search. These had been photocopied and were added to the 1980 investigation and incident reports (referenced here as Haywood 1980). The evacuation and stopping of road, river, and rail traffic were the major points of most of the articles. The leak was said to be small enough that it posed no threat to the offsite public. The total amount of hydrogen sulfide estimated to have been released as a result of the leak was 0.5 ton (Haywood 1980).

The incident report mentions that previous dispersion studies had predicted that hydrogen sulfide concentrations of 500 ppm or greater could exist several miles away from the 400-Area if 1 ton of hydrogen sulfide was released and the wind velocity was low (Haywood 1980).
Table 17-32 compiles hydrogen sulfide release estimates from different sources.

Table 17-32. Hydrogen Sulfide Release Estimates

Year	Amount (ton y^{-1})	Basis of the estimate	Reference
1960	40	Incident report	Ellett (1960)
1973	150	General process losses and flare tower	Reinig et al. (1973)
1980	0.5	Incident report	Haywood (1980)

Although the heavy water production plant was shutdown permanently in 1981 (DOE 1987), D-Area continued to do heavy water reprocessing, called heavy water rework in many documents (Arnett et al. 1993). Long before the first air emissions inventory was conducted, the GS process was no longer in operation. Recent release estimates from the AIRS database will not be useful for estimating releases in the early years when large amounts of hydrogen sulfide were being used to make heavy water.

In recent years, the largest source estimated in the AIRS database for hydrogen sulfide was the degassifiers at the water treatment plant, used to remove sulfur and other compounds from the water. Emissions estimates for these facilities in 1985 are shown in Table 17-33. Routine releases of hydrogen sulfide from groundwater treatment were included in the AIRS database. For example, emissions estimates for the 183-K Buildings that make up the groundwater treatment plant were described in the K-Area calculations. Groundwater was treated for steam generation, reactor cooling, and domestic use, which involved degassification, clarification, pH adjustment, and treatment with biocides (primarily sodium hypochlorite). The water contained sulfides at a concentration of about 0.9 mg L^{-1}, which were removed by the degasifiers that were designed to remove carbon dioxide. Hydrogen sulfide emissions from the degasifiers were calculated from the flow of groundwater and concentration of sulfides per gallon, assuming all of the sulfides were liberated as hydrogen sulfide. The emission rate calculated for 183-K was 0.09 lb h^{-1} hydrogen sulfide, which equals a maximum emission of 0.39 ton y^{-1} or 0.197 ton y^{-1} for each unit (Radian 1992b). The actual emissions estimate for all nine units in 1985 totaled 3.05 ton y^{-1}.

Table 17-33. Emissions Estimates for Nine Water Degasifiers Operating in 1985

Degasifier	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
Each of two 183-C filter and softener plant degasifier	8.20×10^{-2}	5.60×10^{-2}
282-H Powerhouse degasifier	2.60	2.60
Each of two 183-K filter and softener plant degasifier	1.97×10^{-1}	1.97×10^{-1}
Each of two 183-L filter and softener plant degasifier	1.25×10^{-1}	8.50×10^{-2}
Each of two 183-P filter and softener plant degasifier	1.60×10^{-1}	1.10×10^{-1}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

The Standard 8 results submitted to SCDHEC said that in 1991, hydrogen sulfide was released from 30 sources in A-Area, B-Area, C-Area, F-Area, H-Area, K-Area, L-Area, P-Area, and S-Area. The maximum 24-hour average Site boundary concentration was calculated to be 0.201 μg m^{-3}. The ambient air standard was 140 μg m^{-3} (Dukes 1993). In summary, Reinig et al. (1973) estimated that 150 ton y^{-1} may have been routinely released from D-Area from 1952–1973. Two accidental releases released an additional 40 and 0.5 ton, in 1960 and 1980, respectively, most of which burned (Ellett 1960; Haywood 1980). From 1952–1982, a total of 4690 ton of hydrogen sulfide may have been released based on the assumption that 150 ton were released each year from 1952–1982. After 1982, emissions were probably less than 3.5 ton y^{-1}, primarily from the aeration of groundwater. Although the uncertainty in these release estimates is great, there was not enough information to quantify the uncertainty associated with these release estimates.

Lead

Most of the lead used onsite was probably used as shielding material. Leaded oil was used as a lubricant for the uranium extrusion press and lead was emitted into the air from this process. A three to one mixture of oil and lead powder was used as a lubricant for the extrusion process in 321-M. About 9 qt of leaded oil was used each day. About 6 ton of lead was used in the year 1985, 4.5 ton in 1986, and approximately 1.7 ton in 1987 (Westinghouse 1987a). Lead fume emissions from these processes have not been well characterized, and the potential for their emissions has not been assessed (Faugl 1996a). Industrial hygiene records indicate that worker exposures to metal fumes from the 321-M extrusion process were minimal and the process was not an occupational hazard. The air around the extrusion press was vented outside. Lead concentrations in workroom air were less than 5.3 $\mu g\ m^{-3}$ in 1985 (DOE 1987).

In 1967, an air sampling program for lead was initiated in M-Area. Measurements of lead and carbon monoxide were taken twice daily for 18 days. The average concentration was reported to be 0.16 $mg\ m^{-3}$ for lead with a footnote that said, "only two positive samples, indicating a very clean atmosphere." The report section about monitoring was titled "air purity," but the text did not state whether the sampling was done out of concern for industrial hygiene or environmental releases. The report did not indicate where the samples were taken and it was not clear whether the samples were from the stack or ambient air (Du Pont 1967). A 1987 report describing ambient air quality monitoring onsite and offsite said that lead was not monitored because the potential release was insignificant compared to the standard (Mikol et al. 1988).

There is little information on lead released to the air before 1985. The emissions estimates in the AIRS database included lead released from M-Area and smelting, lead pots, and small welding and cutting operations at various locations onsite (Faugl 1996g). Welding and painting operations were estimated to release less than 10^{-3} ton y^{-1} total. About four times as many emissions points are listed for 1995 than for 1985, 1987, and 1990, and almost all of these were welding machines, welding booths, and welders. Table 17-34 presents the lead releases in the AIRS Database and Table 17-35 lists lead emissions by source.

The largest emission estimated in 1990 was lead oxide from the tank farm, at 2.40×10^{-3} ton y^{-1} actual estimated emissions. These emissions were probably from maintenance work that involved the removal or application of lead paint.

Lead has also been released from the combustion of fuels containing lead. The emissions estimate for the large 200-H emergency power generator, actual emissions assuming 2080 hours of operation each year was 2.82×10^{-6} ton y^{-1} for lead (Westinghouse 1996a).

The air quality permit application estimated that the two 784-A boilers released a maximum total of 3.87×10^{-3} ton y^{-1} of lead, based on each boiler burning 8500 ton of coal or 17,000 ton y^{-1} for the two boilers (Westinghouse 1996a). If we assume that coal with a similar lead content was burned Site-wide, as much as 0.114 ton y^{-1} of lead could have been released during the years when about 500,000 ton y^{-1} of coal was being burned. The coal crushing operation at 784-A was also evaluated for the air quality permit. The maximum emissions for several different pieces of coal-handling equipment and the coal pile, assuming operating at capacity of 66 ton h^{-1} totaled 1.05×10^{-3} ton y^{-1} for lead, based on the amount of coal burned (Westinghouse 1996a). Actual emissions estimates for metals from the fuel oil-fired package boilers in K-Area included lead with 1.65×10^{-4} ton y^{-1} (Westinghouse 1996a).

Table 17-34. Key Lead Releases in the AIRS Database

Year and source description	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1985 total	9.97×10^{-3}	4.68×10^{-3}
F-Area tank farm, lead oxide gas	2.40×10^{-3}	2.40×10^{-3}
H-Area coal storage pile	1.50×10^{-3}	8.70×10^{-5}
H-Area Building 284 powerhouse ash sluice sump	1.67×10^{-4}	3.65×10^{-5}
H-Area Manufacturing Building Number 3, 234-H Fabricated metals machining	5.20×10^{-3}	1.74×10^{-3}
K-Area coal pile	4.70×10^{-5}	4.70×10^{-5}
K-Area coal pile runoff basin	4.70×10^{-5}	4.70×10^{-5}
N-Area Lead Pouring Building 711-04 lead melting pot	0	5.36×10^{-8}
1987 total	9.97×10^{-3}	4.68×10^{-3}
F-Area tank farm, lead oxide gas	2.40×10^{-3}	2.40×10^{-3}
H-Area coal storage pile	1.50×10^{-3}	8.70×10^{-5}
H-Area Building 284 powerhouse ash sluice sump	1.67×10^{-4}	3.65×10^{-5}
H-Area Manufacturing Building Number 3, 234-H Fabricated metals machining	5.20×10^{-3}	1.74×10^{-3}
K-Area coal pile	4.70×10^{-5}	4.70×10^{-5}
K-Area coal pile runoff basin	4.70×10^{-5}	4.70×10^{-5}
1990 total	9.97×10^{-3}	4.68×10^{-3}
1990 values are the same as 1987 with the addition of		
H-Area Building 284 powerhouse ash sluice sump	1.67×10^{-4}	3.83×10^{-5}
N-Area Lead Pouring Building 711-04 lead melting pot	0	2.68×10^{-8}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

The amendment to the air quality permit application included handwritten calculation sheets for lead emissions for the lead melter in Building 711-4N. All particulate from the pot was assumed to be lead and the emission included melting and pouring. Estimates were based on the amount of lead melted and an emission factor. The lead melter held about 16,000 lb of lead in two pots (Westinghouse 1996a). Lead has been melted and molded as needed. Apparently, no operating records were kept before July 1991. Records for 1994 were compiled by International Technology Corporation for the operating permit application; they suggested that monthly quantities of lead melted ranged from 0 to 15135 lb. The total amount melted in 1994 was estimated to have been 45,005 lb. The operating procedures indicate that lead was heated for about 1 hour until it was 700°F, then it was poured through a pipe into a mold. Exhaust was pulled from the enclosure for each pot, combined, ducted through a high-efficiency particulate air (HEPA) filter and exhausted out the stack. The maximum emissions estimate for the N-Area melting pot was 3.5×10^{-5} ton y^{-1} (Westinghouse 1997c). This emissions estimate is about 600 times higher than the emissions estimate reported in the AIRS database (Faugl 1996g). Further information on the lead melter has not been found.

The Standard 8 results submitted to SCDHEC said that in 1991, lead was emitted from 26 sources in A-Area, D-Area, H-Area, K-Area, N-Area, and S-Area. The estimated maximum quarterly Site boundary concentration was calculated to be 0.0015 μg m^{-3}. The ambient air standard was 1.50 μg m^{-3} (Dukes 1993).

Table 17-35. Sources of Lead Emission Estimates for Selected Years[a]

Emission source	Year	Actual[b] emission estimate (ton y^{-1})
H-Area coal storage pile	1985	8.70×10^{-5}
	1987	8.70×10^{-5}
	1995	1.77×10^{-5}
H-Area powerhouse	1985	3.65×10^{-5}
	1987	3.65×10^{-5}
H-Area manufacturing building	1985	1.74×10^{-3}
	1987	1.74×10^{-3}
	1995	1.74×10^{-4}
K-Area coal pile	1985	4.70×10^{-5}
	1987	4.70×10^{-5}
K-Area coal pile storage runoff	1985	4.70×10^{-5}
	1987	4.70×10^{-5}
F-Area tank farm	1985	2.40×10^{-3}
	1987	2.40×10^{-3}

[a] Source: Faugl (1996g).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

From 1987 to 1995, the TRI, reported to the EPA and SCDHEC, included estimates of the pounds per year of lead released from the SRS, shown in Table 17-36. We do not know the reason for differences between years or why the release reported in 1995 was so low. The emissions from coal consumption do not appear to be included in the TRI estimates.

Table 17-36. Toxic Release Inventory Release Estimates for Lead (per year)[a]

Year	Air emissions (lb y^{-1})
1989	120
1990	12
1992	29
1993	76
1994	8
1995	1

[a] Source: Westinghouse (1996b).

It is likely that in years with no amount reported, some amount below the reporting limit was released (Westinghouse 1996b).

In summary, we did not obtain sufficient information to determine lead releases from the M-Area extrusion process or gasoline combustion. The annual total in the AIRS database for 1985, 1987 and 1990 was 4.68×10^{-3} ton y^{-1} and accounted for welders, lead melting pots and metal machining (Faugl 1996g). Lead emissions from coal burning may have ranged from 0.045 to 0.114 ton y^{-1} depending on the year. The lead melting pot emission estimate used for the operating permit application was 3.5×10^{-5} ton y^{-1}. These emissions total about 0.05–0.119 ton y^{-1} or 238 lb y^{-1} compared to 120 lb reported to the EPA for the 1989 TRI.

An attempt was made to calculate uncertainty for the lead releases, based on the information available in the AIRS database, the TRI release estimates, and the permit application estimates. Very little information was provided about the basis of release estimates, making it quite difficult to quantify the uncertainty. Although we have had much success providing uncertainty estimates for releases from coal burning, only one estimate of lead released per ton of coal burned was found, and the uncertainty related to that estimate was unknown. The distribution of uncertainty in the release estimates produced from using only the ranges of estimates was quite narrow and misleading in terms of the total uncertainty in these releases. The lack of information precluded any calculations of uncertainty and the range of releases presented is provided as the best available information on lead emissions.

Manganese Compounds

Manganese dioxide was used in the separations area head end processes. Most of the manganese was discharged to the liquid waste tanks. The separations area processes did not release notable amounts of manganese to the air. Potassium permanganate solutions were used in D-Area and in small amounts in many laboratories. Releases to surface water are described in Chapter 18. Manganese was measured in ash basin effluents, but manganese releases to the air do not appear to have been monitored.

Manganese emissions estimates were entered into the AIRS database for a number of grinding and cutting operations in A-Area, F-Area, H-Area, N-Area, S-Area, and T-Area; H-Area and K-Area coal storage and handling; water filtration and treatment; F-Canyon and H-Canyon stacks; and combustion sources. Table 17-37 lists the total emissions for several years. Some of the highest emissions estimates were for machining in H-Area manufacturing (Faugl 1996f).

Table 17-37. Key Sources of Manganese Emissions Estimates in the AIRS Database [a]

Emission source	Year	Actual[b] emission estimate (ton y^{-1})
A-Area boiler house	1995	1.22×10^{-4}
A-Area ash pile	1995	5.21×10^{-4}
H-Area coal storage pile	1985	5.60×10^{-5}
	1987	5.60×10^{-5}
	1995	5.72×10^{-5}
H-Area powerhouse	1985	4.63×10^{-5}
	1987	4.63×10^{-5}
H-Area manufacturing building	1985	1.73×10^{-4}
	1987	4.95×10^{-4}
K-Area coal pile	1985	3.00×10^{-5}
	1987	3.00×10^{-5}
K-Area coal storage runoff area	1985	3.00×10^{-5}
	1987	3.00×10^{-5}

[a] Source: Faugl (1996f).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Most of the emissions points in the AIRS database for manganese were for grinding, cutting, torch cutting, belt sanders, metal machining, turning, and drilling, and other similar maintenance facility and machine shop operations. Estimates for the coal operations in D-Area and A-Area were also listed and are shown in Table 17-38.

Table 17-38. Manganese Releases to the Air in the AIRS database for 1985, 1987 and 1990[a]

Year and source description	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985		
H-Area manufacturing Building 232		
232-H hood metallography		0
234-H hood cutting		0
234-H radiological equipment repair	1.05×10^{-2}	1.73×10^{-4}
234-H finishing operations	1.43×10^{-5}	1.43×10^{-5}
234-H inert finishing operations	1.73×10^{-6}	1.73×10^{-6}
234-H fabricated metals machining	2.62×10^{-2}	8.83×10^{-3}
238-H milling and machining hood	2.35×10^{-3}	1.70×10^{-5}
238-H lathe hood	2.35×10^{-3}	2.59×10^{-5}
K-Area coal pile	3.00×10^{-5}	3.00×10^{-5}
K-Area coal pile runoff basin	3.00×10^{-5}	3.00×10^{-5}
1987 and 1990		
H-Area coal storage pile	9.50×10^{-4}	5.60×10^{-5}
H ash sluice sump	2.12×10^{-4}	4.63×10^{-5}
H-Area manufacturing Building 232		
232-H hood metallography	6.0×10^{-4}	1.44×10^{-4}
234-H hood cutting	3.80×10^{-3}	1.78×10^{-4}
234-H radiological equipment repair	1.05×10^{-2}	1.73×10^{-4}
234-H finishing operations	1.56×10^{-5}	1.56×10^{-5}
234-H inert finishing operations	3.19×10^{-6}	3.19×10^{-6}
234-H fabricated metals machining	2.64×10^{-2}	8.83×10^{-3}
238-H milling and machining hood	2.35×10^{-3}	1.64×10^{-5}
238-H lathe hood	2.35×10^{-3}	3.29×10^{-5}
Coal transfer operation	1.11×10^{-4}	3.30×10^{-6}
Coal storage pile	3.29×10^{-5}	1.23×10^{-5}
Coal crushing operation	3.24×10^{-3}	0
788-A ash pile	6.10×10^{-4}	5.21×10^{-4}
484-D coal storage pile-coal transfer	4.42×10^{-2}	3.29×10^{-3}
484-D coal storage pile	4.44×10^{-2}	3.48×10^{-3}
484-D coal storage pile coal reject pile	1.64×10^{-6}	5.79×10^{-7}
488-D ash basin - disposal basin	9.41×10^{-3}	8.02×10^{-3}
488-D ash basin - coal reject handling	1.63×10^{-4}	1.62×10^{-4}
488-D ash disposal basin	3.66×10^{-3}	0
H-Area coal transfer	9.27×10^{-5}	3.09×10^{-6}
K-Area coal pile	1.86×10^{-5}	1.86×10^{-5}

[a] Source: Faugl (1996f).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

The highest emissions estimates for all years were for the C-Area, Building 717 grinders and dust collectors used in the contaminated maintenance facility at 0.029 ton y^{-1}. Followed by 0.0088 ton y^{-1} for fabricated metals machining in 234-H (Faugl 1996f).

Table 17-39. AIRS Database Manganese Total Emissions[a]

Total	Maximum	Actual[b]
1985	6.05×10^{-2}	9.79×10^{-2}
1987	6.52×10^{-2}	6.95×10^{-2}
1990	6.56×10^{-2}	6.95×10^{-2}
1992	2.84×10^{-2}	5.61×10^{-3}

[a] Source: Faugl (1996f).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

There appears to be an error in the total maximum emissions estimates, which are less than the actual, because actual values were given, but the maximum values were zero, for several of the metal and pipe cutting and grinding operations. The manganese emissions estimate for the 200-H emergency power generator, actual emissions, was 1.05×10^{-6} ton y^{-1}, assuming 2080 hours of operation each year. Actual emissions estimates for metals from the fuel oil-fired package boilers in K-Area included manganese with 2.59×10^{-4} ton y^{-1}. The coal crushing operation at 784-A was also evaluated for the air quality permit. The maximum emissions for several different pieces of equipment and the coal pile, assuming operating at capacity of 66 ton h^{-1}, totaled 3.38×10^{-3} ton y^{-1} for manganese based on the amount of coal burned (Westinghouse 1996a). This suggests that 0.099 ton y^{-1} may have been released during the years when 500,000 ton y^{-1} of coal was burned.

At the time of the 1996 permit, the F-Canyon was not operating and actual emissions were reported as zero. The combined F-Canyon stack maximum controlled emission estimates assuming 24 h d^{-1} releases of manganese oxide totaled 2.38×10^{-6} ton y^{-1} based on engineering calculations (Westinghouse 1996a). We have no information about releases from the use of permanganate in laboratories and we have no evidence that any releases occurred. From 1987 to 1995, the TRI, reported to the EPA and SCDHEC, included estimates of the pounds per year of manganese compounds released from the SRS.

Table 17-40. Manganese Compound Release Estimates from the Toxic Release Inventory

Year	Air emissions (lb y^{-1})	Ton y^{-1}
1988	190	0.095
1989	190	0.095
1990	150	0.075
1993	42	0.021
1994	31	0.015

It is likely that in years with no amount reported, some amount below the reporting limit was released (Westinghouse 1996b).

Most of the routine releases of manganese came from metal cutting, grinding, machining, and finishing operations and coal burning operations. Releases were probably less than 0.099 ton y^{-1}, or less than 200 lb y^{-1}. They may have ranged from about 0.07 ton y^{-1} to 1.9 ton y^{-1}. Again, the combination of the AIRS database information, release estimates from coal burning and the TRI release estimates did not provide enough information to effectively quantify uncertainty for manganese releases. The estimates presented are our best estimate.

Mercury

Mercury is a naturally occurring metal released into the atmosphere from deposits in soil and rock and from combustion of coal. Mercury in the environment can exist in three valence states in inorganic and organic compounds and the elemental or liquid mercury form. Elemental mercury can volatilize from soil, water, and waste.

Inhalation, ingestion, or skin absorption of mercury can cause neurological damage. Inorganic mercury, such as mercury salts, also damages the nervous system. Chronic exposure to mercury salts and mercury vapor may cause kidney damage, and neurological effects. Epidemiological studies suggest that mercury is not a carcinogen. Mercury can cause birth defects. Organic mercury is readily transported across the placental barrier. Mercury can cause damage to the central nervous system, causing impaired learning and behavior disabilities.

Mercury vapor and mercury bound to particulates is readily transported through the air. In the environment, mercury can be transformed by microorganisms in sediments to organic methyl mercury, which bioaccumulates up the food chain. Methyl mercury in fish is often the environmental exposure pathway of greatest concern for exposures to the public. Methyl mercury causes nervous system toxicity. Unborn children and children under the age of 6 are most sensitive.

Atmospheric mercury pollution has emerged as one of the leading environmental issues of the 1990s. Mercury in the atmosphere occurs almost exclusively as Hg(0), elemental mercury, but it may be oxidized and deposited as mercury ions and salts. The Hg^{2+} and Ch_3Hg^{+} ions are complexed by hydroxide, chloride, sulfide, and humic acids in surface water and sediments. The cycling, transformation, and bioaccumulation of mercury are complex. Understanding some of the Site-specific environmental fate characteristics of mercury will be important if mercury is evaluated further in later phases of the dose reconstruction project.

This section summarizes what has been documented about the use and release of mercury at SRS facilities and addresses the releases to air from each facility or process.

Overview of Mercury Use and Release

All plant areas, except possibly the reactor areas, have released mercury to the ground or surface streams during use in the aluminum dissolution process, in laboratories as a chemical reagent, and as a necessary component of process equipment (Horton 1974a). Mercury has been excluded from all reactor areas to prevent reactions with aluminum in fuel and other components (Du Pont 1972a).

Mercury was used in the separations areas as a process catalyst for aluminum dissolution (as a catalyst to increase the rate at which aluminum dissolves in nitric acid) in H-Area and to much less of an extent in F-Area. It also served to remove chlorides that, if not removed, corrode stainless steel in tanks and processing equipment (Kvartek et al. 1994; Pickett et al. 1989). The addition of mercuric nitrate was also reported to decrease the releases of ^{131}I (Ice 1973; Dodgen and Sykes 1971; Du Pont 1967). The separations areas also used large quantities of sodium hydroxide (caustic), of which mercury was an impurity (Horton 1974b).

Mercury has been used in mechanical and diffusion pumps to handle tritium gas in the tritium facilities. Before 1968, old pumps and any mercury drained from the tritium facility pumps were buried in the burial grounds. Various Site researchers have estimated that the tritium facility disposed of approximately 10,000 kg of mercury in the burial grounds (Kvartek et al. 1994; Horton 1973; Westinghouse 1992). Mercury has also been used in many kinds of equipment in laboratories and other facilities onsite. The use and potential for mercury release from each of these facilities is discussed in more detail in the following sections.

Mercury discharged in liquid effluent went primarily to underground storage tanks and the seepage basins before the Effluent Treatment Facility (ETF) began operation in 1988. Mercury was also released to the air through the separation's process stacks. Mercury in separations effluent discharged to the seepage basins and contaminated groundwater underneath the basins, which outcrop to Four Mile Creek and flows to the Savannah River. Mercury releases to surface water are described in Chapter 18. The results and interpretation of monitoring of water, sediments, and fish for mercury is discussed in Chapter 20.

Mercury Use for Separations in the 200-H and 200-F Areas

Mercury was first used in H-Area for the HM process used to recover enriched uranium from spent aluminum-uranium reactor fuel in 221-H in 1959. About 7 kg of mercury was added to the large dissolver, and about 5 kg of mercury was added to the small dissolver in 221-H for each run (Kvartek et al. 1994). Mercury was first used to recover ^{238}Pu and ^{237}Np in the 221-H frames process in 1961. Mercury was initially used in 221-F to dissolve plutonium-aluminum targets and scrap in 1965. Mercury was also used during the recovery of plutonium from scrub-alloy received from Rocky Flats in 1984. About 105 kg of mercury was used to dissolve aluminum and precipitate chlorides in a typical charge.

Kvartek et al. (1994) summarized the concentrations of mercury charged to the H-Area dissolver for various campaigns from 1959–1985. These data were derived from a report titled, *Mercury Requirement for Separations Processes by* Pickett et al. (1989). Carlisle Pickett, the author of the report, and a chemical engineer in H-Area was interviewed by *RAC* researchers on two separate occasions. He provided us with copies of information from a waste reduction study, tables of flowsheets, chemical makeup tank data, and other estimates similar to those summarized in the 1989 memo. Mercury concentrations that were used ranged from 0.0025 to 0.04 moles/liter (M). The highest concentrations were used before 1962 to dissolve plutonium-aluminum targets and Mark VI-J fuel. In March 1985, the mercury concentration in the dissolvers was reduced to 0.002 M to minimize the amount of mixed hazardous waste generated (Kvartek et al. 1994), but no suitable replacement for mercury in the process has been found.

Kvartek et al. (1994) also published a table of estimates of the amounts of mercury used in the chemical separations processes from 1974–1980 based on information in essential materials

transaction reports. A total of 2500 kg was used in F-Area in 1985, 1986, 1987, 1988, 1989, and 1992. H-Area use is summarized in Table 17-41. No mercury was reported to have been used in H-Area in 1978, 1980, 1981, 1991, and 1992. Inventory adjustments resulted in a net gain in the inventory of mercury (negative amounts used) in 1990 and 1993.

Table 17-41. Mercury Use (kg) in the F-Area and H-Area Canyons by Year (Kvartek et al. 1994)

Year	221-H	221-F	Total	1% (emissions/ consumption)
1974	3600	No data available	3600	36
1975	4300	No data available	4300	43
1976	3300	No data available	3300	33
1977[a]	2700	No data available	2700	27
1978	No data available	No data available	-	
1979[a]	240	No data available	240	2.4
1980	No data available	No data available	-	
1981	No data available	No data available	-	
1982	2600	No data available	2600	26
1983	2900	No data available	2900	29
1984	4800	No data available	4800	48
1985	4800	620	5420	54.2
1986	1500	280	1780	17.8
1987	1100	300	1400	14
1988	0	680	680	6.8
1989	0	560	560	5.6

[a] partial year inventories

An average of 2449 was used in H-Canyon during the 13 years for which data was reported, and an average of 488 kg was used in F-Canyon after 1985 when mercury was used in the dissolution and head end processes. Less mercury would have been used from 1960 to 1964.

Mercury was used in the H-Canyon process as mercuric nitrate catalyst in the dissolution process. The catalyst destroyed the passive aluminum oxide surface that forms on fuel and can hinder dissolution. Some of the mercury added to the dissolvers as a catalyst was released as a vapor through the 292-H and 292-F stacks. A 1985 description of the dissolving process said that mercury was boiled for 1 hour in nitric acid in a tank to make up the catalyst. The fuel and nitric acid were preheated in the dissolvers, then the mercuric nitrate was added. It immediately reacted and mercury was vaporized. The solution in the dissolvers was then heated for about 22 hours after the catalyst was added. After dissolution was complete, the solution went to the head end system in preparation for the first cycle of solvent extraction. The 11.3E evaporator was part of the head end system. The aluminum, fission products, mercury, and other waste materials remained in the aqueous waste stream, the volume of which was decreased using the 9.1E and 9.2E evaporators. Most of the mercury in the process liquid waste was eventually sent to the high activity waste tanks. Mercury in evaporator overheads was sent to the seepage basins (Franklin 1985).

Information on the amount of mercury used, discharged to the seepage basins, or routed to the waste tanks does not seem to be adequate for using a materials balance approach to estimate releases.

Mercury vapors were released from the dissolvers, process waste evaporators, and the catalyst makeup tank. Most of the mercury emissions exhausted through the 292-H or 292-F stack. The 1987 DOE Environmental Survey states that mercury was released to the air from the H-Area separations and tritium facilities 292-H main stack, 232-H stacks 1 and 2, 234-H stack, 242-H evaporator stack, 241-H as well as the 241-F stacks and 242-F stack. The survey team thought there was potential for stack emissions of mercury to be inhaled by the surrounding population (DOE 1987).

H-Area Mercury Monitoring Program

A characterization program for the H-Canyon stack emissions was initiated in 1984 to identify mercury sources and to determine the amount of mercury being released from the stack.

A monitoring program, described in Franklin (1985), was established to measure emissions to the 292-H stack and to correlate the emissions to 221-H canyon operations. Six potential sources of mercury emissions from the HM process were identified: the catalyst makeup tank; the 6.1D and 6.4D dissolvers; and the 9.1E, 9.2E, and 11.3E evaporators. All of the six pieces of processing equipment that could potentially emit mercury vapors were exhausted by the vessel vent system. The air in the vessel vent system was passed through a reactor to remove iodine and a glass wool filter to remove particulates before passing through the sand filter and exhausting out the 292-H stack (Franklin 1985).

Mercury released through the stack during routine operations of the 6.1D and 6.4D dissolvers and the 9.1E, 9.2E, and 11.3E evaporators was monitored using a model 411 gold film mercury vapor analyzer manufactured by the Jerome Instrument Corporation modified for continuous monitoring. The mercury vapor monitor was installed in the 292-H stack sampling room, and the sample point was located at the 50-ft elevation point. Samples were taken at 15-min intervals at various times from January–April 1985. The milligram per cubic meter amounts were converted to pounds per hour based on the average flow rate of 217,000 ft^3 min^{-1} through the stack. Hourly averages were calculated and graphed. The data were presented as a series of graphs of daily data. The spikes and dips were not labeled and we cannot correlate concentrations with process activities. Maximum and minimum values for the entire study are difficult to determine. The report of the study by Franklin (1985) said that a good correlation between mercuric nitrate catalyst addition to the 6.4D dissolver and mercury emission levels was observed. He said there was generally a significant spike visible on the graph at the time of the catalyst addition, while startup of evaporators and makeup tank did not result in a spike (Franklin 1985). The 6.1D dissolvers operated on average only four times per month, so they contributed much less to the total release. The catalyst makeup tank and evaporators had little effect on the total release. Franklin (1985) estimated a yearly emission of 64.5 lb (29.3 kg) based on 15 dissolutions per month for the first quarter of 1985. This emission rate was calculated from data obtained during a period of relatively high production. The maximum theoretical capacity of the 221-H canyon during that time was 24 dissolutions per month, which would have resulted in a mercury emission rate of 104 lb y^{-1} (47.3 kg y^{-1}) (Franklin 1985). Franklin (1985) noted that previous data reported had indicated a release of about 38 lb y^{-1}, but no reference for this value was given.

The monitoring study was used to demonstrate compliance with air pollution regulations. The South Carolina regulatory limit for mercury emissions was said to have been 0.1 ton y^{-1} or 200 lb y^{-1} in 1985 (Franklin 1985).

The H-Canyon started a program to reduce mercury in March 1985. The amount of mercuric nitrate added to the dissolvers was decreased by 60% (Franklin 1985).

The mercury monitor has been out of service since the 1985 study (DOE 1987). Mercury consumption in H-Area was about 5000 lb during the first quarter of 1985. The measured emissions to the air were less than 50 lb during this time (DOE 1987). These measurements suggest that nearly all of the mercury in the process was incorporated into liquid waste and about 1% (50/5000) was released into the air. If we apply this factor to the mercury reported to have been used in the canyons (Kvartek et al. 1994), then we can predict the kilograms per year emitted shown in Table 17-41. Assuming 2.5 kg y^{-1} was released in 1978, 1979, 1980, and 1981; 1 kg y^{-1} was released from 1954—1958; and 36 kg was released each year from 1954–1973, a total of 895 kg (1% of the total amount used) is the predicted release. This averages to about 29 kg y^{-1} over 31 years. The uncertainty in such an estimate is very large. The uncertainty in applying 4-months of sampling data to 20 years of operations and the uncertainty in the estimates of the amount of mercury used are difficult to quantify.

The DOE Environmental Survey Report from 1987 mentions a mercury monitor that had been removed from 292-H stack for repair, but it was suppose to have been reinstalled when it was repaired (DOE 1987). As far as we know, monitoring data have not been collected since this study. However, in 1996, plans were made to collect stack monitoring data, including mercury concentrations from F-Area, which recently begun processing. As of September 1997, funding to perform stack monitoring for nonradiological emissions had not been obtained (Villa 1997).

Kvartek et al.. (1994) estimated that in 1988 an average of 2.7 kg (5.9 lb) of mercury per year was released from the 292-H stack, and a maximum theoretical discharge of 4.8 kg y^{-1} (106 lb y^{-1}) was released (Kvartek et al.. 1994). At this time, the amount of mercury used for dissolving aluminum had been reduced. Estimates of mercury release before the reduction were 29 kg y^{-1} (63.8 lb y^{-1}) with a maximum theoretical discharge of 47 kg y^{-1} (103 lb y^{-1}) (Kvartek et al.. 1994).

Mercury was also collected by the separations area waste evaporators. There were two evaporators in both the F and H Waste Management Areas. Each evaporator had two air emission points: the vessel vent and the building exhaust. DOE (1987) reported that air emissions from the F-Area and H-Area evaporators had not been characterized. Franklin (1985), which included the three H-Area evaporators, was not mentioned.

Operating Permit Release Estimates for H-Area

Mercury vapor emissions occur as a result of the addition of mercuric nitrate catalyst $Hg(NO_3)_2$ to each dissolver batch. The mercury emissions for the Part 70 permit application were calculated for the time period when the mercury reduction program initiated after 1985 was in place. The calculations were based on actual monitoring of the 291-H stack for mercury emissions. According to the permit, mercury emissions from the 291-H stack were monitored on March 19 and 20, 1987. Emissions included in the permit application used this monitoring data and referenced two memos from M.G. Franklin to T.G. Cambell and to J.G. McKibbin, dated March 1988 and March 1985. A report dated August 1985 was located and is included in the

Phase I database (Franklin 1985), but the memo from Franklin in 1988 or any other reports about the 1985 or 1988 monitoring results were not found.

Based on the amount of fuel run through the dissolver during the time of the sampling, Radian estimated that for Mark 16B fuel with 227 kg of aluminum and 0.0021 M mercuric nitrate in 14,000 L of dissolver solution, at a use rate of 9.54 kg run^{-1}, 14 runs mo^{-1}, 12 mo y^{-1}, 1603 kg of mercuric nitrate catalyst was added, which corresponds to the measured emission of 6.3 lb y^{-1} (2.9 kg y^{-1}). Other charges to the dissolver were analyzed. For other fuels, at 370 kg aluminum per run, 10.5 kg of mercuric nitrate per run was used for 20 runs mo^{-1} and 12 mo y^{-1}, resulting in an actual use of 2527 kg y^{-1}. Assuming the same emission rate as for Mark 16B fuel, the estimated uncontrolled emission was

$$\frac{6.3 \text{ lb y}^{-1}}{1603 \text{ kg y}^{-1} \text{ used}} \times 2527 \text{ kg. y}^{-1} \text{ used} = 9.9 \text{ lb y}^{-1} = 4.95 \times 10^{-3} \text{ ton y}^{-1} \ .$$

The maximum uncontrolled emission from the dissolver was calculated by extending the estimate from 7200 hr y^{-1} actual operation to 8760 hr y^{-1}, resulting in 12 lb y^{-1} (6.05×10^{-3} ton y^{-1}).

In their 1993 H-Area air emissions calculations notebook, Radian assumed that no emissions of mercury occurred from the dissolution step of the process because mercuric nitrate "forms a large nitrate complex that remains in solution. On aluminum surfaces Hg^{+2} is reduced to Hg^{0} which forms an amalgam with Al^{+3} in strong acid solutions which says that the *in situ* retention of Hg^{+2} as a catalyst in the acid solution is a contributing factor in the formation of NO gas which is vented from the dissolvers." Radian (1993) referenced Cotton and Wilkinson's Advanced Inorganic Chemistry, 2nd edition, pp. 520-521 and WSRC-TR-91-606, Purex Process Chemistry, 1991, which *RAC* was unable to locate, in support of this assumption. A special stack sampling study conducted in 1985 suggests mercury was released from the evaporators and the dissolvers (Franklin 1985). A study of emissions from the Idaho Chemical Processing Plant, which used a similar dissolution process, suggests that most of the mercury remains in the liquid waste (Herbst 1979).

Radian (1993) described the use of mercury in the dissolving process. Mercury was gravity fed to the mercuric nitrate storage tank and dissolved in the tank with concentrated HNO_3, forming $Hg(NO^3)_2$ and H_2. Concern about hydrogen emissions from the reaction was expressed, but the mercury nitrate complex was thought to be nonvolatile and there was thought to be no mercury above the solution in the tank. The mercury charging station for mercuric nitrate production was also described. Elemental mercury was poured from a flask into the charging station, which gravity fed into the mercuric nitrate storage tank. For the air inventory, Radian estimated actual mercury vapor losses from the charging operation using the EPA's AP-42 equation for organic liquid transfer losses. Radian estimated the vapor pressure of mercury under these conditions to be 1.26×10^{-5} atm at 25ºC and calculated emissions using the dissolver 'demand data' for mercuric nitrate (Radian 1993). They estimated 0.00125 lb of mercury was released per 10^3 gal transferred. The mass (m) of mercury processed was calculated from dissolver charge records using the equation:

$$m\ 100\%\ Hg = M_{Hg} \times (lb/453.6\ g) \times \Sigma(V_{dis} \times M_{Hg}) \quad (17\text{-}1)$$

where
M_{Hg} = molecular weight of mercury (200.16 g mol^{-1})
M_{Hg} = molarity of mercury in mol L^{-1} for each batch
V_{dis} = volume of dissolver solution in L for each batch.

The molarity of mercury charged to the dissolver varied with the type of target dissolved. A table in the Radian report indicates that for the 1985 estimate, they had obtained information on 13 different types of targets dissolved, the V_{dis} for each target, the number of batches run for each type of target, and the M_{Hg} for the dissolving solution used for each target. The total amounts were summed to 9026.8 lb of 100% mercury processed into mercuric nitrate or 79.58 gal of mercury, resulting in a transfer loss of (0.00125 lb 10^{-3} gal) × 79.58 gal mercury or 9.948×10^{-5} lb of mercury emitted from transfer operations during 1985. The hourly emission rates reported in the AIRS database were calculated from this value using the assumption that that mercury was transferred into the mercuric nitrate tank a maximum of 16 hr y^{-1} (Radian 1993).

The 242-25H evaporator process accounted for mercury emissions of 1.55×10^{-4} ton y^{-1}, based on airflow, capacities, and throughputs. Emission estimates for the mercury mixing station in 222-H, also called the Canyon Bulk Chemicals Facility, were 1.96×10^{-8} ton y^{-1}, maximum. This was based on a maximum use of mercuric nitrate of 3.8 lb h^{-1} for dissolving (Westinghouse 1996a).

Operating Permit Releases Estimates for F-Area

Mercury vapor was released from the F-Area dissolver because mercury catalysts were added to process the Rocky Flats scrub alloy fuel. The permit application stated that actual measurements of mercury from the H-Canyon 292-H stack on March 19 and 20, 1987, were used to estimate releases from F-Canyon processes. The dissolver batch corresponding to the measurements was characterized as containing 227 kg of aluminum and 0.0021 M mercuric nitrate in 14,000 L of dissolver solution running at an average of 14 dissolutions mo^{-1}. The amount of mercury released was proportional to the amount used in the dissolver and the amount of aluminum present because mercury amalgamates with aluminum. The HM process was estimated to use 9.5 kg of mercury per HM run or 1603 kg y^{-1}. About 38,173 kg of aluminum was processed each year. The actual, measured amounts of mercury emitted under these conditions was 6.3 lb y^{-1} (2.9 kg y^{-1}) (Westinghouse 1996a).

In the HM process, mercuric nitrate was not used for the head end strike. However, processing of the Rocky Flats scrub alloy involved adding mercuric nitrate to the dissolver and mercury vapor emissions from the head end process. In F-Area, 384 lb of mercury was added per dissolver run and 200 lb per strike in the head end process for similar processing. Processing of the Rocky Flats fuel was different because of concerns about plutonium criticality safety. Based on fuel composition and operating procedures limiting the amount of plutonium processed, the amount of catalyst used was calculated to be 109 kg per run for the dissolver and 57 kg per run for the head end. Correlated with measured emissions from the Mark 16B fuel, an actual emission of 16 lb y^{-1} from the dissolver and 8 lb y^{-1} from the head end was calculated, or 24 lb or 0.012 ton y^{-1} combined. The maximum emission from both, based on 24 h day^{-1} operation, was

estimated to be 59 lb y^{-1} or 2.95×10^{-2} ton y^{-1}. At peak production, about 1125 lb of mercury was added to the dissolver and head end for each run of Rocky Flats scrub alloy fuel. The dissolver was calculated to emit 72 lb y^{-1} based on the amount used. Emissions estimated based on the amount of aluminum dissolved yielded a much lower estimate, 1.13 lb y^{-1}. Therefore, the more conservative method was chosen and 72 lb y^{-1} (3.6×10^{-2} ton y^{-1}) is the reported actual uncontrolled emissions for the process. This was based on three runs per month, 12 mo y^{-1}, 30 h run^{-1}, and 1080 h y^{-1} (Westinghouse 1996a).

F-Area and H-Area Evaporators

The permit application reported an emission rate of 1.59×10^{-7} ton y^{-1} for mercury from the 242-1F evaporator. The permit listed all of the evaporators and overhead receiver tanks in F-Area and H-Area, a total of 22 facilities. Based on feed rates, airflow rates, tank volumes, and vapor pressures, actual emission estimates for mercury totaled 2.17×10^{-5} ton y^{-1} for F-Area and 8.66×10^{-5} ton y^{-1} for H-Area. The total for both areas was 1.08×10^{-4} ton y^{-1}. Included in these estimates are all of the 242-F and 242-H evaporators, all of the receiver tanks, the 241-H diversion box and pump tank, the 241-H-100H waste transfer facility tanks, 242-25H evaporators, 242-3F CTS, 242-21H CTS, 241-70H pump tank and Pits 5 and 6, and 241-18H CTS pump tank (Westinghouse 1996a).

Releases from the ETF stack from chemical mixing tank, filter cleaning, and waste concentrate tank were estimated to total 3.48×10^{-10} ton y^{-1} of mercury.

The emissions estimate for the 200-H emergency power generator, actual emissions assuming 2080 hours of operation each year, was 6.70×10^{-7} ton y^{-1} for mercury (Westinghouse 1996a).

Air Emissions Inventory Estimates for F-Canyon and H-Canyon

Mercury estimates for the canyon stacks were discussed in the permit application and the calculational document for H-Area, but they were not in the AIRS database for the years examined (Faugl 1996h). *RAC* asked Westinghouse to search the AIRS database again, specifically for canyon stack releases. A search of the AIRS database entries for mercury found mercury emissions were estimated for the separations area in 1994 and 1995. Emission estimates for the F-Canyon stacks were first seen in 1994. All of the actual emissions were reported to be zero, which was expected because the facility was not operating at the time. The emission estimates for maximum design capacity for F-Canyon were 0.099 ton y^{-1} for the dissolver and 0.192 ton y^{-1} for the head end exhaust in 1994 and 1995 (Faugl 1996e). The AIRS database maximum design capacity emissions estimates for 1995 for H-Canyon were 0.0195 ton y^{-1} for the dissolver and 0.030 ton y^{-1} for the head end operations (Faugl 1996e). Based on process history, we would expect that the emissions from H-Area would have been greater than from F-Area. The AIRS database estimates of 0.0495 ton y^{-1} for H-Area and 0.29 ton y^{-1} for F-Area do not seem to be representative for most years. It could be that the F-Area emissions were calculated using the assumption that the plant was processing Rocky Flats scrub alloy fuel at full capacity.

Air Emissions Inventory Estimates for Other Sources

The AIRS database contained emissions for the H-Area and K-Area coal piles and many diesel generators and pumps with a total of less than 4×10^{-5} ton y^{-1} actual emission in 1990 (Faugl 1996h). Some of the key sources are listed in Table 17-42.

Table 17-42. Mercury Emission Estimates in the AIRS Database

Year and source description	1985 and 1987		1990	
	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1985 and 1987				
F-Area seepage basin	2.14×10^{-2}	2.14×10^{-2}	2.14×10^{-2}	2.14×10^{-2}
Old F-Area seepage basin	2.31×10^{-3}	2.31×10^{-3}	2.31×10^{-3}	2.31×10^{-3}
H-Area seepage basins	1.47×10^{-10}	1.47×10^{-10}	1.85×10^{-10}	1.85×10^{-10}
723-A met lab basin	1.00×10^{-6}	1.00×10^{-6}	1.00×10^{-6}	1.00×10^{-6}
H-Area coal storage pile	5.70×10^{-5}	5.70×10^{-5}	5.70×10^{-5}	5.70×10^{-5}
H-Area powerhouse ash sluice sump	4.79×10^{-6}	4.79×10^{-6}	4.79×10^{-6}	4.79×10^{-6}
K-Area coal pile	1.80×10^{-6}	1.80×10^{-6}	1.80×10^{-6}	1.80×10^{-6}
K-Area coal pile runoff basin	1.80×10^{-6}	1.80×10^{-6}	1.80×10^{-6}	1.80×10^{-6}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Table 17-43 presents the totals in the AIRS database, which did not appear to include the H-Canyon and F-Canyon stack releases.

Table 17-43. Total Mercury Releases from the AIRS Database

Totals	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1985	2.54×10^{-2}	2.38×10^{-2}
1987	2.54×10^{-2}	2.38×10^{-2}
1990	3.17×10^{-2}	7.26×10^{-3}
1992	9.20×10^{-2}	2.36×10^{-3}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

In the AIRS database, the H-Canyon stack maximum design capacity emissions estimates for 1995 were 0.0195 ton y^{-1} for the dissolver and 0.03 ton y^{-1} for the head end. The F-Canyon estimates were 0.0997 ton y^{-1} for the dissolver and 0.192 ton y^{-1} for the head end. These are the largest emissions estimates reported.

Seepage Basins

Mercury was discharged to the seepage basins with low activity waste and evaporator overheads. Some of the mercury probably evaporated into the air. We did not find reports of monitoring or investigations about mercury released to the air from the H-Area or F-Area seepage basins.

The Old F-Area seepage basin was also included in the Part 70 Operating Permit Application. The 1.02-acre area, in place since 1954, was estimated to have released 2.31×10^{-3} ton y^{-1} mercury based on a concentration of mercury of 0.32 ppm, the highest concentration detected, and data on wind speed, depth, area, and temperature. The model CHEMDAT7 was used. The emission rate was estimated for 1993 and 1994. This estimate corresponds to that listed for the Old F-Area basin in the AIRS database for 1985 and 1987 (Faugl 1996h). The Ford-Area seepage basin was treated similarly, but a mercury emission estimate of zero was given (Westinghouse 1996a). Emissions for the H-Area seepage basins were listed in the AIRS database printouts (Faugl 1996h). The H-Area calculations did not describe how the values for the seepage basins were calculated (Radian 1993). The estimate was likely based on surface area and was calculated using an approach similar to that described in the permit application for the Old F-Area seepage basin. The 1985 actual emissions estimate of 1.4×10^{-10} ton y^{-1} presumably corresponds to a time period when the canyons were operating at near maximum capacity. If this amount was released each year from the H-Area seepage basin, then about 5.3×10^{-9} kg total might have been released over the 36-year period between 1954 and 1989.

Tritium Facilities

The tritium production facilities, 232-H and 234-H, used mercury in several types of process pumps such as Sprengel pumps, Edwards mercury diffusion pumps, and CEC mercury booster ejection pumps. These mechanical and diffusion pumps were used as a part of the tritium facilities gas handling system. The mercury generated a vacuum used to transfer tritium gas and evacuate process equipment. Several different types of tritium pumps have been used over the years. They all have reservoirs containing 3 to 105 kg of circulating mercury. The mercury deteriorates from oxidation and reaction with pump components and must be changed occasionally. The waste mercury may have contained a small amount of tritium and most was apparently buried in the radioactive burial ground (Horton 1973). In the 1980s and 1990s, some of the mercury pumps were replaced with oil diaphragm-type pumps (DOE 1987).

In a memo justifying discontinuation of biological monitoring in H-Area, Karoly (1985) reviewed potential sources of mercury exposure for workers and estimated the mercury inventory in equipment at various facilities. He reported that diffusion pumps at 232-H, contained from 6 to 300 lb of mercury per pump. Four diffusion columns in 232-H contained 30 lb per column and were changed out once every 2 years. Seal pots in the inert gas system for 232-H and 234-H contained 200 lb per pot and required little or no maintenance. Nine diffusion pumps in 234-H contained from 6 to 120 lb per pump, and four mechanical pumps in 234- H contained 160 lb each. Merrick scales in the 184 C, K, and P powerhouses and in 3/700-Areas contained about 0.5 L of mercury per scale. These were closed systems that should not have released mercury to the environment. In addition, about 1700 lb of mercury was stored at 234-H in polyethylene bottles inside a hood and about 1.5 ton was stored in 232-H in 55-gal drums in a chemical storage

area (Karoly 1985). Mention of 232-H maintenance operations in logbooks and other documents refers to changing mercury in pumps during pump maintenance. Deteriorated mercury was drained and the pump refilled in an air supply hood in the 1970s and 1980s. Waste mercury was bottled for disposal. Workers did not measure how much was released to the air from these activities. Shift logbooks and special work permits also mentioned leaks in pumps and maintenance of mercury-containing equipment. The Spengle pumps were drained and repaired in hoods in a contained area (Du Pont 1959). Although most of the concern centered on radiological contamination, reports suggested that mercury was occasionally monitored for industrial hygiene purposes and it was not reported to be a problem in any of the reports reviewed.

According to Kvartek et al. (1994), Schmitz 1989 reported the mercury inventory in the tritium facilities in 1989 was 2200 kg of contaminated mercury in storage, 860 kg in pumps, 110 kg uncontaminated fresh mercury in storage, and 140 kg of mercury in other sources and in 1992, Rowan (in a personal communication with Kvartek et al. (1994), reported 28 pumps, with a total capacity of 241 kg of mercury, were operating in 232-H.

In a technical memorandum given to RAC by Ed Kvartek, Johnson (1983), reported the 1983 Mercury Inventory Record for the Tritium Facilities, compiled from essential materials transaction reports. After 1968, when the burial of mercury waste was stopped, the amount of mercury used in the facilities dropped to 7530 pounds (3200 lb from 1968–1972 and 4330 lb from 1973–1983). The decrease was attributed to reuse of unoxidized mercury drained from pumps. Before 1968, all of the mercury drained from pumps (about 20,000 pounds) was buried as waste (Johnson 1983).

Data compiled by Kvartek et al.. (1994) suggest that about 10,200 kg of mercury was used by the tritium facilities from 1960 to 1987. The highest amount reported was 1300 kg in 1963, followed by 1000 kg in 1982. Zero use was reported for 1979. No amount was reported for 1978, 1980, 1981, and 1986 because “no information was available”(Kvartek et al. 1994). Excluding these 4 years, the average annual use appears to have been about 424 kg y^{-1} for the 28-year period. In an attempt to estimate the amount of mercury buried in the burial ground, Horton (1973) compiled the “amounts consumed since 1960 . . . recorded in the Essential Materials Transactions Report in the Separations Department,” referencing Du Pont reports DPSP-60-19 through DPSP-72-19 for 1960 through 1972. The total kilograms used each year is reproduced in Table 17-44. The records for 1966 and 1967 were said to have been destroyed, and consumption estimates for these years were made using an interpolated average from 1965 and 1968 values (Horton 1973).

Table 17-44. Mercury Reported to Have Been Used By the Tritium Facilities (kg)

Year	Mercury use in the tritium facilities reported by Kvartek et al. (1994)	Mercury use in the tritium facilities reported by Horton (1973)
1954–1960	Not reported	Not reported
1960	600	604
1961	900	895
1962	960	959
1963	1300	1259
1964	730	727
1965	530	525
1966	500	502
1967	500	502
1968	480	480
1969	240	239
1970	200	204
1971	150	148
1972	380	384
1973	130	Not Reported
1974	77	Not Reported
1975	790	Not Reported
1976	14	Not Reported
1977	68	Not Reported
1978	No data available	Not Reported
1979	0	Not Reported
1980	No data available	Not Reported
1981	No data available	Not Reported
1982	1000	Not Reported
1983	450	Not Reported
1984	180	Not Reported
1985	32	Not Reported
1986	No data available	Not Reported
1987	36	Not Reported

Kvartek et al. (1994) thought releases to the air from the tritium facility process stacks were small. Releases from tritium facilities were not routinely monitored. Engineering calculations in 1988 estimated that stack emissions from the facilities were less than 0.2 kg of mercury per year (Kvartek et al. 1994).

The release of mercury vapors from mercury-containing process pumps used to transport tritium and other gases through the process and metal fumes from the target furnace in the H-Area tritium facilities were not measured. Pumps in both 232-H and 234-H released mercury into the process streams through volatilization and entrainment (DOE 1987). Mercury was also present in the tritium gas distribution piping. Mercury was removed at various points using gold-foil traps designed to collect mercury in the piping. About 3 to 10 traps were removed each year. The gold traps could contain 3 to 6 g of mercury, but traps and old piping were not a significant source of mercury from the tritium facilities (Kvartek et al. 1994).

No controls for mercury were applied to the process stacks. Although stack testing for mercury has been proposed, it does not appear to have ever been conducted and mercury emissions from the facilities were not measured. The DOE Environmental Survey team felt the tritium facilities had the potential to release more than 200 lb y^{-1} (0.1 ton y^{-1}) (DOE 1987).

Emissions from the tritium facilities were not described in detail in the unclassified version of the permit application, but they were included in the totals from the AIRS database.

Separations Area Waste Tanks

Most of the mercury put into the H-Area processes came out in the radioactive liquid waste, which was said to contain about 0.5 g L^{-1} mercury (DOE 1982, 1987). Most of the mercury used in the dissolvers remained in the dissolver waste solutions and was transferred to the underground waste tanks. It is estimated that in H-Area, where the majority of the aluminum dissolving was done, 80 ton of mercury had been discharged to the waste tanks as of 1971 (Du Pont 1971a). An assessment in 1988 and 1989 estimated that the underground waste tanks contained from 73,000 kg to 91,000 kg (or about 100 ton) of mercury from separations area wastes (Kvartek et al. 1994). Another evaluation published in 1994 stated that waste solvent tanks at the Solid Waste Disposal Facility (SWDF) contained spent canyon solvents that contained up to 13 mg L^{-1} mercury, and approximately 80,000 kg of mercury was contained in high level waste tanks (Kvartek et al. 1994). The underground tanks were continuously exhausted to prevent the buildup of flammable gases. Mercury in the vapor space above the liquid waste would have been released in this exhaust, but how much mercury may have been released is unknown. As far as we can determine, mercury vapor in the waste tank exhaust has not been measured. Mercury can evaporate into the air space in waste tanks and be vented into the air through the tank ventilation systems. In answers to questions asked in the 1980s about mercury release from the tanks, Site engineers reported that the potential for emissions of mercury from the tank ventilation systems was not known (Albenesius 1992). Studies have shown that most of the mercury settled to the bottom of the sludge in the tanks and very little has been released (Kvartek et al.. 1994). The sludge in the tanks was reported to contain about 1.6 weight percent mercury hydroxide (Ebra and Wiley 1984).

In the *Action Plan for the Resolution of findings in the DOE-HQ Environmental Survey of SRS*, W.C. Reinig (1989) noted the survey finding that " atmospheric mercury emissions from the Tritium Facility and waste tank farms have not been characterized and may represent significant sources of environmental contamination and a potential human health risk." No further action was recommended because the SRS believed that the only significant source was from the H-Canyon dissolvers. Measured to be about 6 lb/yr. They reported that that H-Canyon was using about 16 per cent of the mercury used in previous years and the air emissions had been reduced from 64.5 lbs (30 kg)/yr in 1986 (maximum theoretical capacity of 104 lbs/yr) to 8.3 lbs (3.8 kg)/yr in 1987 (maximum theoretical capacity of 10.8 lbs/yr). Reinig (1989) stated that a worse case engineered calculation for the Tritium Facility demonstrated that less than 0.5 lb/yr could be released and that other mercury sources were considered insignificant (Reinig 1989).

The operating permit application contained estimates of mercury released as a result of waste tank purges in F-Area and H-Area. The total estimate from all 22 of the F-Area tanks listed was 4.48×10^{-4} ton y^{-1}. The total for the 29 H-Area waste tanks was 4.05×10^{-4} ton y^{-1} for mercury, actual emission estimates. The total for both areas was 8.53×10^{-4} ton y^{-1} (Westinghouse 1996a).

Mercury in the Burial Grounds

Until the end of 1968, all of the mercury drained during pump maintenance and replacement was buried as waste (Johnson 1983). It was usually buried in 1-L polyethylene bottles that were placed in metal cans and buried in 643-E, of the SWDF, formerly called 643-G, and also referred to as the burial ground (Orebaugh and Hale 1976).

Beginning in 1968, metallic impurities and oxidized mercury in the mercury were removed through decanting and the mercury was reused. As a result of this recycling, the amount of mercury buried was reduced and no new mercury has been added to the tritium facilities inventory since 1987 according to Kvartek et al.. (1994).

Several reports estimate that between 1956 and 1968, before recycling mercury drained from the pumps was begun, the tritium facility disposed of about 10,000 kg of mercury in the 643-E SWDF (Westinghouse 1992). After 1968, mercury trapped in the gold traps, collected from leaks or spills, or that could not be drained from equipment, continued to be buried until 643-E was filled in 1972 (Kvartek et al.. 1994).

In 1973, Horton estimated that 10 ton (20,000 lb or about 9100 kg) of mercury had been buried since startup. Horton (1973) explained that the quantities buried had not been recorded and his estimate was an upper limit estimate based on mercury use. He considered that of the 3200 lb used from 1968–1972, about 1000 lb was recovered from spills and was in storage. The remaining 2200 lb might have existed as unmeasured increased inventory in the process facilities or may have been buried in discarded process equipment (Horton 1973). Horton (1973) reported that mercury burial was stopped in 1974. The burial containers were expected to remain intact for several decades and routine monitoring to detect transport of mercury from the burial ground was not recommended at the time (Horton 1973). In the years after 1974, the mercury burial estimate determined by Horton was used by others and no additional information to improve the estimate was offered (Kvartek et al.. 1994; Orebaugh and Hale 1976; Albenesius 1992).

Waste liquid mercury was placed in a 1-L polyethylene bottle and surrounded by two polyethylene bags. Two or three bottles in bags were then placed in a 5-gal steel can. These were buried throughout 44 acres of the low-level beta gamma waste trenches in 643-G burial ground. In 1973, Hale recognized that volatilization of metallic mercury (Hg^{o}) from the burial ground into the air would be a concern if the containers in which the mercury was placed failed, and he noted that the depth of soil cover required so that this would not be a concern was unknown (Hale 1973).

Orebaugh and Hale (1976) mathematically modeled transport using 9000 kg of mercury as the source term corresponding to the 10 ton of mercury said to have been buried in trenches by Horton (1973). They examined the soil redox potential, pH characteristics, and inorganic chloride and sulfate concentrations and concluded that mercury in the soil was in a stable complex. The modeling took into account the soil moisture, mercury solubility, soil composition, burial depth, soil porosity, and permeability to water and gases of the trench fill soil and surrounding and underlying soil. The soil had been studied extensively over the years because of a concern about leaching of buried radioactive materials. Experiments were conducted to measure mercury vaporization from soil and the diffusion of mercury vapor through soil with varying moisture contents. Mercury solubility was also determined experimentally. In the course of these experiments, the researchers determined that mercury on colloids could be an important transport mechanism for mercury in soil. They found that transport could occur through vaporization into

the air or transport in water of both dissolved mercury in water percolating through the soil and mercury on oxide colloids of iron and silicon in soil water. They concluded that colloidal suspension was the dominant mode for transport of mercury from the burial grounds. A worst case estimate of possible vapor transport to the atmosphere (which assumed that all of the mercury in bottles, bags, and steel cans was released to the soil) was 5 mg h^{-1}, a flux considered by the authors to be insufficient for any environmental impact (Orebaugh and Hale 1976; Kvartek et al. 1994).

As far as we know, waste mercury packaged in bottles, bags, and cans has not been released to the soil or to the air from the SWDF. We have characterized the burial of mercury to the extent possible. At this time, developing a better source term for releases to the air from the burial grounds is not feasible because of the lack of accurate burial records, releases are not likely to have been large, and mercury buried appears to have remained in the burial ground.

Mercury from Coal Burning

Coal contains varying amounts of mercury that are released as a vapor when coal is burned. Coal-fueled boilers have been used at the SRS to generate steam to heat buildings, operate process equipment, and produce electricity. The Site burned large amounts of coal over the years. Mercury is of concern for release from coal burning plants because, unlike many of the other toxic metals, it is not effectively removed by common particulate control measures. A summary of estimates of the coal consumed since 1972 is provided in the section on coal in this chapter.

Mercury releases from coal have not been measured, but they were estimated by Horton (1974a) and also by Kvartek et al. (1994). Horton (1974a) estimated average mercury releases from the Site powerhouses based on a concentration of mercury in coal of 1 ppm. He estimated that the D-Area powerhouse burned 450,000 ton of coal and released 900 lb (410 kg) of mercury per year, and that all other powerhouses at the SRS burned 215,000 ton of coal and released 430 lb (195 kg) of mercury each year. He compared this to the South Carolina Electric and Gas Company's Urquhart Station, which burned 587,000 ton of coal each year and released 1170 lb (532 kg) of mercury.

Kvartek et al. (1994) used a concentration of 0.12 ppm of mercury in coal and calculated the amount of mercury released from 1980–1993 using the assumption that all of the mercury in the coal volatilized and was released. Interestingly, the amount of coal burned reported by Kvartek et al. (1994) for these years was higher than the amounts reported in the annual reports. Table 17-45 presents the estimates of mercury releases that Kvartek et al. (1994) and Horton (1974a) compiled.

Kvartek's estimates are about 10 fold less those based on Horton's estimate because Horton (1974a) estimated that 9.1×10^{-4} kg of mercury was released for each ton of coal burned and Kvartek et al. (1994) estimated that 1.08×10^{-4} kg ton^{-1} was released. Horton (1974a) said that coal in the U.S. averaged 1 ppm mercury, as opposed to Kvartek's estimate of 0.12 ppm said to be a coal vendors estimate. We can speculate that Kvartek's estimates might be more accurate because more was understood about mercury emissions from coal in 1994 than in 1974 and emissions factors may have been more refined. However, we know nothing about the quality of the coal burned in various years and how much mercury it contained. The EPA's emissions factors for mercury released from coal burning range from 9.7×10^{-5} to 1.3×10^{-4} lb ton^{-1} burned, much closer to the Kvartek et al. lower estimates than to the Horton larger estimates.

Unfortunately, mercury emissions from the powerhouses were not evaluated for the operating permit application nor included in the AIRS database. We have no information on coal burned between 1952–1972. We know that less than 500,000 ton of coal was probably burned each year before 1972, probably much less in the early years when the reactor areas were still under construction.

Table 17-45. Mercury Emission Estimates for the Powerhouses

Year	Coal burned (ton)	Mercury release estimates reported by Kvartek et al. (1994) (kg)	Mercury release estimates calculated using EPA AP-42 emission factors[a] (kg)	Mercury release estimates calculated using Horton's (1974) data (kg)[b]
1972	500,000		21.8–29.5	455
1973	500,000		21.8–29.5	455
1974	500,000		21.8–29.5	455
1975	500,000		21.8–29.5	455
1976	500,000		21.8–29.5	455
1977	500,000		21.8–29.5	455
1978	500,000		21.8–29.5	455
1979	500,000		21.8–29.5	455
1980	500,000	48	21.8–29.5	455
1981	500,000	51	21.8–29.5	455
1982	500,000	47	21.8–29.5	455
1983	460,000	50	20.3–27.2	418
1984	460,000	49	20.3–27.2	418
1985	455,000	49	20.0–26.9	414
1986	455,000	48	20.0–26.9	414
1987	453,000	49	19.9–26.8	412
1988	374,000	41	16.5–22.1	340
1989	227,000	25	10.0–13.4	206

[a] EPA emissions factors range from 9.7×10^{-5} to 1.3×10^{-4} lb ton^{-1} or 4.41×10^{-5} to 5.91×10^{-5} kg ton^{-1} of coal burned.

[b] Estimated mercury released based on annual report coal consumption and the factor used by Horton (1974a) of 1×10^{-4} kg released per ton of coal burned.

If we assume that 500,000 ton of coal were burned each year from 1952–1972 (a conservative assumption), and use the EPA's range of emission factors from the AP-42 publication (EPA 1988), then we can estimate that a total of about 1816–2455 kg (2.0–2.7 ton) of mercury was released from coal burning from 1952–1989, for an average of about 46.5–63 kg y^{-1} (0.05–0.07 ton y^{-1}). The emission factor used by Horton (1974a) would result in release estimates ten fold greater than these.

In 1974, Spanish moss along the Savannah River was collected and the mercury content was measured. Horton (1974a) concluded that the effects of the SRS powerhouses on moss concentrations seemed small when compared to moss concentrations adjacent to Bush Field (the Augusta airport) and the stretch of industrial plants along the river known as the 'miracle mile'.

The coal crushing operation at 784-A was evaluated for the 1996 air quality permit application. The maximum emissions for several different pieces of equipment and the coal pile, assuming operation at a capacity of 66 ton h^{-1}, totaled 1.09×10^{-5} ton y^{-1} for mercury based on the amount of coal processed. Actual emissions estimates for metals from the fuel oil-fired package boilers in K-Area also included a value for mercury at 5.55×10^{-5} ton y^{-1} (Westinghouse 1996a).

Mercury Used in Laboratory, Experimental, and Other Support Facilities

Mercury has been and still is a commonly used laboratory chemical, used as a standard and reagent for many applications. Mercury is found in thermometers, manometers, barometers, switches, relays, pressure monitors, lights, batteries, and other equipment. In the 1993 inventory, 11 facilities reported having from 0.5 to 5000 kg of mercury onsite (Kvartek et al. 1994). The Site reported that discharges from experimental, laboratory, and process support facilities were very low. The 1990 Air Emissions Inventory lists 98 emission points for mercury including storage tanks, process stacks, ash disposal, coal boilers, and an incinerator (Kvartek et al. 1994).

Releases from Other Sources

Other instances of mercury mentioned in industrial hygiene or other reports have been noted. "A mercury vapor problem in 484-D was recognized by the Instrument Department and Health Physics" was noted in the June 1955 Monthly Report for the Explosives Department (Du Pont 1955). This was likely to have been an industrial hygiene concern. A Works Technical Report from April 1977 mentions bioassay of D-Area employees who routinely handled mercury. All of the employees were negative, but bioassays were to be done annually (Du Pont 1977b). This suggests that mercury was used in D-Area in large enough quantities and routinely enough to be of concern for worker exposure (Du Pont 1977b). Other records that explain how mercury was used or released in D-Area have not been discovered. Several workers with knowledge of historical operations in D-Area could not recall a use for mercury. They speculated that mercury in river water taken by the 400-Area to use for the powerhouse and heavy water processes may have been a concern for workers working in the water treatment plant.

Another small source of mercury emissions, noted in the Part 70 Operating Permit Application Amendment No. 3 from 1997, was a fluorescent lamp disposer with a maximum emission estimate of 0.00313 ton y^{-1} for mercury (Westinghouse 1996c).

Summary of Mercury Releases to Air

In summary, both Frankin (1985) and Kvartek et al. (1994) estimated that an average of 29 kg y^{-1} (0.03 ton y^{-1}) and a maximum of 47 kg y^{-1} (0.05 ton y^{-1}) was released from 292-H before 1985. Kvartek estimated an average of 2.7 kg y^{-1} (2.9×10^{-3} ton y^{-1}) and maximum of 4.8 kg y^{-1} (5.3×10^{-3} ton y^{-1}) was released from 292-H after 1988. In 1987, the DOE Environmental Survey team believed that the tritium facilities had the potential to release 0.1 ton y^{-1} (DOE 1987). Kvartek et al. (1994) predicted a release of less than 2.5×10^{-3} ton y^{-1} for the tritium facilities. There is no evidence that mercury in the burial grounds has been released to the air.

The air permit estimates for the H-Area and F-Area waste tank purges totaled 8.5×10^{-4} ton y^{-1}. We might add 0.05–0.07 ton y^{-1} from coal burning for most years.
Release estimates are summarized in Table 17-46.

Table 17-46. Summary of Estimates for Mercury Releases to Air

Source of releases	Source of estimate	Actual estimate or lower estimate (ton y^{-1})	Maximum estimate or higher estimate (ton y^{-1})
F-Area and H-Area	AIRS database (Faugl 1996h); Permit Application (Westinghouse 1996a); Kvartek et al. (1994)	0.03	0.3395
Tritium facilities	Kvartek et al. (1994) and DOE Survey (DOE 1987)	0.0025	0.1
Waste tanks	Permit Application (Westinghouse 1996a)	8.5×10^{-4}	8.5×10^{-4}
Coal burning	EPA 1988	0.05	0.07
Total		0.083	0.51

The uncertainty and error in the estimates derived from essential materials and coal inventories, estimates of mercury content of coal, waste tanks, seepage basin sediments, and canyon use and release data are not readily quantifiable. The variability of calculated values are at least an order of magnitude. There is a 10-fold difference between different reported estimates for mercury releases from coal burning. There is a similar difference between estimates on the air emissions from the canyon**.**

In an attempt to quantify uncertainty in releases of mercury, we utilized the combined information from releases of mercury from stacks, tritium facilities, waste tanks, coal burning, and other miscellaneous sources. The AIRS database and permit applications yielded information on releases from the stacks and miscellaneous sources. For use in uncertainty calculations, we created triangular distributions of the AIRS database estimates based upon the actual release, used to represent the most likely value, and the maximum release, used to represent the boundary of the triangular distribution.

Uncertainty in releases from the tritium facilities was large as a result of two release estimates from independent sources that were nearly three orders of magnitude different from one another. The DOE estimate was assumed to be the least likely, and was used as a boundary to the triangular distribution, with the release developed from engineering calculations used as most likely.

Separations area waste tanks had two different release estimates quoted in available literature, one from Kvartek and one from the operating permit application.

Releases from coal burning were estimated by multiplying the estimated coal burned at the Site each year by a distribution of estimates for total mercury released per ton of coal burned. This distribution of estimates was derived from the total percentage of mercury in coal reported by the Site throughout the years as well as some of the AP-42 estimates for releases per ton burned.

The average mercury release per year was fitted to a lognormal distribution with a geometric mean of 0.30 ton y^{-1} and a geometric standard deviation of 1.38. The 5^{th} and 95^{th} percent estimates of this distribution were 0.18 ton y^{-1} and 0.51 ton y^{-1}, respectively. The 95^{th} percentile

matches the maximum release estimated by simply adding together the maximum release estimates.

This estimate for uncertainty in mercury releases is, however, based only on available release information. There is non-quantifiable uncertainty associated with using release estimates for a few years to estimate releases for all years, as well as the uncertainty of operations in the 1950s and 1960s as they compare to the 1980s.

No ambient air monitoring near the SRS was conducted for mercury as far as we know. A limited amount of modeling, needed for compliance with air quality regulations, has been done. In 1993, the maximum 24-hour average concentration of mercury in the air at the Site boundary, modeled using the EPA's Industrial Source Complex Short Term (ISCST) model, was estimated to average about 0.0024 μg m^{-3}, considerably below the SCDHEC ambient air standard of 0.25 μg m^{-3} (Dukes 1993). However, 1993 was certainly not a year of maximum or even moderate production for the canyons.

In their report, *Assessment of Mercury in the SRS Environment*, Kvartek et al. (1994) concluded that no significant releases of mercury to the air were likely to have occurred. They believe that any releases would have been well below the SCDHEC ambient standard based on process knowledge. Kvartek et al. (1994) published an estimate of the predicted a maximum concentration of mercury at the Site boundary of 0.014 μg m^{-3}, also below the standard. The calculated daily amount inhaled did not exceed the EPA's reference concentration for mercury. The summed oral and inhalation hazard index for an offsite individual was 0.03 (Kvartek et al. 1994). A hazard index $\geq$1 indicates a concern for potential health effects.

Nickel

Three nickel electroplating tanks in Building 313-M used a plating solution of nickel sulfate, nickel chloride, and boric acid. Nickel in air in M-Area has not been monitored and did not seem to be an industrial hygiene concern. M-Area calculations done for the air emissions inventory included graphite from lubricants, aluminum and lithium from various processes, and ammonia from aquadag; they did not include nickel or lead from lubricant oils or nickel plating. The nickel electroplating process was said to result in negligible aerosol emissions because of the high efficiency of the plating process. Reports from the U.S. Air Force and American Airlines studies were cited as the basis for the assumptions used for calculating emissions. A worst case emission for the process was estimated to be 5.8 lb y^{-1} for 1985–1990 based on estimates from a less efficient chromium-plating process (Radian 1992a).

Nickel emissions reported in the AIRS database were primarily from welders and diesel generators and pumps. The AIRS database included nickel emissions from generators; coal operations; and many metals fabricating, machining, and finishing operations. Nickel releases were calculated for the H-Area and K-Area coal piles and 232-H manufacturing processes. The coal crushing operation at 784-A was also evaluated for the air quality permit. The maximum emissions for several different pieces of equipment and the coal pile, assuming maximum operating at capacity, totaled 1.27×10^{-3} ton y^{-1} for nickel based on the amount of coal burned (Westinghouse 1996a). Using the relationship assumed for the A-Area boilers, burning 500,000 ton of coal per year site-wide would correspond to a nickel emission of 0.037 ton y^{-1}. Actual emissions estimates for metals from the fuel oil-fired package boilers in K-Area included nickel

with 3.3×10^{-4} ton y^{-1} (Westinghouse 1996a). Some of the key emissions estimates are summarized in Table 17-47.

Table 17-47. Emissions Estimates for Nickel in the AIRS Database

Year and source description	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1985		
Coal storage pile H-Area	1.30×10^{-3}	7.70×10^{-5}
H-Area 284 powerhouse ash sluice pump	2.54×10^{-4}	5.53×10^{-5}
H-Area manufacturing Building 232		
232-H hood metallography	Blank	0
234-H hood cutting	Blank	0
234-H radiological equipment repair	1.97×10^{-3}	3.25×10^{-5}
234-H finishing operations	8.59×10^{-5}	8.59×10^{-5}
234-H inert finishing operations	1.04×10^{-5}	1.04×10^{-5}
234-H fabricated metals machining	1.56×10^{-1}	5.21×10^{-2}
238-H milling and machining hood	1.41×10^{-2}	1.55×10^{-4}
238-H lathe hood	1.41×10^{-2}	1.55×10^{-4}
H-Area tank farm field welding operations	Blank	Blank
H-Area diesel generators	Blank	Blank
K-Area coal pile	4.20×10^{-5}	4.20×10^{-5}
K-Area coal pile runoff basin	4.20×10^{-5}	4.20×10^{-5}
1987		
Coal storage pile H-Area	1.30×10^{-3}	7.70×10^{-5}
H-Area 284 powerhouse ash sluice pump	2.54×10^{-4}	5.53×10^{-5}
H-Area manufacturing Building 232		
232-H hood metallography	3.30×10^{-3}	7.92×10^{-4}
234-H hood cutting	2.09×10^{-2}	9.79×10^{-4}
234-H radiological equipment repair	1.97×10^{-3}	3.25×10^{-5}
234-H finishing operations	9.38×10^{-5}	9.38×10^{-5}
234-H inert finishing operations	1.91×10^{-5}	1.91×10^{-5}
234-H fabricated metals machining	1.56×10^{-1}	5.21×10^{-2}
238-H milling and machining hood	1.41×10^{-2}	9.86×10^{-5}
238-H lathe hood	1.41×10^{-2}	1.97×10^{-4}
K-Area coal pile	4.20×10^{-5}	4.20×10^{-5}
K-Area coal pile runoff basin	4.20×10^{-5}	4.20×10^{-5}
1990		
H-Area manufacturing Building 232		
234-H finishing operations	9.38×10^{-5}	9.32×10^{-5}
234-H inert finishing operations	1.91×10^{-5}	8.60×10^{-6}
234-H fabricated metals machining	1.56×10^{-1}	5.21×10^{-2}
238-H milling and machining hood	1.41×10^{-2}	9.42×10^{-5}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Table 17-48 presents nickel emission estimates in the AIRS database by source. The totals are shown in Table 17-49.

Table 17-48. Emissions Estimates for Nickel in the AIRS Database, by Source[a]

Emission source	Year	Actual[b] emission estimate (ton y^{-1})
H-Area coal storage pile	1985	7.70×10^{-5}
	1987	7.70×10^{-5}
	1995	2.15×10^{-5}
H-Area powerhouse	1985	2.54×10^{-4}
	1987	2.54×10^{-4}
H-Area manufacturing building	1985	5.21×10^{-1}
	1987	5.21×10^{-1}
	1995	1.61×10^{-2}
H-Area reclamation building	1985	2.82×10^{-2}
	1987	2.82×10^{-2}
	1995	2.51×10^{-2}
K-Area coal pile	1985	4.20×10^{-5}
	1987	4.20×10^{-5}
K-Area coal pile runoff area	1985	4.20×10^{-5}
	1987	4.20×10^{-5}

[a] Source: Faugl (1996i).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Table 17-49. Total Nickel Releases[a]

Year	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985	3.49×10^{-1}	7.03×10^{-2}
1987	3.76×10^{-1}	7.22×10^{-2}
1989	3.86×10^{-1}	6.94×10^{-2}

[a] Source: Faugl (1996i).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

The highest emissions for 1985 were from the fabricated metals machining in 234-H, followed by field welding operations in the H-Area tank farm and diesel generators in the H-Area diesel house. The air quality permit emissions estimate for the 200-H emergency power generator, actual emissions assuming 2080 hours of operation each year, was 1.32×10^{-6} ton y^{-1} for nickel (Westinghouse 1996a).

Nickel plating in M-Area was not a significant source of nickel releases to the air. Nickel releases from metal cutting, machining and finishing operations, welding, and combustion sources were probably less than 0.4 ton y^{-1}. We estimate that total emissions may have ranged from actual to maximum estimates of 0.11 – 0.423 ton y^{-1}. These ranges are the only information available for nickel releases. Uncertainty could not effectively be calculated from the point values.

Nitric Acid

Nitric acid was used in large quantities in H-Area, F-Area, M-Area, CNX, TNX, and other areas as a process chemical. Many of the reactions involving nitric acid produced nitrates, which were discharged in liquid effluents, and oxides of nitrogen, which were discharged to the air. Some of the process exhaust was subject to control devices that reduced emissions, such as an acid scrubber, condenser, or nitrogen oxides absorption column. Much of the nitrogen oxide emissions to the air were uncontrolled. Many processes released both nitric acid fumes and nitrogen oxides and often the magnitude of the release of one was correlated to the other. Nitric acid and nitrogen dioxide releases from the SRS have been determined based on process data, opacity readings, and stack monitoring. Ambient air monitoring data, described in Chapter 19, is useful for determining how nitrogen dioxide produced onsite may have affected concentrations offsite.

Inhaled nitric acid reacts in the upper respiratory tract. Exposure to high doses of nitric acid causes lung irritation and may exacerbate lung diseases like asthma.

Air Emissions Estimates

Nitric acid emission estimates were included in the AIRS database (Faugl 1996j). Process emissions are shown in Table 17-50, and key emissions are shown in Table 17-51. The highest estimate was for a nitric acid storage tank used in 245-H for regeneration of resin, with an actual emissions estimate of 8.76×10^{-2} ton y^{-1}. In 1985, 1987, and 1990, 20 laboratory hoods and two glove boxes for the A-Area Radiological and Environmental Laboratory Process and Production, Building 735, were listed with an actual emissions estimate of 2.05×10^{-2} ton y^{-1} each. Nine laboratory hoods were listed with an emissions estimate of 1.56×10^{-2} ton y^{-1} each, totaling 31 hoods with a total actual emission estimate of 0.59 ton y^{-1}. In 1992, the number of laboratory hoods for A-Area decreased to 13, with actual emissions estimates totaling 6×10^{-2} ton y^{-1}. Ten emission points were listed for the F-Canyon, but all of the estimates given were zeros. In 1990, the M-Area emission points were listed with the same maximum value as the years before, but they were given an actual value of zero (Faugl 1996j).

Table 17-50. Process Emissions Estimates for Nitric Acid in the AIRS Database[a]

Year and source description	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985		
H Bldg 245 Resin regeneration building nitric acid tank	8.76×10^{-2}	8.76×10^{-2}
M-Area: Canning Building 313 core recovery HNO3 etch	2.05×10^{-7}	1.74×10^{-7}
Canning Building 313 slug nitric etch	6.48×10^{-3}	5.49×10^{-3}
Canning Building 313 Apl station 6 post etch nitric	3.22×10^{-3}	0
Canning Building 313 Apl station 7 post etch nitric	3.22×10^{-3}	0
Canning Building 313 Apl station 8 post etch nitric	3.22×10^{-3}	0
Canning Building 313 Apl etch line station 13	6.15×10^{-7}	0
Canning Building 313 Apl etch line station 14	6.15×10^{-7}	0
Canning Building 313 Apl etch line station 15	3.11×10^{-2}	0
Alloy Building 320 nitric acid tank	1.00×10^{-4}	1.00×10^{-4}
T-Area Semiworks Building 678 nitric acid storage tank	4.0×10^{-4}	4.0×10^{-4}
1987		
F-Area Canyon Stack Acid Recovery 607 Building 291	2.50×10^{-3}	2.50×10^{-3}
F-247-F Naval fuels glove boxes	6.0×10^{-4}	6.0×10^{-4}
H Bldg 245 resin regeneration building nitric acid tank	8.76×10^{-2}	3.76×10^{-4}
M-Area: Canning Building 313 core recovery HNO3 etch	2.05×10^{-7}	9.51×10^{-8}
Canning Building 313 slug nitric etch	6.48×10^{-3}	3.01×10^{-3}
Canning Building 313 Apl station 6 post etch nitric	3.22×10^{-3}	8.24×10^{-3}
Canning Building 313 Apl station 7 post etch nitric	3.22×10^{-3}	8.24×10^{-3}
Canning Building 313 Apl station 8 post etch nitric	3.22×10^{-3}	8.24×10^{-3}
Canning Building 313 Apl etch line station 13	6.15×10^{-7}	1.57×10^{-8}
Canning Building 313 Apl etch line station 14	6.15×10^{-7}	1.57×10^{-8}
Canning Building 313 Apl etch line station 15	3.11×10^{-2}	7.94×10^{-4}
Alloy Building 320 nitric acid tank	1.00×10^{-4}	1.00×10^{-4}
1990		
F-Area Canyon Stack Acid Recovery (unit) 607, 291-F	2.50×10^{-3}	2.50×10^{-3}
F-247-F Naval fuels glove boxes	6.0×10^{-4}	6.0×10^{-4}
H Bldg 245 resin regeneration building nitric acid tank	8.76×10^{-2}	3.49×10^{-4}
H-Area acid storage tank	1.13	2.65×10^{-2}
M-Area Alloy Building 320 nitric acid tank	1.00×10^{-4}	1.00×10^{-4}
M-Area: Canning Building 313 core recovery HNO3 etch	2.05×10^{-7}	0
Canning Building 313 slug nitric etch	6.48×10^{-3}	0
Canning Building 313 Apl station 6 post etch nitric	3.22×10^{-3}	0
Canning Building 313 Apl station 7 post etch nitric	3.22×10^{-3}	0
Canning Building 313 Apl station 8 post etch nitric	3.22×10^{-3}	0
Canning Building 313 Apl etch line station 13	6.15×10^{-7}	0
Canning Building 313 Apl etch line station 14	6.15×10^{-7}	0
Canning Building 313 Apl etch line station 15	3.11×10^{-2}	0

[a] Source: Faugl (1996j).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Table 17-51. Key Emissions of Nitric Acid in the AIRS Database by Source[a]

Emission source	Year	Actual[b] emissions estimate (ton y^{-1})
F-Area Canyon stack acid recovery	1985	2.50×10^{-3}
F-Area Canyon stack acid recovery	1987	2.50×10^{-3}
F-Area Canyon stack - second cycle	1992	6.4×10^{1}
F-Area Canyon stack - feed prep	1992	7.7×10^{-4}
H-Area Canyon resin regeneration	1992	1.24×10^{-4}
H-Area chemical storage tanks	1992	9.97×10^{-1}
H-Area tanks	1992	2.62×10^{-2}
T-Area Chemical Semiworks and Pilot Plant, five emission points	1985	2.0×10^{-3}
	1987	2.0×10^{-3}
	1990	2.4×10^{-3}
TNX Chemical Semiworks	1992	1.0×10^{-3}

[a] Source: Faugl (1996j).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

The total nitric acid emissions reported in the AIRS database are shown in Table 17-52. One of the largest single estimates for 1992 was the M-Area Alloy Building acid tank with 2.0×10^{1} ton y^{-1} for actual and maximum emissions. This source had an emissions estimate of 1×10^{-4} ton y^{-1} in the AIRS database for 1985, 1987, and 1990. The increased emissions estimate for this source and the estimates for the F-Canyon second uranium cycle, which totaled 6.4×10^{1} ton y^{-1}, accounted for the larger estimate in 1992. The H-Canyon stack emissions were not included. The estimates for 1985 and 1987 might have been larger than the 1992 estimates if these emissions points had been included because the production for the canyons and M-Area was greater in 1987 than in 1992.

Table 17-52. Total Nitric Acid Emissions Estimates[a]

Totals oxides of nitrogen	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985	1.10	6.03×10^{-1}
1987	1.10	6.26×10^{-1}
1990	2.20	6.22×10^{-1}

[a] Source: Faugl (1996j).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

M-Area Nitric Acid Releases. M-Area Nitric Acid Releases were included in the AIRS database estimates. Emissions included in the operating permit application applied to storage tanks but not operations.

Worksheets contained in Radian (1992a) for calculating nitrogen oxide emissions included complicated calculations for nitric acid releases that assumed a process rate of 75,000 gal y^{-1} for the plating line acid scrubber. The process used caustic etch tanks and nitric etch baths. To estimate potential releases, Radian (1992a) determined the number of cores per shift and the number of cores processed per month and used the concentration of materials, volumes in the tanks, tank surface areas, and material balance information (found in the degreaser logbook, DPSOLs, and material balance or essential materials logbooks for 1983). The emissions from the hot and cold water rinse tanks (used before and after cleaning, etching, and plating processes) were assumed to be negligible. Nitric acid tank emissions were said to have been very small because of the low vapor pressure of the solutions.

Storage tank emissions, calculated using AP-42 equations for working and breathing losses, were calculated using information on the throughput, temperature, tank design, and vapor pressure of contents. The standing losses because of tanks breathing and working losses because of vapor displacement during filling were added to the emissions. These loses are most important for aboveground tanks that were not insulated and expand and contract daily because of temperature changes (Radian 1992a). This was applicable because nitric acid was stored in fixed roof storage tanks in M-Area. The throughput for these tanks was reported to be 27,000 gal in 1985, 30,000 gal in 1986, 25,000 gal on 1987, 44,000 gal in 1988, 20,000 gal in 1989, and 28,000 gal in 1990. Using data on the fill rates, transfer rates, venting, and temperature changes, a maximum working loss for the tanks was calculated to be 1.73 lb y^{-1} in 1985. The breathing losses, calculated assuming the tanks were one-half full, totaled 10.80 lb y^{-1}. Another spreadsheet in the documentation for M-Area air emissions contained maximum working and breathing losses for five nitric acid and nitric acid waste tanks. These totaled 6.8 lb y^{-1} for 1985, 7.8 lb y^{-1} for 1986, 7.05 lb y^{-1} for 1987, 6.9 lb y^{-1} for 1988, and 6.58 lb y^{-1} for 1989. Calculations of throughputs for acids and caustic were handwritten and seem to be based on use records, monthly receipts, and information obtained from employee interviews.

H-Area Nitric Acid Releases Calculated for the Operating Permit Application. Nitric acid (50% HNO_3) is used to dissolve aluminum-clad fuels. The nitric acid and mercuric nitrate catalyst were heated to boiling, or a maximum of 110°C, to increase the dissolution rate. Nitrogen dioxide generated in the dissolver reacted with water in the off-gas condenser to form nitric acid, which returned as a condensate to the dissolver. Not all of the nitrogen dioxide generated was converted to nitric acid. The nitric acid emissions from the dissolver were calculated assuming (a) the off-gas was 50°C, (b) dissolving accounts for 20 hours of a 30-hour dissolving cycle, (c) 10% of the nitric acid added to the dissolver was excess and was available for emission, and (d) 20 runs per month were conducted. For calculating nitric acid emissions, Radian (1993) assumed that 45 ton y^{-1} of nitrogen dioxide was emitted from the dissolver. The iodine reactor, which used silver nitrate to convert iodine in the off-gas to silver iodide or iodate, produced nitric acid. Based on stoicheomtery, one iodine reactor was estimated to produce about 0.026 lb y^{-1} of nitric acid. The actual emissions for nitric acid from the dissolvers in H-Area totaled 1.05×10^{-5} ton y^{-1} for the iodine reactor and 0.036 ton y^{-1} for the dissolver (Westinghouse 1996a).

Emissions of nitric acid from the head end process (based on tank capacity, throughput, and vapor pressure) were said to have been negligible. Maximum emission of nitric acid from the first cycle extraction was calculated to be 0.822 ton y^{-1}. Based on flow rates, tank working volumes, and vapor pressures, Radian (1993) estimated that a maximum of 720 lb y^{-1} of nitric acid was emitted from process vessels associated with the first cycle. Second uranium cycle losses were estimated to be 1.72 ton y^{-1} maximum, and the second neptunium/plutonium cycle emissions of nitric acid were calculated to be 1.43 ton y^{-1} maximum. Solvent recovery processes were estimated not to release nitric acid or nitrogen dioxide (Radian 1993). The solvent recovery processes consisted of three separate solvent recovery systems, one for each extraction cycle, which removed radioactive contaminants and chemical degradation products from solvent using alkaline and acid washes.

The frame waste recovery system in H-Area, which purified and concentrated ^{238}Pu solutions, used nitric acid. The maximum throughput was reported to be run in 1984. The 1984 throughput was used to determine emissions estimates for the Title V Permit Application. Based on stoichiometry, throughputs, column feed rates, and maximum operating temperatures allowed for worker safety concerns, a release estimate 1.77 ton of nitric acid maximum emissions was estimated based on 1984 throughputs (Westinghouse 1996c).

The maximum nitric acid emissions from the acid recovery unit in 221-H were estimated to be 0.019 ton y^{-1} based on pump, tank, and column capacities. H-Canyon rerun process nitric acid releases from all of the process vessels were estimated to be 1.72 ton y^{-1} maximum (Westinghouse 1996c). The H-Canyon general purpose evaporator was not thought to have emitted nitric acid or nitrogen dioxide. Maximum nitric acid emissions from the Segregated Solvent facilities were estimated to be 0.012 ton y^{-1} because of solvent washing. No emissions were found to be worth reporting for the permit application for the H-Area sumps and water handling facility.

The emissions calculation for the third-level cold feed process, old HB-Line facility decontamination and decommissioning activities, and the enriched uranium system are Unclassified Controlled Nuclear Information and were not copied. They were available for *RAC* review and the emissions were included in the AIRS database values that *RAC* compiled.

The acid recovery unit in Building 221-H concentrated dilute nitric acid that had been used as a scrubbing or solvent wash solution in the H-Canyon. The process components that could have contributed to emissions were the nitric acid receiving tank, the recovered nitric acid storage tank, recovered nitric acid run tanks, overhead condensate tanks, and the nitric acid evaporator column. The evaporator column is sealed and vapor losses from dilute nitric acid tanks were assumed to be nearly zero. Transfer losses and breathing losses from the tanks were calculated for each tank based on the target class data for 13 different types of targets dissolved in 1985 and using the AP-42 equations for liquid storage tanks, tank dimensions, and nitric acid vapor pressure of 0.039 mm Hg. The total losses were estimated to be 40.92 lb for the nitric acid tanks in 1985 (Radian 1993).

Estimates of releases from the cold feed preparation area in 222-H, where reagents were formulated for use in the canyons, were made for 1985. The area operations were vented through the process vessel vent system to the 291-H stack. The cold feed preparation area housed four dilute nitric acid tanks. Radian (1993) estimated that the 1000-gal nitric acid tank at 245-H had an estimated maximum emission of 1.15×10^{-4} ton y^{-1} nitric acid. The four 17,700-gal nitric acid tanks in place since 1953 in 211-H had maximum emissions totaling 4.06×10^{-1} ton y^{-1}. The

permit application for the H-Canyon from 1995 reported maximum controlled emissions for nitric acid to total 12.1 ton y^{-1} based on engineering calculations (Westinghouse 1996c).

F-Area Nitric Acid Releases Calculated for the Operating Permit Application. Actual uncontrolled working volume losses of nitric acid were calculated to be 0.516 ton y^{-1} for the F-Area dissolver and head end processes. The nitric acid releases from the dissolver were calculated accounting for the condenser, which returns most of the nitric acid vapors to the dissolver. The condenser also converts some of the nitrogen oxides to nitric acid, but this was not considered to reduce the nitrogen dioxide estimates, which were meant to be conservative. However, to maximize the nitric acid release estimates, it was assumed that all of the nitrogen oxides emitted were converted to nitric acid. Nitric acid releases from the iodine reactor, the makeup tanks, and the B-Line waste tanks were included in the permit application estimates. Controlled emissions for nitric acid were calculated assuming the F-8 column had a 90% efficiency. The engineers thought that sufficient water was used so that the F-8 absorber could absorb 100% of the nitric acid released from the dissolvers and the iodine reactor, and 90% was thought to be a conservative value. The actual, controlled emission estimate for nitric acid from these processes was estimated to be 0.052 ton y^{-1}. Emissions for the head end process were calculated using Raoult's Law and throughputs through the process vessels. The maximum air emissions were estimated to be 10.1 ton y^{-1}. The first cycle maximum emissions for nitric acid were 2.37 ton y^{-1}. The second uranium cycle losses of nitric acid were estimated to be 0.73 ton y^{-1}. The second plutonium cycle losses of nitric acid were estimated to be 1.88 ton y^{-1}. Emissions from the solvent recovery system were estimated to be 0.45 ton y^{-1}; the low activity and high activity waste systems for 221-F were not thought to have released nitric acid into the air.

FB-Line, in Building 221-F, made plutonium buttons from a dilute nitrate solution. FB-Line tanks and vessels were enclosed in cabinets or glove boxes. The line included four major processes and four vacuum venting systems. The vessel vent vacuum system was preceded by Teflon filters and used a venturi scrubber to scrub the off-gas, which contained nitrous oxides and nitric acid. This system also used a caustic scrubber to neutralize the nitric acid vapors. Actual emissions for nitric acid from the FB-Line were estimated to be 1.94×10^{-5} ton y^{-1}. Estimates of maximum emissions from the cold feed nitric acid tanks used for the FB-Line totaled 4.2×10^{-2} ton y^{-1} (Westinghouse 1996c).

Maximum nitric acid emissions from the acid recovery unit in 221-F, which concentrated nitric acid evaporator overheads by vacuum distillation to 50% for reuse, were reported to be 0.0198 ton y^{-1}. The five 221-F nitric acid storage tanks maximum emissions estimates totaled 6.05×10^{-1} ton y^{-1}. Emissions estimates for tanks in 222-F totaled 1.77×10^{-2} ton y^{-1}. All of these exhausts flowed into the wet cabinet exhaust, which went through a series of prefilters, HEPA filters, and a sand filter then out the 291-F stack.

Other emissions for F-Area included those for the segregated solvent facilities, with a maximum nitric acid emissions estimate of 0.0556 ton y^{-1} nitric acid (Westinghouse 1996a).

At the time of the 1996 air permit application, the F-Canyon was not operating and actual emissions were reported as zero. The combined F-Canyon stack maximum emission estimates, assuming 24 hour a day releases of nitric acid, totaled 16.3 ton y^{-1} based on engineering calculations (Westinghouse 1996a). This compares to a maximum design capacity controlled

emission estimate total for nitric acid from F-Area, including the canyons of 9.89 ton y^{-1} in the AIRS database for 1995 (Faugl 1996e).

Other Areas. In the AIRS database for 1985, 1987, and 1990, 29 laboratory hoods and two glove boxes were listed as emission points for nitric acid for the Radiological and Environmental Laboratory Process and Production, Building 735. Actual emissions estimates totaled 0.59 ton y^{-1} (Faugl 1996j). A nitric acid maximum emission of 4.6 0 × 10^{-6} ton y^{-1} was given for the Par Pond Laboratory in 1994 (Westinghouse 1996a).

From 1987 to 1995, the TRI, reported to the EPA and SCDHEC, included estimates of the pounds per year of nitric acid released from the SRS. The TRI estimates shown in Table 17-53 are lower than the actual AIRS database emission estimates.

Table 17-53. Toxic Release Inventory Release Estimates for Nitric Acid[a]

Year	Air emissions (lb y^{-1})	Ton y^{-1}
1987	71000	35.5
1988	54100	27
1989	19000	9.5
1990	8000	4
1991	3601	1.8
1992	3601	1.8
1993	37000	18.5
1994	32050	16
1995	224	0.1

[a] Source: Westinghouse (1996b).

Obviously, there is a big difference between actual emission and maximum design emission estimates for nitric acid. Estimates calculated for the AIRS database and permit application suggest that 30–150 ton y^{-1} were released in 1985–1992. Thirty ton is the total of the lowest actual emissions in the permit application (primarily 16.8 ton for H-Area, 12.1 ton for F-Area, and the total actual emission estimates for M-Area in the AIRS database of 2.85 × 10^{-2} ton y^{-1} plus other smaller emissions in the AIRS database). The 150-ton estimate is the highest annual estimate in the AIRS database, which was 86 ton y^{-1} for 1992 and included an emissions estimate for the F-Canyon stack but not the H-Canyon stack. If the H-Canyon stack releases were similar to those predicted for the F-Canyon stack, as much as 64 ton y^{-1} should be added to the emissions estimate, for a total of 150 ton y^{-1}. It is likely that releases in the past were similar and may have been less because 1985 was one of the highest years for M-Area as well as the canyon's production.

Total nitric acid releases had such a small range as to make uncertainty calculations from the release estimates misleading. Not all sources of uncertainty could be quantified well enough to make this a worthwhile calculation.

The Standard 8 results submitted to the SCDHEC said that in 1991, nitric acid was emitted by 47 sources in A-Area, B-Area, F-Area, H-Area, M-Area, S-Area, and TNX. The maximum

24-hour average Site boundary concentration was calculated to be 50.95 μg m^{-3}. The ambient air standard was 125 μg m^{-3}.

Oxides of Nitrogen

Because various forms of nitrogen oxides can occur together in the air and many are chemically convertible, the compounds (which include nitric oxide [NO], nitrogen dioxide [NO_2], nitrous oxide [N_2O], nitric acid [HNO_3], and other nitrogen oxides) are generally designated NO_x or oxides of nitrogen.

Most of the oxides of nitrogen are produced from combustion sources and is initially produced as nitric oxide, which is generally rapidly oxidized to nitrogen dioxide. Nitric oxide and nitrogen dioxide are chemically reactive and of public health interest. Many of the emissions estimates in the Title V Permit Application and in the AIRS database are given for nitrogen oxides or oxides of nitrogen that may include nitric oxide and nitrous oxide as well as nitrogen dioxide, which is the compound of most concern. Most of the nitric oxide released is oxidized to nitrogen dioxide. Also, several reports suggest that the canyon operators did air sparging of the evaporator to improve retention of acid in the dissolver by oxidizing nitric oxide to nitrogen dioxide (Du Pont 1974b). Since nitrogen dioxide is the toxic pollutant of most concern, we will assume that all of the oxides of nitrogen are nitrogen dioxide unless otherwise indicated.

Depending on the concentration, the presence of nitrogen dioxide in air is indicated by a light yellow to reddish brown color. Inhaled nitrogen dioxide affects the lungs at low levels of exposure, possibly decreasing pulmonary protective mechanisms. Nitrogen dioxide does not appear to be a carcinogen. In general, studies on humans suggest that levels <1 ppm do not cause significant changes in pulmonary function in normal, healthy adults. Epidemiological studies of people exposed to nitrogen dioxide in indoor and outdoor air have found both positive and negative associations with a number of acute respiratory conditions. No definitive conclusions about health effects caused by nitrogen dioxide have been drawn from such studies.

Oxides of nitrogen were released from many facilities at the SRS that used nitric acid. The facilities that used the largest amounts were the 200-F and H-Canyons and B-Line processes, the 300-M Area fuel fabrication facilities, and the TNX and CMX pilot plants. Nitrogen dioxide was also released from the power plants, the Naval Fuels Manufacturing Facility, and many small combustion engines.

The AIRS database releases for oxides of nitrogen were compiled for 1985, 1987, 1990, and 1992 and are presented in Table 17-54 (Faugl 1996k).

Table 17-54. Total Oxides of Nitrogen Emissions Estimates[a]

Totals oxides of nitrogen	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985	2.73×10^3	3.55×10^2
1987	2.92×10^3	4.69×10^2
1990	3.06×10^3	3.64×10^2

[a] Source: Faugl (1996k).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Process releases and releases of most concern are listed in Table 17-55.

Table 17-55. Process Releases of Oxides of Nitrogen in the AIRS Database

Year and source description	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
1985		
F-Area canyon stack, Bldg 291 second uranium cycle	4.93×10^{1}	4.93×10^{1}
F-Area canyon stack, Bldg 291 solvent recovery	2.5×10^{-3}	2.5×10^{-3}
L-Area reactor building, 105 reactivity/model	2.37×10^{-6}	1.04×10^{-5}
M-Area		
Alloy Building 320 diesel generator	3.6×10^{1}	1.00×10^{-1}
Canning Building 313 core recovery HNO3 etch	6.60×10^{-1}	5.60×10^{-1}
Canning Building 313 slug nitric etch	1.27	1.08
Canning Building 313 Apl station 6 post etch nitric	1.36	0
Canning Building 313 Apl station 7 post etch nitric	1.36	0
Canning Building 313 Apl station 8 post etch nitric	1.36	0
Canning Building 313 Apl etch line station 13	2.76	0
Canning Building 313 Apl etch line station 14	2.76	0
Canning Building 313 Apl etch line station 15	1.36	0
Alloy Building 320 Nitric acid tank	2.19	5.20×10^{-1}
N-Area Central Shops burn pit, open wood burning pit	2.46	2.46
T-Area		
Pilot Plant Building geometrically favorable dissolver	0	2.7×10^{-1}
Pilot Plant Building incinerator	2.83×10^{-1}	3.55×10^{-4}
DWPF Semiworks Building process tank	8.10	1.40×10^{-1}
Glass Melter Building stack	Blank	1.90×10^{-1}
1987		
F-Area canyon stack, Bldg 291 second uranium cycle	4.93×10^{1}	4.93×10^{1}
F-Area canyon stack, Bldg 291 solvent recovery	2.5×10^{-3}	2.5×10^{-3}
Glove boxes, Naval Fuels F-Area Building 247	9.90×10^{1}	9.90×10^{1}
H-Area hood metallography. 232 manufacturing building	9.40×10^{-3}	1.65×10^{-3}
L-Area reactor building, 105 reactivity/model	2.37×10^{-6}	1.04×10^{-5}
M-Area		
Alloy Building 320 diesel generator	3.6×10^{1}	1.00×10^{-1}
Canning Building 313 core recovery HNO3 etch	6.60×10^{-1}	3.00×10^{-1}
Canning Building 313 slug nitric etch	1.27	5.90×10^{-1}
Canning Building 313 Apl station 6 post etch nitric	1.36	3.50×10^{-2}
Canning Building 313 Apl station 7 post etch nitric	1.36	1.36
Canning Building 313 Apl station 8 post etch nitric	1.36	3.50×10^{-2}
Canning Building 313 Apl etch line station 13	2.76	7.10×10^{-2}
Canning Building 313 Apl etch line station 14	2.76	7.10×10^{-2}
Canning Building 313 Apl etch line station 15	1.36	3.50×10^{-2}
Alloy Building 320 nitric acid tank	2.19	3.40×10^{-1}
T-Area		
Pilot Plant Building geometrically favorable dissolver	0	0
Pilot Plant Building incinerator	2.83×10^{-1}	3.19×10^{-3}
DWPF Semiworks Building process tank	8.10	1.40×10^{-1}
Glass Melter Building stack	Blank	1.17

Table 17-55. Process Releases of Oxides of Nitrogen in the AIRS Database

Year and source description	Maximum (ton y^{-1})	Actual[a] (ton y^{-1})
Building 682		
Manufacturing building precipitate reactor tank	3.70×10^{-2}	0
Manufacturing building organic evaporator tank	3.70×10^{-2}	0
1990		
F-Area canyon stack, Bldg 291 second uranium cycle	4.93×10^{1}	4.00×10^{1}
F-Area canyon stack, Bldg 291 solvent recovery	2.5×10^{-3}	0
Glove boxes, Naval Fuels F-Area Building 247	9.90×10^{1}	9.90×10^{1}
H-Area hood metallography. 232 Manufacturing Building	9.40×10^{-3}	1.65×10^{-3}
M-Area		
Alloy Building 320 diesel generator	3.6×10^{1}	1.00×10^{-1}
Canning Building 313 core recovery HNO3 etch	6.60×10^{-1}	0
Canning Building 313 slug nitric etch	1.27	0
Canning Building 313 Apl station 6 post etch nitric	1.36	0
Canning Building 313 Apl station 7 post etch nitric	1.36	0
Canning Building 313 Apl station 8 post etch nitric	1.36	0
Canning Building 313 Apl etch line station 13	2.76	0
Canning Building 313 Apl etch line station 14	2.76	0
Canning Building 313 Apl etch line station 15	1.36	0
Alloy Building 320 nitric acid tank	2.19	1.60×10^{-1}
N-Area Central Shops burn pit, open wood burning pit	2.46	2.46
DWPF Semiworks		
IDMS feed preparation	1.60	1.40×10^{-1}
IDMS melter and off-gas system	1.40	2.50×10^{-1}
Manufacturing Building 682 precipitate reactor tank	3.70×10^{-2}	3.46×10^{-3}
Manufacturing Building 682 organic evaporator tank	3.70×10^{-2}	3.46×10^{-3}

[a] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Many of the emissions estimates for the generators were higher than the estimates for production processes listed above. The highest process emission in 1985 was the second uranium cycle discharge to the 291-F stack at 49 ton y^{-1}. Emissions estimates were not given for the H stack or any H-Canyon process except the diesel generators for the canyon exhaust fan house and in the HB-Line. This is because different contractors were responsible for reporting emissions from F-Area, and although the processes are similar, emissions estimates were often different. In this case, H-Area canyon process emissions may not have been submitted. Estimates for key sources were compiled from AIRS database excerpts for 1985, 1987, and 1995 and are presented in Table 17-56.

Table 17-56. Nitrogen Dioxide Emission Estimates for Key Sources from AIRS Database

Emission source	Year	Actual[b] emission estimate (ton y^{-1})
A-Area boiler house	1985	177.
	1987	219.
	1995	121.
D-Area powerhouse	1985	886.
H-Area powerhouse boiler 1	1985	128.
	1987	64.5
	1995	15.6
H-Area powerhouse boiler 2	1985	63.9
	1987	63.9
	1995	14.7
K-Area powerhouse	1985	256
	1987	354
K-Area package boiler	1995	1.87
Central Shops burning pit	1985	2.46
	1995	3.64
F-Area canyon stack	1985	49.3
	1987	48.6
	1995	0.00000199
H-Canyon exhaust fan	1985	0.507
	1987	0.507
	1995	1.35
H-Canyon HB-Line	1985	1.04
	1987	1.04
	1995	0.367
H-Canyon HB-Line (another emission point)	1985	0.0299
	1987	0.0299
	1995	0.305
H-Area manufacturing building	1987	0.00165
	1995	0.000293
M-Area canning building	1985	1.64
	1987	2.5
M-Area alloy building	1985	0.520
	1987	0.340
T-Area Pilot Plant building	1985	0.000761
	1987	0.000756

[a] Source: Faugl (1996k).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

M-Area Releases of Oxides of Nitrogen

Large quantities of nitric acid were used in M-Area. Although several reports estimate the amount of nitric acid and nitrates released to the M-Area process sewers in liquid effluent, nitrogen dioxide releases from the stack because of the nitric acid processes were not estimated until the air emissions inventory was taken in the late 1980s. The primary releases to the air from processes in building at M-Area were nitric acid (mist) and oxides of nitrogen, primarily from the nitric acid etching and cleaning (Du Pont 1971b). Air exhaust was subjected to an acid scrubber, which may have been put into place in the mid-1970s. A Du Pont report from 1973 stated that these emissions were recently reduced to one-tenth of their former quantity through process changes (Du Pont 1973b).

Nitric acid was used for etching in 321-M and 313-M processes. The DOE Environmental Survey (DOE 1987) said that nitric acid and nitrogen oxide from the 321-M cleaning room were estimated to be about 8 lb h^{-1} based on a stack emission test. They also said that nitric acid and nitrogen oxide emissions from the 313-M plating line were uncontrolled until 1987, when a water scrubber was to be used in the new plating line. The emissions from etching and core recovery processes in 313-M were controlled by the water scrubber and were estimated to be 14 lb h^{-1} maximum based on stack tests (DOE 1987). The scrubber efficiency was thought to be about 50%, but it was not accounted for in the 1983 estimates (DOE 1987). The stack emission testing was attributed to Clayton Environmental in 1983. We found and contacted a company called Clayton Environmental. Current employees thought the company previously had an office in Atlanta, but their library in Michigan did not contain copies of any studies conducted for the SRS in 1983. M-Area and Environmental Protection Department personnel did not recall or have copies of these testing reports. The actual maximum emissions estimates, including scrubber controls were 7.94 lb h^{-1} for 321-M and 5.57 lb h^{-1} for 313-M. Average emission estimates were 2.6 lb h^{-1} and 3.0 lb h^{-1}. The nitrogen oxides emissions from 300-Area were said to have been low compared to those from separations or the powerhouses.

M-Area emissions estimates in the AIRS database included 2 ton from M-Area canning and 0.34 ton from the M-Area alloy building in 1987. Oxide of nitrogen emissions were calculated for 17 nitric acid process tanks in M-Area. A stack test of the Building 321-M cleaning line detected nitrogen dioxide at 4.0 ppm, which Radian (1992a) thought corresponded to about 0.81 lb hr^{-1}. Nitrogen oxides were evolved from the nitric acid etch tank during the reduction of nitric acid or from the oxidation of the metal parts. Emissions from other tanks were scaled to match the cleaning line tank based on the amount of nitric acid used in the tank for which the stack test was done. The total mass of nitric acid was used to account for variations in nitric acid concentrations and tank volumes. The cleaning line operated at the highest temperatures of any process, so the estimates were thought to be worst case (Radian 1992a). The actual emission estimates for nitrogen oxides from the worksheets for 17 emission points in M-Area were summed and are shown in Table 17-57. The maximum design emission estimates for 1985–1990 totaled 20.97 ton y^{-1}.

Table 17-57. Actual Emission Estimates for Nitrogen Oxides in M-Area from the Air Emissions Inventory Worksheets[a]

Year	Actual[b] emission estimate (ton y^{-1})
1985	5.64
1986	6.02
1987	3.86
1988	1.81
1989	0.194

[a] Source: (Radian 1992a).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

The largest emission was from the nitric acid etch tank, followed by the core recovery nitric etch, both of the 313-M old plating line (Radian 1992a).

In 1967, an air sampling program for nitrogen oxides was initiated in M-Area. Nitrogen dioxide was continuously monitored over an 18-day period, and the average concentration was 0.06 ppm. The location where the samples were taken was not indicated, and it was not clear whether the samples were from the stack or ambient air (Du Pont 1967). The annual ambient air quality standard is currently 0.053 ppm.

F-Area and H-Area Release of Oxides of Nitrogen

Both dissolving and denitration processes in the separations areas produced visible emissions of nitrogen oxides. Concentrations of nitrogen oxides released from the dissolver were sufficient to produce a visible yellowish-brown plume from the stack. Emissions from the dissolvers were not continuous, but they peaked during dissolution of each charge to the dissolver.

The dissolver off-gas was set up to be exhausted through a water scrubber column, but materiel could be steam-jetted to the stack if the dissolver overflowed. The dissolver could overflow if dissolving proceeded at a greater rate than recovery of the nitric acid. When this happened, the off-gas was routed to the stack and a brown plume of nitrogen dioxide could be seen. Everett Sheldon (Sheldon 1996) estimated that perhaps 20% of the time the off-gas was diverted directly to the stack.

Reinig et al. (1973) studied the emissions and reported that dilution was sufficient to keep air concentrations far below standards except during extreme inversions. Compliance with air quality standards was generally achieved by using opacity meters or visual opacity readings.

A reviewer at CDC noted that many of the equations used to explain the nitric acid and nitrogen dioxide emission estimates submitted for the Operating Permit Application were not balanced. We are reluctant to modify the equations for fear this might mislead the reader because the equations, as written, were used to calculate the emissions estimates. The stoichiometry appeared to be correct for the relevant products.

H-Area Releases of Nitrogen Oxides

The 221-H uranium aluminum separations used the HM process to recover irradiated uranium (^{235}U) from aluminum clad-uranium targets using chemical dissolving in nitric acid, chemical precipitation of silica and other impurities, and concentration of metals (called the head end treatment), which was followed by two-cycle extraction of the dissolved uranium. Nitrogen oxide was generated during dissolution. Dissolving was aided by a mercuric nitrate catalyst ($Hg[NO_3]_2$). The reactions result in the evolution of nitrogen, oxides of nitrogen, nitrous oxide (N_2O), and traces of hydrogen:

$$Al + 3.75HNO_3 \rightarrow Al(NO_3)_3 + 0.225NO + 0.15N_2O + 0.11\ N_2 + 1.9H_2$$
$$U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + NO_2 + 2H_2O$$

The potential amount of N_2O formed and lost to the air per pound of aluminum discharged to the dissolver, calculated using a stoichiometric mass balance, was approximately 0.2447 lb of N_2O per pound of aluminum. All N_2O formed was assumed to have been vented to the 291-H stack. The off-gas condenser was thought to convert some of the nitrogen oxide to nitric acid, which condensed and was recycled to the dissolver. The conversion of nitrogen oxide to nitric acid was probably variable and would have been affected by the reaction rate, the temperature of the off-gas, presence of oxidation catalysts, residence time, and other parameters. Because the conversion was very uncertain and the amount converted was unknown, a conservative approach would be to assume that all of the NO formed was vented to the process vessel vent system. A stoichiometric mass balance based on reaction above and the 1983 technical manual data, predicted that 0.25 lb of NO was lost to the exhaust per pound of aluminum for aluminum dissolution and 0.025 lb of NO was formed per pound of uranium from uranium dissolution.

An example calculation provided by Radian (1993) for the air emissions inventory assumed 251.52 kg of aluminum and 42.24 kg of uranium per charge (Mark 22 target class), a molarity of 3.31 mole L^{-1} for HNO_3 and 0.0125 mole L^{-1} for $Hg(NO_3)_2$ L^{-1}, a total volume of 14,000 L in the dissolver, and a total dissolving time of 22 hours. Using these values and the relationships described above, they calculated 135.69 lb of N_2O were emitted per batch or 6.17 lb h^{-1}. If one batch were dissolved each day, the rate might be 5.65 lb h^{-1} for each 24-hour period, or 135.69 lb d^{-1}. Using an estimate of 50,084 kg of aluminum, they calculated that 326,859 gal of raw metal solution was put through the first cycle uranium extraction in 1985. The most annual separation activity over the period of the emission inventory occurred in 1985, so these 1985 24-hour emissions rates were used as the ‘design’ rates for reporting. In 1985, 164 dissolver batches were processed in H-Canyon (Radian 1993).

For the permit application, H-Area dissolver emissions were calculated using maximum fuel quantities charged per year. Of the three dissolvers, 6.4D was the largest and was used to provide the maximum emissions. The actual emissions estimates were based on 20 dissolver runs per month of fuel containing 370 kg per batch of aluminum and 50.6 kg per batch ^{235}U with a dissolving time of 20 hours per batch. The maximum case was obtained from a one-time dissolver run of an offsite fuel containing 546 kg of aluminum and 50.6 kg of uranium per batch. The aluminum content was estimated from interviews with H-Area engineers. They were conservative estimates predicted to overestimate the amount of nitrogen oxides released. The maximum dissolver capacity and 24-hour a day operation was assumed. It was assumed that all of the oxides of nitrogen were nitrogen dioxide and that the condenser that condensed nitric acid vapor and

returned it to the dissolver did not convert any of the nitrogen dioxide evolved to nitric acid. There is excess oxygen in the process, so it is reasonable to assume that all of the NO was converted to NO_2. From process stoichiometry, it was calculated that 0.244 lb of N_2O was evolved per pound of aluminum charged, 0.392 lb of NO_2 was evolved per pound of aluminum charged, plus 0.474 lb of NO_2 per pound of uranium charged. This results in actual, worst case, uncontrolled emission of 44.66 ton y^{-1} for NO_2 and 23.9 ton y^{-1} for N_2O, assuming 20 hours per batch dissolving time. The maximum uncontrolled emission assuming 8760 hours of continuous operation was 76.5 ton y^{-1} for NO_2 and 42.9 ton y^{-1} for N_2O (Westinghouse 1996c).

Calculations for the dissolution of Rocky Flats scrub alloy, which contains plutonium, was found to be less than the uranium fuels. Therefore, all calculations were performed for the MK16B, considered to be the worst or bounding case. Radian (1993) estimated controlled emissions based on controls by three devices between the dissolver and the 291-H stack: the condenser, iodine reactor, and the fiberglass filter. The oxides of nitrogen that were formed in the dissolver and were not condensed were discharged through the stack. The efficiency of the condenser for converting nitrogen oxide to nitric acid was thought to be about 20%; therefore, about 80% of the oxides of nitrogen generated in the dissolver was released. The condenser was excluded as a pollution control device, but it was considered as a part of the dissolver process. For the conservative estimates in the air permit application, controlled emissions were said to equal uncontrolled emissions.

The head end process involves a permanganate strike according to the reaction:

$$Mn(NO_3)_2 + 2\ KMnO_4 + 2\ H_2O \rightarrow 5\ MnO_2 + KNO_3 + HNO_3$$

the centrifuge cake dissolution proceeds according to

$$MnO_2 + NaNO_2 + 2\ HNO_3 \rightarrow Mn(NO_3)_2 + NaNO_3 + H_2O$$

None of the products of these reactions was said to contribute to the air emissions inventory. Evolution of nitrogen dioxide at a maximum rate of about 10 lb y^{-1} was estimated from the addition of sodium nitrite to nitric acid in the gelatin strike tank. Compared to 44 ton y^{-1} from the dissolver, this amount seems negligible (Radian 1993). Interestingly, the permit application conservatively assumed that 5% of the dissolver off-gas was due to the head end process; therefore, 0.05 × 44.66 ton = 2.23 ton y^{-1} of oxides of nitrogen that was attributed to the head end. The Title V operating permit calculations led to actual emission estimates for the dissolver of 44.6 ton y^{-1} of nitrogen dioxide (Westinghouse 1996c). A weekly progress letter from October of 1959 said that analytical data were being collected on buildup of nitric acid in 291-H stack catch tank. The acid was formed by absorption of nitrogen oxides in condensing moisture in the stack plenum, which drains to the catch tank. The acid in the tank contributed about 24 gal of waste volume per day. It was hoped that operation of an acid absorber might reduce the amount of acid and decrease the waste volume (Martens et al. 1959). The dissolver off-gases from dissolution were being processed through the acid absorber by 1959, but another report suggests that before 1959, the dissolver off-gases were discharged directly to the stack (Du Pont 1959b). The acid buildup in the stack catch tank was compared with buildup when the dissolver off-gases were discharged directly to the stack. The data obtained indicated that the buildup in the stack catch tank was approximately 850 lb of 12% nitric acid per day, or 100 lb of 100% nitric acid per day

(Martens et al. 1959). This report suggests that about 100 lb d^{-1} or about 18 ton y^{-1} of nitric acid could have been removed from the air exhaust by the acid absorber.

The frame waste recovery system in H-Area, which purified and concentrated ^{238}Pu solutions, used nitric acid. The maximum pounds per run was reported in 1984. The 1984 throughput was used to determine emissions estimates for the Operating Permit application. Based on stoichiometry, throughputs, column feed rates, maximum operating temperatures allowed for worker safety concerns, a release estimate of 17.2 ton of nitrous oxide, and 0.39 ton of nitrogen dioxide and maximum emissions were estimated, using the 1984 throughputs (Westinghouse 1996c).

A conservative estimate of the nitrogen dioxide emissions from the H-Canyon rerun process, based on the amount of ferrous sulfamate used in the frames waste recovery process (a maximum of 334.3 ton y^{-1}), was calculated to be 20.6 ton y^{-1}. This upper bound limit assumes maximum processing of 24 hours per day and that all the NO formed was converted to nitrogen dioxide (Westinghouse 1996a).

The H-Canyon high and low activity waste processes that result in discharges to the canyon stack were also considered for the operating permit application. These processes included evaporation and waste neutralization. Nitrogen dioxide was evolved from sodium nitrite added to the LAW (Low Activity Waste) and HAW (High Activity Waste) evaporator feed tanks to eliminate the ferrous sulfamate. The H-Area LAW evaporators, combined were estimated to emit a maximum of 6.32 ton y^{-1}, and the HAW evaporators emission estimates totaled 2.64 ton y^{-1} for nitrogen dioxide (Westinghouse 1996c). The H-Canyon general purpose evaporator was not thought to have emitted nitric acid or nitrogen dioxide.

The emissions estimate for the 200-H emergency power generator, actual emissions assuming 2080 hours of operation each year, was 1.47×10^{-1} ton y^{-1} for oxides of nitrogen (Westinghouse 1996a).

The HB-Line converted aqueous neptunium and plutonium solutions from the canyon processes into dry oxide powders through ion exchange removal, acid oxidation, and dehydration and crystallization in a calcining furnace. In 1993, Radian estimated the amount of nitrogen dioxide emitted per pound of neptunium processed in 1985. The exact process chemistry was not available to Radian in the unclassified documentation, but a probable reaction stoichiometry was assumed, and solution volumes and throughputs were used to make the calculations. Actual annual emissions were estimated to be 0.0472 ton y^{-1} of nitrogen dioxide (Radian 1993).

The permit application for the H-Canyon from 1995 reported maximum controlled emissions for oxides of nitrogen to be 89.7 ton y^{-1}.

F-Area Releases of Nitrogen Oxides

The F-Canyon cycles, solvent recovery system, waste, acid recovery, evaporators and other process equipment were similar to those in H-Area. The recycle vessel vent system, process vessel vent system venting exhausted through the sand filters then the stack were the same as described for H-Area.

The overall profile of nitrogen oxide emissions for the F-Area separations process main stack (291-F) was evaluated in 1983. The approximate ratio of emissions of nitrogen oxide from the dissolution and denitration parts of the process was said to have been 8:1. Nitric acid fumes from both processes were recovered in the acid recovery unit and recycled as 50% nitric acid. The

nitrogen oxide emissions from 291-F were subject to a State permit limit of 180 lb h^{-1} annual average. Releases were estimated using mass balance calculations and facility production schedules. A stack test was conducted in 1983 to look at increased nitrogen dioxide from a proposed process modification. The data suggested that without the acid recovery unit, maximum emissions during the dissolution process were up to twice the hourly limit of 180 lb h^{-1}, but the average emissions for the entire process cycle appeared to be below the annual emissions limit. The efficiency of the replacement acid recovery column installed at this time was estimated to be twice that of the old column, so nitrogen oxide emissions were expected to be well within permit limits. The permit conditions did not require monitoring of nitrogen oxide emissions. The uranium denitrators were equipped with evacuators that bypass the acid recovery unit and exhaust directly to the sand filter and stack during a process emergency. The facility was suppose to report the use of the evacuators for more than 6 minutes to the State because of a concern about exceedance of the opacity limitation (DOE 1987). The tests and reports about them were cited in the DOE (1987) survey, but the reports referenced for the tests, attributed to Roberts in 1984 and Clayton Environmental in 1983, were not found by *RAC*. We also searched local phone directories and asked directory assistance for Augusta, Georgia, Aiken, South Carolina, and Atlanta, Georgia, areas for the consulting firms said to have been involved in testing in 1983, and could not find any reference to Clayton Environmental. Robert and Company of Atlanta may have done the monitoring but current personnel could not locate any reports or any employees with knowledge of monitoring done at the SRS. No documentation about these tests has been found. The permit conditions apparently do not require monitoring of nitrogen oxide emissions and no recent emissions data are available.

F-Area had two dissolvers of the same size: 6.1D and 6.4D. Very rarely did they operate at the same time, and emissions calculations for the permit assumed one dissolver operated. The maximum nitrogen dioxide emissions were thought to have been associated with processing of Mark 31A and B fuels. A dissolver run of 15 metric ton of uranium Mark31A contained about 856 lb of aluminum cladding, and 15 metric ton of Mark 31B fuel contained 794 lb of aluminum. The maximum dissolver capacity was 27 buckets or 18 metric ton of uranium targets. Decladding generally took 6–8 hours and dissolving was done for 20 to 22 hours. Minimum time of 26 hours per run was used as a conservative estimate. Maximum emissions were calculated assuming 18 metric ton of uranium per run at 26 hours per run for 8760 hours per year. However, the historical data reported that the highest amount of targets dissolved in a year was in 1976, which totaled 1352.8 metric ton, less than 25% of the theoretical maximum used (8760/26 × 18 or 6064 metric ton). Processing of different fuel, like the Rocky Flats scrub alloy, was considered and different assumptions were applied (for example, the plutonium containing targets do not go through the decladding step). As with H-Area, the F-Area condenser was not assumed to convert nitrogen oxide to nitric acid; it was only assumed to condense nitric acid vapors and return them to the dissolver.

Aluminum-clad uranium fuel assemblies were loaded in to the dissolver and declad by dissolving in sodium hydroxide followed by the dissolving of uranium metal in 50% nitric acid. Gaseous emissions included ammonia and oxides of nitrogen. The stoichiometry is such that 1 mol of uranium yields 2.42 of nitrogen dioxide. The maximum evolution of nitrogen dioxide was predicted to be 9.2 ton per run at maximum dissolver capacity. The actual uncontrolled emissions estimate based on 1944 metric ton of uranium each year was 993.6 ton y^{-1}. The actual uncontrolled emissions for the Rocky Flats scrub alloy fuel was 8.33 ton y^{-1}. Because this was

much less, in amount per time than the SRS fuel, the Rocky Flats fuel was not considered further, and the conservative assumption that all fuel was like the maximum fuel was used in subsequent calculations (Westinghouse 1996a).

The head end process permanganate strike and centrifuge cake dissolution forms nitrates and manganese compounds, none of which were thought to contribute to air emissions. Ruthenium particles and oxides of nitrogen from foaming during slurry dissolution in the strike tank were noted. Engineers estimated that the nitrogen oxides released from the head end process would not exceed 5% of the dissolver emissions, and the estimates reported in the tables of the air permit were simply 5% of the dissolver emissions or $0.05 \times 993.6 = 49.7$ ton y^{-1} actual uncontrolled emissions of nitrogen dioxide from the head end process.

Denitration was done at the F-Canyon A-Line. The facility converted uranium nitrate solutions to uranium trioxide powder. Uranium solution was concentrated using continuous then hydrate evaporators. The A-Line process vessels and the hydrate evaporators were vented through the recycle vessel vent system fiberglass filters then sand filters to the stack. The off-gas from the denitration pots was discharged from the stack after flowing through a series of scrubbers, coolers, and a nitrogen oxides absorption column (the same column used for the dissolver off-gas) (Westinghouse 1996a). The A-line denitration step converted uranyl nitrate to uranium trioxide by thermal decomposition, which evolved nitrogen dioxide. The A-Line nitrogen oxide removal system, also called the F-8 column, removed water soluble nitrogen dioxide from the off-gas. The F-8 column was the most effective control device in the process, with an efficiency of 45–70% reported by the vendor who sold the unit to the SRS. The air quality permit application reduced the emission estimate for nitrogen dioxide by 45% or $993.6\ (1 - 0.45) = 556.5$ ton y^{-1} for the dissolver and 5.0 ton y^{-1} from the head end to estimate actual controlled nitrogen dioxide emissions. How the emissions estimate for the head end was calculated to be 5 ton y^{-1} based on this reduction is not clear. A 45% reduction of 49.7 ton y^{-1} should result in the release of 27 ton y^{-1} (which equals 5% of 556.5 ton y^{-1}); however, 5 ton y^{-1} was the estimate reported for the F-Area head end process in the Operating Permit Application.

Based on stoichiometry of producing uranium trioxide from uranyl nitrate hexahydrate, 692.5 ton of nitrogen dioxide per year was the controlled maximum emissions estimate calculated for the denitrator facility. This assumed two denitrator pots were operating simultaneously and the F-8 column had an efficiency of 45%. The A-line evaporation and purification and hydrate evaporation systems were calculated to have released no nitrogen dioxide or nitric acid to the air.

Nitrogen dioxide was also created by adding sodium nitrate to the evaporator feed tanks, a part of the low activity and high activity waste handling systems. Maximum uncontrolled emissions were estimated to be 13.72 ton y^{-1} from the high activity waste and 10.81 ton y^{-1} from the low activity waste, for a total of 24.53 ton y^{-1}. No actual emissions were given (Westinghouse 1996a).

FB-Line, in Building 221-F made plutonium buttons from a dilute nitrate solution. FB-Line tanks and vessels were enclosed in cabinets or glove boxes. The line included four major processes and four vacuum venting systems. The vessel vent vacuum system was preceded by Teflon filters and used a venturi scrubber to scrub the off-gas, which contained nitrous oxides and nitric acid. This system used a caustic scrubber to neutralize the nitric acid vapors. Actual emissions of nitrogen oxides from the FB-Line were reported to be zero in 1996, but the maximum controlled emission estimates were 1.39 ton y^{-1} in the permit application.

A 1982, environmental assessment for the Naval Reactors Fuel Materials Facility estimated that the emission rate of nitrogen oxides to the air would be 0.1 ton y^{-1} (DOE 1982). Emissions for the Naval Fuels Manufacturing Facility were included in the AIRS database (Faugl 1996e) and are shown in Table 17-54.

F-Area emissions of nitric acid and nitrogen dioxide estimated in the AIRS database in 1994 and 1995 were reviewed. Most of the actual emissions were estimated as zero, indicating the facility was not operating. However, maximum design capacity estimates were given for 59 emission points, including 0.052 ton y^{-1} nitric acid, 42.9 ton y^{-1} nitrous oxide, and 76.5 ton y^{-1} nitrogen dioxide for the dissolver off-gas and 3.83 ton y^{-1} for the head end. The rest of the emission points for the canyon processes were totaled, including the first and second uranium cycle and all the vessel vents and other exhaust points that comprise the 50 sources that contributed to the canyon stack emissions. The maximum design capacity-controlled emissions for nitric acid totaled 9.89 ton y^{-1}. Actual emissions were listed for 11 sources, which were tanks and other equipment, and they totaled 0.76 ton y^{-1}. The maximum emissions for nitrogen dioxide totaled 13.5 ton y^{-1}, and the actual emissions totaled 0.24 ton y^{-1}. The maximum design capacity emissions for nitrous oxide totaled 2.9 ton y^{-1} and the actual emissions were estimated at 0.395 ton y^{-1} (Faugl 1996e).

In summary, the uncontrolled actual emissions for nitrogen dioxide from F-Canyon included 994 ton y^{-1} from the dissolvers and 49.68 ton y^{-1} from the head end process. Controlled actual emissions were estimated to be 557 ton y^{-1} from the dissolvers and 5.0 ton y^{-1} from the head end process. The total emissions for the individual sources described in the permit application were 73–90 ton. At the time of the 1996 permit, the F-Canyon was not operating and actual emissions were reported as zero. The combined F-Canyon stack maximum controlled emission estimates, assuming 24 hour a day releases of oxides of nitrogen, totaled 2530 ton y^{-1} based on engineering calculations (Westinghouse 1996a). By far, this estimate from the permit application, was the largest emission estimate given in any of the documents reviewed.

Nitrogen Dioxide from the Power Plants

From 1972 to 1985, estimates of nitrogen oxide emissions from the coal burning power plants, reported in the annual reports, were said to have been within standards. Emissions estimates were not given. After 1977, control of total suspended particulates and oxides of nitrogen was assessed using opacity meters in the powerhouse stacks. The 1986 annual report is the first to mention opacity standards, which were set by SCDHEC at 40%. The 1986 annual report states," the day-to-day control of total suspended particulates and oxides of nitrogen is maintained with the use of opacity meters in all of the powerhouse stacks. These measurements indicated that the SRP boilers were within limits greater than 99% of the time in 1986." Opacity was limited to 40% for stacks in existence before January 1, 1986. Stacks put in use after that date were to be held to a standard of 20% opacity. The 1986 environmental report also says that, "all facilities were within applicable federal and state standards except for occasional high opacity results from the F-Area separations process stack. The acid absorber column for the F-Area separations process stack had deteriorated and required renovation in 1986. After renovation was complete, the opacity requirement was met" (Ziegler et al. 1987). Oxides of nitrogen from the power plants were reported to have been within applicable standards in 1987 and 1988 (Mikol et al. 1988; Davis et al. 1989).

The 1989 environmental report mentions that the 291-F stack occasionally exceeded the opacity standard and renovations of the acid absorption column were underway to ensure compliance in the future. However, all of the coal burning power plant stacks were said to have been in compliance.

The 1992 annual report estimated emissions of nitrogen dioxide to be 3767 ton from the coal-fired boilers (which burned 243,627 ton of coal that year [corresponding to an emission factor of 30.9 lb ton^{-1}]; 17.2 ton from the fuel-oil fired boilers; and 142.6 ton from diesel equipment. These estimates were said to have been based on AP-42 calculations and opacity monitoring (Arnett et al. 1993).

K-Area coal consumption and emissions estimates of uncontrolled nitrogen dioxide emissions for 1985–1990 were included in the air emissions inventory and are summarized in Table 17-58.

Table 17-58. Estimates of the Coal Consumed and Uncontrolled Emissions of Nitrogen Dioxide Each Year for K-Area[a]

Year	Tons of coal consumed	Tons of nitrogen dioxide per year
1985	40886	255.5
1986	52394	327.5
1987	56638	354
1988	56449	352.8
1989	18717	117
1990	8064	50.4

[a] Calculated by Radian (1992b) for the air emissions inventory.

Nitrogen dioxide emissions from the two boilers in K-Area were not controlled. In 1992, nitrogen dioxide emissions were derived graphically from source test data compiled from KVB, Inc. in support of EPA research on the formation of nitrogen dioxide. A nitrogen content of 1.20%, which was the average content reported for 1988, was used for the emissions estimates. Handwritten calculations described stoichiometric oxygen requirements and said that the nitrogen dioxide emissions were calculated using a computer program written for this purpose. The calculation was said to use the 95% confidence level of the KVB Inc. data and to assume a worst case, 3% excess oxygen scenario. The resulting uncontrolled emissions estimate was 12.5 lb nitrogen dioxide per ton of coal burned. Radian (1992b) stated that the EPA's AP-42 value for NOx was 7.5 lb ton^{-1} of coal burned (Radian 1992b).

The two coal-fired stoker boilers in A-Area had two opacity monitors: one in the No. 2 boiler exhaust duct and one in the stack. However, these monitors were not used for compliance purposes. The units were exempted from continuos opacity monitoring because they produced less than 250 million BTUs. Analyses and calculations of the K-Area boilers suggest that 117.5 ton of nitrogen dioxide was produced from burning 17,000 ton of coal (Westinghouse 1996a) or 13.8 lb of nitrogen dioxide per ton of coal burned (Westinghouse 1996a).

Generally, site-specific data or vendor analysis-based emission factors are preferred over literature values. If we assume, based on the reported emissions, that the emissions factor for nitrogen dioxide released from coal burned at the SRS ranged from 12.5 to 31 lb ton^{-1}, the estimates of emissions from coal burning in Table 17-59 could be made.

Table 17-59. Estimates of the Nitrogen Dioxide Released Based on the Amount of Coal Burned Each Year

Year	Estimate of coal burned each year	Range of nitrogen dioxide emissions predicted (ton y^{-1})
1954–1972	≤500,000	3125–7750
1972–1982	500,000	3125–7750
1983	400,000	2500–6200
1984	400,000	2500–6200
1985	455,000	2845–7053
1986	439,700	2750–6815
1987	453,000	2831–7021
1988	373,935	2337–5795
1989	227,017	1418–3518

Other Nitrogen Dioxide Emissions

The AIRS database contained emissions estimates for oxides of nitrogen from emergency diesel generators, diesel compressors, welders, diesel engines, welders, and other equipment. Most of the diesel generator and engine emissions were estimated to be less than 1 ton y^{-1}, but the contribution from all of these sources was significant. In 1985, sources included 58 emergency diesel generators, 2 portable gasoline generators, 2 diesel engines, 55 diesel and gasoline generators, a diesel compressor, 9 diesel pumps, 1 welder, and 1 lead melting pot. In 1990, emissions were given for 76 emergency diesel generators, 3 portable gasoline generators, 3 engines, 67 diesel and gasoline generators, 1 diesel compressor, 11 diesel pumps, 1 welder, and 1 lead melting pot. In 1992, 117 welders were listed. This was probably because of the search criteria, which may have excluded welders from the printout in the earlier years. The totals reflect all of these sources. The lead melter used No. 2 fuel oil and also released notable amounts of nitrogen oxides (about 0.47 ton y^{-1}) (Faugl 1996k).

Facilities associated with the vitrification processes, operated in the 1990s, are not within the scope of this study. An example of one of these processes with relatively large releases is the F-Area rerun process. It involved processes of denitration, oxalate precipitation, oxalate kill, dissolution of the precipitate in nitric acid, steam stripping, formic acid denitration, and concentration using an evaporator. The nitric acid going through this process is used at several different concentrations, volumes, and temperatures. The emissions were considered to be uncontrolled because fiberglass and sand filters of the process vessel vent system do not remove nitrogen dioxide or nitric acid. The maximum emissions were estimated to be 784 ton y^{-1} of nitrogen dioxide and 0.039 ton y^{-1} of nitric acid in 1995 (Westinghouse 1996a).

Summary of Release Estimates for Nitrogen Dioxide

The actual emissions estimates in the AIRS database for 1987 totaled 469 ton. This included most of the key emissions from F-Area, H-Area, M-Area, and T-Area and relatively conservative estimates of releases from generators, engines, welders, and other equipment. The 1992 annual report suggested diesel equipment produced 143 ton y^{-1} (Arnett et al. 1993). The AIRS database

estimates did not include the D-Area coal burning. We might add 1418–7750 ton y^{-1} to the estimate to account for coal burning in 1987. As much as 70 ton y^{-1} of nitrogen dioxide may have been released from open burning operations (described near the end of this chapter). The permit application suggested releases of 6–21 ton y^{-1} for M-Area, 73–90 ton y^{-1} for H-Area, and 588–1068 ton y^{-1} for F-Area. A stand alone section of the permit applications also provided a very high total of 2530 ton y^{-1} for F-Area. Taken together, the range of estimates spans from (a) 2086 to 10,534 ton y^{-1} if the high of the 2530 ton y^{-1} permit application estimate for F-Area is used as a maximum or (b) 2086 to 9072 ton y^{-1} if an estimate of 1068 ton y^{-1} is used for the maximum for F-Area. For some operations, these ranges apply to releases in the 1985 to 1987 time frame. This is especially important for considering pollution control equipment that may not have been in place in earlier years. However, actual releases for all time periods, including the mid-1970s when the maximum amount of coal was burned and the canyon production was high, should fall within the range that was determined by adding together many maximum emission estimates. This represents more of a worst case than a best case scenario. A release of 2086–10534 ton y^{-1} for the 35 years between 1954 and 1989 totals 73,010–368,690 ton of nitrogen dioxide.

Uncertainty was calculated for these releases using the estimates from the AIRS database, permit applications, and engineering calculations, and coal releases. Although the very large estimate for releases from F-Area is not expected to approximate a true value, doing an uncertainty calculation allowed us to include it on the tail of the F-Area release distribution. The distribution of total oxides of nitrogen released per year was lognormal with a geometric mean of 6050 ton y^{-1} and a GSD=1.23. This distribution represents a range of releases from 4320–8480 ton y^{-1} of nitrogen dioxide. Using uncertainty calculations to estimate releases decreased the total range of possible values somewhat. Since the total range of estimated releases in the preceding paragraph is assumed to represent a worst case type scenario as a result of some very large point estimates, this distribution of values narrows the potential release estimates into what are probably more realistic estimates.

The Standard 8 results submitted to SCDHEC said that in 1991, 295 sources from all areas at the SRS released nitrogen dioxide. The estimated maximum annual average Site boundary concentration was calculated to be 125.4 μg m^{-3}. The ambient air standard was 100 μg m^{-3}. This suggested that if all operations were operating at maximum, nitrogen dioxide emissions could exceed standards at the Site boundary. The Environmental Protection Department staff submitting the report to SCDHEC felt that the exceedances were due to extremely conservative approaches being used in the modeling analysis and they planned to remodel for the standards using more accurate operating data and system configurations. They also said they planned to develop a control strategy plan for the D-Area Powerhouses (Dukes 1993).

Several accidents involving nitric acid spills and explosions have been reported. Two 'red-oil' explosions have occurred at the plant. These are described briefly, but well, in Durant (1978). In both cases, operators did not realize that tributyl phosphate was present in the uranyl nitrate solutions being processed. In January 1953, an evaporator in Building 678-G at TNX exploded during concentration of a uranyl nitrate and nitric acid solution. Tributyl phosphate and AMSCO diluent were present in the evaporator charge, and the explosion was a result of an exothermic reaction between tributyl phosphate and the nitrate or nitric acid or both. An experimental program was conducted after the explosion to learn more about how violent reactions may have been produced. The explosion destroyed the evaporator, ripping the pot into six pieces, and damaged the roof and siding of the building. Two minor injuries were said to have been

sustained. The operator present at the time of the explosion later said he saw orange colored fumes evolving from the top of the column and heard rumbling and roaring. The total capacity of the evaporator was 1300 gal in the shell and pot plus 525 gal in the column. No mention of chemical releases because of this incident was made in the report (Colven et al 1953). A later summary of the incident in Durant (1978) estimated that 1800 gal of solution was being evaporated at the time of the explosion, but that the deacidification was carried out in several batches of about 500 gal each. Three batches had been successfully processed. The fourth and final charge had contained the 70 gal heel of the original solution plus 160 gal of previously evaporated material diluted with water.

The other accident occurred 22 years later, on February 12, 1975, in an A-Line facility denitrator (calciner), which was used to convert uranyl nitrate solution to uranium trioxide powder. The A-Line incident involved fires from the ignition of gases that were evolved from the denitrator. Damage to the building required 6 months to repair (Durant 1978). The incident report does not specifically address releases of chemical or radioactive materials to the air or surface water.

Sulfur Dioxide

Sulfur dioxide was formed by combustion processes. Releases from the powerhouses, lead melting pots, incinerators, and engines all contributed sulfur dioxide to the air.

The AIRS database search for emissions of hydrogen sulfide, sulfuric acid, and sulfur dioxide were run together as sulfur compounds. The largest source of sulfur dioxide, the D-Area powerhouse stacks, were not included. Sulfuric acid emissions were listed for battery storage, sulfuric acid tanks, neutralization tanks, acid tanks, and wash tanks. Some of the larger sulfur dioxide emissions were given for the Central Shops Burn Pit, with maximum and actual emissions estimates of 0.55 ton y^{-1}, and the lead melting pot, with an actual emission estimate of 2.3×10^{-3} ton y^{-1}. In 1987, the Naval fuels glove boxes were listed with an actual and maximum emissions estimate of 1.6 ton y^{-1} (Faugl 1996n). Several fire-training pits were listed after 1990 with actual emissions of 2.1×10^{-3} ton y^{-1}. The AIRS database releases for oxides of sulfur were compiled for 1985, 1987, and 1990 and are shown in Table 17-60. Total process emissions of sulfur dioxide, sulfuric acid, and hydrogen sulfide are shown in Table 17-61.

Table 17-60. Sulfur dioxide emissions from the AIRS Database by Source[a]

Emission source	Year	Actual[b] emission estimate (ton y^{-1})
A-Area boiler house	1985	304
	1987	400
	1995	673
D-Area Powerhouse	1985	2530
H-Area Powerhouse Boiler 1	1985	306
	1987	306
	1995	86.6
H-Area Boiler House 2	1995	81.5
K-Area Powerhouse	1985	769
	1987	1060
K-Area Package Boiler	1995	6.73
Central Shops Burning Pit	1985	0.550
	1995	0.258
H-Canyon exhaust fan	1985	0.044
	1987	0.044
	1995	0.022
H-Canyon HB-Line	1985	0.010
	1987	0.010
	1995	0.00597
H-Canyon HB-Line (another emission point	1985	0.0299
	1987	0.0299
	1995	0.00401

[a] Source: Faugl (1996n).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

Table 17-61. Total Sulfur Compound Emissions Estimates Reported in the AIRS Database[a]

Total sulfur compounds	Maximum (ton y^{-1})	Actual[b] (ton y^{-1})
1985	4.34	4.05
1987	5.36	5.11
1990	6.0	5.66
1994	114.0	19.9

[a] Source: Faugl (1996n).
[b] Actual emissions are those predicted under typical operating capacities and times. Maximum design capacity emissions are calculated using maximum throughputs and capacities, assuming 24 hours per day and 365 days per year operating times.

The operating permit application included emissions of sulfur dioxide for the large generators. For example, the emissions estimate for the 200-H emergency power generator (actual

emissions assuming 2080 hours of operation each year) was 2.93×10^{-3} ton y^{-1} for oxides of sulfur (Westinghouse 1996a). The lead melter described in the permit application used No. 2 fuel oil and also released notable amounts of sulfur dioxide (7.44 ton y^{-1}) (Westinghouse 1996a).

The HB-Line converted aqueous neptunium and plutonium solutions from the canyon processes into dry oxide powders through ion exchange removal, acid oxidation, and dehydration and crystallization in a calcining furnace. In 1993, Radian estimated the maximum amount of sulfur dioxide emitted per pound of neptunium processed in 1985. The exact process chemistry was not available to Radian in the unclassified documentation, but a probable reaction stoichiometry was assumed and solution volumes and throughputs were used to make the calculations. Actual annual emissions were estimated to be 0.0167 ton y^{-1} of sulfur dioxide (Radian 1993).

Sulfur dioxide was formed from the burning of hydrogen sulfide discharged to the flare tower from the heavy water facility in D-Area (Rusche 1973). How much was never reported, but emissions were have said to have been very small compared to D-Area powerhouse emissions.

Sulfur dioxide emission from M-Area, H-Area, and F-Area were due to combustion engines, furnaces, and maintenance equipment and were not the result of sulfur compounds used in the processes. A document describing the design of the Fuel Production Facility in F-Area described potential sulfur dioxide releases from the calcining process. Uranium was to be loaded onto sulfur-bearing ion exchange resin then the resin was calcined to produce U_3O_8. Much of the sulfur would have exhausted out the stack. The maximum load, worst case emissions were calculated to be about 12,403 kg y^{-1} or about 13.7 ton. Average and actual emissions would be much less than this because the facility did not intend to operate at maximum load and it was predicted that about one-half of the sulfur in the calciner exhaust may be carbonyl sulfide rather than sulfur dioxide (Allender 1985). No other reference to this production facility was found. Site personnel in the Environmental Protection Department could not recall any operations of this type in separations or the Naval Fuel Facility. It may be that the facility was designed but not built nor operated.

In 1967, an 18-day air sampling program was conducted in M-Area; it measured an average concentration of 0.02 ppm sulfur dioxide in air. The purpose of the sampling, why sulfur dioxide was a concern, and where the samples were taken are not indicated (Du Pont 1967). The National Ambient Air Quality Standard is currently 0.03 ppm annual average concentration and 0.14 ppm over 24 hours.

Sulfur Dioxide Emissions from Power Plants

According to the DOE Environmental Survey, the sulfur dioxide emission limit of 3.5 lb/10^6 BTU heat input was met in the 1980s by the use of low-sulfur coal, and no pollution control equipment for sulfur dioxide was ever applied to any of the boilers (DOE 1987). It seems likely that in the 1950s and 1960s some of the coal purchased had higher sulfur content, and emissions would have been greater than they were in the more recent past and currently. Higher sulfur content coal may have been somewhat balanced by fewer tons of total coal burned in earlier years.

At some point after about 1970, the specifications required a sulfur content of less than 2% (Garvin 1996). The pulverized coal used at 400-D was of lower quality than the stoker coal that was crushed and blown into the boilers (Smith 1996). Sulfur contents reported in the annual reports also suggest that stoker coal was lower in sulfur than pulverized coal (Du Pont 1983).

The amount of coal burned before 1972 is unknown. The annual environmental reports have summarized the status of power plants onsite and reported the amount of coal burned and the approximate sulfur content of the coal. The reports gave estimates of the emissions of sulfur dioxide, nitrogen dioxide, and fly ash particulates in the early and mid-1970s. Beginning in 1972, each year the reports gave estimates of emissions of carbon monoxide and volatile organic compounds (VOCs). Attempts to locate more primary data on sulfur analysis of coal and coal receipt or storage information were not successful. Records of this type were not found in the Phase I database search. Essential materials ledgers for D-Area and the other powerhouses were not located. In 1996, Tom Thome, Stan Smith, and H.S. (Sid) Willis, who worked onsite in power engineering or previously for the Power Department; Robert Garvin and Mal Schroeder, who worked in D-Area; and retired workers Henry Main, Ray Fleming, Leo Shelton, Peter Gray, WB Holt, and Jim King were interviewed about power plant operations, essential materials records, coal inventory and analysis records, and potential releases of chemicals to the environment from the D-Area power plant and other power plants.

The Bureau of Mines did much of the coal analysis in earlier years. The regional office recommended we contact the office in Washington, D.C. Neither office had an idea where we might find records of coal analysis for the SRS.

Sample data sheets from 1987 on the coal analysis were included in materials submitted to supplement the K-Area powerhouse air emissions inventory. The sheets were from Mineral Laboratories, Inc. in Salyersville, Kentucky, and indicated that analysis had been done for Air Techniques, Inc. in Marietta, Georgia. The laboratories indicated that any analysis records they had generated would have been kept for 7 years or less. They had no recommendations for where to find coal analysis records before 1985 (Radian 1992b).

Compliance with the sulfur dioxide emissions standard was determined by estimating an annual emission based on the analysis of the sulfur content of the coal received and the amount of coal burned. This information was reported in the annual reports after 1972. From 1972 to 1975, sulfur dioxide emissions were said to have been within standards. In 1975, eight coal-fired plants were reported to have burned about 500,000 ton of coal that year, with an average sulfur content of 0.9% (Du Pont 1977a). In 1977, sulfur dioxide emissions ranged from 1.63 to 2.12 lb/10^6 BTU, with a weighted annual average of 1.87 lb/10^6 BTU heat input for all power plants (said to be within the emissions standards). In 1978 and 1979, seven coal-fired plants burned about 500,000 ton of coal each year, with an average sulfur content of 1.3% (Du Pont 1979). The emission rate for sulfur dioxide was given as a weighted annual average with a range from 1.55 to 2.50 lb/10^6 BTU and an average of 2.0 lb/10^6 BTU heat input. The South Carolina Emission Standard was 3.5 lb/10^6 BTU heat input in 1978. In 1980, 1981, and 1982, the same volume of coal was reported to have been burned, but the sulfur content was 1.4% (Du Pont 1981, 1983). The sulfur dioxide emissions were broken down into an emission rate for the four pulverized coal boilers, based on a sulfur content of 1.56%, of 2.17 lb/10^6 BTU and for the 15 stoker coal boilers, based on a sulfur content of 0.9%, of 1.30 lb/10^6 BTU (Du Pont 1983). In 1983 and 1984, seven coal-fired plants that burned about 460,000 ton of coal each year, with an average sulfur content of 1.06 and 1.07%, were reported to be operating (Du Pont 1984; Zeigler et al. 1985). In 1985, five coal-fired plants burned a total of 455,000 ton of coal a year with an average sulfur content of 1.05% (Ziegler et al. 1986). In 1986, five coal-fired plants that burned about 439,700 ton of coal each year were described in greater detail and are summarized in Table 17-62.

The sulfur content of the coal burned in 1986 averaged 1.01%, which yielded an average of 1.6 lb of sulfur dioxide per 10^6 BTU input. The sulfur dioxide standards were still 3.5 lb/10^6 BTU heat input in 1986. The 1986 annual environmental report said that, "the content of coal delivered to the site for burning is determined by analyses for sulfur, carbon, ash, water and BTU output." In 1987, five coal-fired plants burned 452,980 ton of coal that averaged 1% sulfur and yielded an average of 1.73 lb of sulfur dioxide per 10^6 BTU input, which was 49% of the South Carolina standard (Mikol et al. 1988). In 1988, the coal plants burned 373,935 ton of coal with an average sulfur content of 1.1%, which yielded an estimate of average sulfur dioxide emissions at 1.77 lb/10^6 BTU input (Davis et al. 1989). Three coal plants burned 227,017 ton of coal in 1989, with an average sulfur content of 2.6%, which resulted in a release estimate of 2.0 lb of sulfur dioxide/10^6 BTU input (Cummins et al. 1990). Three coal-powered plants burned 243,627 ton of coal in 1992, resulting in 7133 ton of sulfur dioxide, assuming a sulfur content of 1.06%. The D-Area power plant boilers also burned 30,922 gal of used oil for energy recovery and 4247 gal of propane for boiler startup. In 1992, the SRS had four package steam generating boilers (three in K-Area and one in P-Area) fueled by No. 2 diesel fuel. These boilers burned 1,718,764 gal of fuel oil in 1992. About 7133 ton of sulfur dioxide was estimated to have been released from the coal-fired boilers, 35.4 ton from the fuel-oil fired boilers, and 9.5 ton from diesel equipment in 1992 (Arnett et al. 1993). Generally, the calculated average emission values in the annual reports seem to be less than or equal to 2.0 lb of SO_2/10^6 BTU heat input.

Table 17-62. Power Plant Location, Number of Boilers, and Capacity[a]

Power plant location	Number of boilers	Boiler capacity 10^6 BTU h^{-1} input
A- Administration Area	2	71.7
D- Powerhouse Area	4	396.0
H-Separations Area	3	71.7
K- Reactor Area	2	194.5
P- Reactor Area	2	194.5
Total	13	928.4

[a] Source: Ziegler et al. (1986)

The coal analysis reported for 1992 suggested that the sulfur content ranged between 0.71–1.82%, averaging 1.06%. If we assume the range of sulfur content varied similarly in other years, then this could be used to approximate an uncertainty range. Radian (1992b) reported that the sulfur content of the coal delivered from 1985 to 1990 varied from 0.81% to 1.24% and averaged 0.97%.

Although the information about capacity is useful for helping to understand the size of the power plants, it is not very useful for estimating releases of pollutants. We know that the boilers did not operate at capacity. Three of four or two of three boilers were usually in operation at one time.

The AP-42 value for sulfur dioxide from coal is 37.8 lb ton^{-1} (EPA 1988). The 784-A two coal-fired stoker boilers have produced steam for A-Area heating since 1953. The capacity of each boiler was 72 million BTU h^{-1}. Particulate emissions were collected in multiple cyclone separators. The units burned about 8500 ton of coal per year each. The air quality permit application estimated that the two boilers released a total of 652 ton of sulfur oxides

(Westinghouse 1996a), which corresponds to an emissions estimate of 77 lb ton^{-1}. In 1992, uncontrolled sulfur dioxide emissions from the two boilers in 184-K were calculated for the air emissions inventory using monthly coal delivery data from 1988 and assuming 97% of the sulfur was converted to sulfur dioxide. The sulfur content of the coal in the 1980s and 1990 varied from 0.81% to 1.24% and averaged 0.97%. The uncontrolled emission estimate for sulfur dioxide from the boilers was 37.6 lb ton^{-1} of coal burned (Radian 1992b). K-Area coal consumption and emissions estimates of sulfur dioxide emissions, which were not controlled for 1985–1990, are summarized in Table 17-63.

Table 17-63. Estimates of the Coal Consumed and Uncontrolled Emissions of Sulfur Dioxide for 1985–1990 for K-Area Boilers[a]

Year	Tons of coal consumed	Sulfur dioxide emissions estimates (ton y^{-1})
1985	40886	769.4
1986	52394	986
1987	56638	1065.8
1988	56449	1062.2
1989	18717	352.2
1990	8064	151.7

[a] Calculated by Radian (1992b) for the air emissions inventory.

The 1992 annual report stated that 7133 ton of sulfur dioxide had been released from burning 243,627 ton of coal (Arnett et al. 1993). This corresponds to an emissions factor of 58.5 lb ton^{-1}. The emissions factors calculated at various time periods for Site coal seem to range from 37 to 77 lb ton^{-1}. The emission factor can also be calculated by converting the emissions reported in the annual reports in terms of lb/10^6 BTU heat input to pounds per ton. The resulting values are shown in the fifth column of Table 17-64.

The AIRS database provided only limited information for uncertainty calculations, but the ranges in the total sulfur released per ton of coal burned, the largest releases of sulfur from the site, allowed the uncertainty in sulfur releases from coal burning to be reasonable well quantified.

The AP-42 value for sulfur released from coal burning of 37.8 lb ton^{-1} is close to the site estimated value derived from the sulfur content in coal during the 1980-90s of 37.6 lb ton^{-1}. From annual reports, from 1977 through 1992, the average of the reported sulfur released per ton of coal burned is 43.5 lb ton^{-1}. In the air quality permit, sulfur releases were estimated at 77 lb ton^{-1}. Because the values from the annual reports are probably the most accurate estimates of sulfur releases for the Site, the average of these values (43.5 lb ton^{-1}) was used as the most likely estimate in a triangular distribution, with 37.6 as the lower limit and 77 as the upper limit. Estimates of releases of sulfur compounds from open burning, as described in the next section, were also added into the release estimate.

The distribution of annual releases of sulfur compounds was lognormally distributed with a geometric mean of 11000 ton y^{-1} and a GSD=1.18. The 5th and 95th percentile values of the distribution were 8470 and 14400 ton y^{-1}, respectively.

The Standard 8 results submitted to SCDHEC said that in 1991, sulfur dioxide was emitted from 282 sources in A-Area, B-Area, C-Area, D-Area, E-Area, F-Area, G-Area, H-Area, K-Area,

L-Area, M-Area, N-Area, P-Area, S-Area, T-Area, and Z-Area. The estimated maximum 3-hour average Site boundary concentration was calculated to be 2319 μg m^{-3}. The corresponding ambient air standard was 1300 μg m^{-3}.

Table 17-64. Coal Consumption, Average Sulfur Content, and Calculated Sulfur Dioxide Releases for 1952–1989

Year	Pounds sulfur dioxide/10^6 BTU heat input	Approximate amount of coal burned in tons[a]	% Sulfur content reported in annual reports	Pounds sulfur dioxide released per ton of coal burned [b]	Central estimate of the range of sulfur dioxide releases (ton y^{-1})
1952–1971	-	<500,000	-	-	<9500
1972	<3.5	500,000	-	-	9500
1973	<3.5	500,000	-	-	9500
1974	<3.5	500,000	-	-	9500
1975	-	500,000	0.9	-	9500
1976	-	500,000	-	-	9500
1977	1.8	500,000	-	45	11250
1978	2.0	500,000	1.3	50	12500
1979	2.0	500,000	1.3	50	12500
1980	1.5	500,000	1.4	37.5	9375
1981	1.5	500,000	1.4	37.5	9375
1982	1.5	500,000	1.4	37.5	9375
1983	1.5	400,000	1.06	37.5	9375
1984	1.6	400,000	1.07	40	8000
1985	1.5	455,000	1.05	37.5	9375
1986	1.6	439,700	1.01	40	8794
1987	1.73	453,000	1.0	43.2	9785
1988	1.77	373,935	1.1	44.2	8264
1989	2.0	227,017	2.6	50	5675
1992		243,627	1.06	58.5	7133

[a] Taken from the Site annual environmental reports

[b] Calculated using 38 lb ton^{-1} emission factor for 1952–1971. A value of 2.5×10^7 BTU ton^{-1} was used for the conversion from lb/10^6 BTU heat input. Vendor analysis in the 1990s suggests that the coal averages about 12,180 BTU/lb or 2.43×10^7BTU/ton (Faugl 1996a). Vendor analysis in the late 1980s suggests 2.6×10^7 BTU/ton (Westinghouse 1996a).

Emissions from Burning

Incineration, open burning, and solvent burning released particulates, sulfur dioxide, oxides of nitrogen, metals, and other chemicals in the air. Emissions of sulfur dioxide, fly ash, and oxides of nitrogen from coal burning are characterized in the sections above. The releases to

surface water from runoff from the coal piles, ash piles, and ash retention basins are addressed in Chapter 18.

The most significant combustion source of concern is the coal-fired powerhouses, the D-Area powerhouse being by far the largest source. The releases to surface water from runoff from the coal piles, ash piles, and ash retention basins are addressed in Chapter 18. Other fuel-burning facilities and equipment have included the beta-gamma radioactive waste incinerator in the 200-H Area, the propane-fired uranium oxide calciners in the 200-F Area A-Line, CMX Pilot Plant test incinerator, and more than 100 diesel generators throughout the facilities. The diesel-powered generators are periodically tested or used for emergency or standby power when electrical power is interrupted. Emissions estimated for diesel-powered generators are included in the Site-wide air emissions inventory and many were included in the AIRS database totals.

Incinerators

Incinerators onsite are a concern because of the potential release of toxic metals and compounds like dioxins. HEPA filters are very effective for controlling particulate and dioxin emissions. Fortunately, because the incinerators were designed to burn radioactive waste, they have been equipped with HEPA filters.

The Consolidated Incineration Facility, in 261-H, began cold runs in 1996 and started operations in March 1997. It consists of a rotary kiln incinerator, a fixed secondary combustion chamber and supporting solid and liquid feed, off-gas treatment, and ash and blowdown solidification systems. It is equipped with several scrubbers and HEPA filters The predicted emissions from this facility are described in the operating permit application submitted in 1996. The ash and blowdown was to be stabilized with Portland cement before disposal. The facility has a 150-ft main process stack and a 42-ft tank farm stack. The off-gas is subjected to coolers, scrubbers, and HEPA filters (Westinghouse 1996a).

The Beta/Gamma Incinerator in Building 230-H is a dual-chambered controlled air incinerator that burns liquid and solid waste, including spent solvent from the canyons, waste oil, rubber, polyvinyl chlorides, and other plastics. Waste oils are suppose to be certified by the generator as free of radioactive materials and toxic components, including lead, chlorinated hydrocarbons, and carcinogenic solvents. Because of the radioactivity of the waste, the exhaust is subject to stringent particulate controls. Pollution control devices include a water quench, baghouse, and HEPA filters (DOE 1987). This incinerator has released hydrochloric acid, nitrogen oxides, and sulfur oxides. Emissions from the incinerator are tested twice a year to comply with State permit requirements. The permit limits emissions of HCL to 30 lb h^{-1}, which was reported to have been easily met because of the limited amount of chlorinated waste and plastics burned. Sulfur dioxide and nitrogen dioxide emissions were said to have been low relative to the powerhouse emissions (DOE 1987; Faugl 1996a).

Interestingly, this facility was not operating during the DOE Environmental Survey conducted in 1986 because of an accident involving the introduction of Halon (a fire extinguisher) into the combustion air (DOE 1987). In December 1986, fumes containing hydrogen fluoride, hydrogen bromide, and bromine were released form the incinerator stack during testing of the Halon 1301 fire suppression system (Jewell 1990). The fumes were detected by construction workers working nearby. This incident demonstrated to the survey team that the incinerator could influence local air quality, and the survey team expected that inadvertent

burning of large amounts of chlorinated plastics could result in increased hydrochloric acid emissions and ground-level concentrations during stable meteorological conditions. They concluded that, "during normal operations with permitted limits the regulated/hazardous emissions from the facility are not significant with respect to other air emissions sources at the site" (DOE 1987).

A test incinerator located at TNX, called the SHIRCO incinerator, was built to help design larger scale incinerators. The incinerator throughput was small and emissions were controlled by a metal filter and three banks of HEPA filters (DOE 1987).

Fuel Burning

The D-Area boilers also burned oil. Waste oil from the reactor areas generated at the powerhouses and from diesel engines used as backup for primary reactor cooling water pumps was disposed of by burning in the 400-D Area powerhouse (DOE 1987). In the 1980s, the 484-D plant was said to have burned about 100,000 lb y^{-1} nonradioactive waste oils, including engine lubricants, kerosene, diesel, and fuel oils. Oils containing lead, chlorinated compounds, cutting oils, or other toxic components were not supposed to be burned. Generators were required to certify that the oil was free of these unsuitable materials before the waste oil could be received. The plant required that the generator provide a certification form that verified the contents of the waste (DOE 1987). Waste oils burned at the 400-D power plant were reported to have been spot checked for polychlorinated biphenyl (PCB) content. The oils were supposed to contain less than 50 ppm PCBs to be accepted for burning (DOE 1987). In 1992, the D-Area power plant boilers burned 30,922 gal of used oil for energy recovery and 4247 gal of propane for boiler startup. In 1992, the SRS also used four package steam generating boilers fueled by No. 2 diesel fuel. These boilers burned 1,718,764 gal of fuel oil in 1992 (Arnett et al. 1993). Releases of sulfur dioxide and oxides of nitrogen from these boilers are included in the AIRS database.

Open Burning

Open burning at the Site included (a) open pan burning of waste solvent at the burial grounds, (b) burning of wood and other waste at the burning and rubble pits, (c) burning of wood and tree slash by the U.S. Forest Service, (d) fire training exercises, (e) burning of scrap lumber, (f) clearing and dead brush disposal, and (g) controlled burning of underbrush by the U.S. Forest Service. Emissions from these activities were determined for the air emissions inventory using EPA emission factors.

Open burning was also addressed in the Part 70 Operating Permit Application. Estimates were calculated by making assumptions about the mass of wood burned in scrap piles, forest, and underbrush. Emission factors chosen for sulfur oxides were 0.4 lb ton^{-1} of scrap lumber and 0.8 lb $acre^{-1}$ for underbrush. Emission factors for nitrogen oxides were estimated to be 2.6 lb ton^{-1} of scrap lumber and 10 lb $acre^{-1}$ for underbrush. For 1994, the Site estimated that 52 fire training exercises were conducted each year, 2800 ton of lumber was burned, and 20,000 acres per year of forest were cleared. U.S. Forest Service-controlled burns in 1994 were also included. Using the EPA AP-42 emissions factors and the estimates of the mass of material burned described above, emissions of oxides of nitrogen were estimated to be 69.9 ton y^{-1} and emissions for oxides of sulfur were estimated to be 5.6 ton y^{-1}. A great deal of uncertainty is associated with

the estimates, but the uncertainty was not quantified. These values are probably conservative. We do not know how burning in 1994 compared with burning the past. Theoretically, 70 ton y^{-1} of nitrogen dioxide and 6 ton y^{-1} of sulfur dioxide could be added to the totals to account for open burning.

Burning and Rubble Pits

Burning and rubble pits were located in Central Shops and in D-Area, F-Area, K-Area, P-Area, R-Area, and L-Area (Westinghouse 1992). Very little documentation on the operation of the burning and rubble pits was found in Phase I. Most of the useful records were characterizations of waste areas prepared recently. The DOE Environmental Survey report (DOE 1987) contained a good summary of what the survey team found out about the pits by reviewing aerial photographs. According to DOE (1987), burnable solid and liquid waste was disposed of in 15 pits between 1951 and 1973. The pits were bulldozed open trenches 8–12 ft deep and 250–400 ft long. The waste was burned only about once a month; therefore, contamination of groundwater beneath these pits has been a concern. In 1973, the pits were no longer used for disposal of chemicals; they were used only as rubble pits until they were filled and covered with soil. Rubble included metal, concrete, lumber, railroad ties, telephone poles, glass, paper, and other solid waste. Most of the pits are located in flat areas away from Site streams, except the P-Area burning and rubble pit, which is about 100 ft from Steel Creek. Steel Creek is in a gorge 75 ft below ground-level, and seeps and springs along the bank suggest that groundwater moves into the creek. A survey done in 1987 found no radioactivity or organic vapor contamination attributable to the pits. No records of pit disposal before 1989 were kept. Estimates were made and published in DOE (1987) using groundwater modeling (PATHRAE model) said to have been done by Du Pont of measured levels of contaminants versus background levels. Table 17-65 summarizes the calculated amounts of some of the chemicals of concern that may have been disposed of in the pits.

Another report prepared for a Comprehensive Environmental Response, Compensation, and Liability Act investigation said that chlorinated solvents and metals (including mercury, zinc, cadmium, nickel, lead, and chromium) have been found in the soil of many of the pits, and solvents, chromium, lead, and manganese have been found in groundwater near many of the pits (Westinghouse 1992).

Determining air emissions from burning in these pits is not possible without more information on what, and how much was burned. The lead disposed of was probably in solid sheeting or other shielding material and may not have been released into the air as a result of burning. Because monitoring indicates groundwater contaminated by these pits is not migrating offsite, the pits were not evaluated further.

Table 17-65. Estimates of Chemicals Disposed of in Rubble Burning Pits[a]

Chemical	Pit	Estimated amount disposed of (kg)
Trichloroethylene	A-Area	1.2
	C-Area	186
	F-Area	7.4
	K-Area	1.0
	P-Area	3.4
Lead	C-Area	5530
	D-Area	204
	P-Area	3300
Chromium	C-Area	9500
Tetrachloroethylene	D-Area	0.1
	F-Area	7.6
	K-Area	3.1
	Central Shops	0.64
	L-Area	0.51
	R-Area	0.37
	P-Area	3.5

[a] Source: DOE (1987). Estimates of the amount of chemicals disposed of in burning rubble pits calculated using groundwater models.

Solvent Use and Solvent Burning

Degraded solvent (tributyl phosphate in kerosene) from the separations areas was stored at the burial ground. After allowing the short-lived fission product activity in the solvent to decay for several years, most of the solvent was burned. Most of the records about solvent burning were concerned with release of radioactivity and burial of radioactive material remaining in the burning pan as residue. Releases of large quantities of black smoke were reported, and slow burning generating less smoke was deemed necessary. A 1971 report stated that, “efforts to burn solvent at suitable rates without smoke generation in burners or incinerators have been unsuccessful because of entrained radioactivity in the combustion gases.” However, the release of radionuclides from solvent burning was said to have been negligible (Ice 1971).

Many of the monthly progress reports between 1956 and 1972 contain a section on the burial ground, which often reported the quantity of solvent transferred to the burial ground and the amount burned. Solvent was burned in an 8 × 8 × 4-ft steel pan with a rain shed over its top (Ice 1971). The pan corroded and was replaced in 1964 by a longitudinally halved 400-gal tank (Du Pont 1974b).

Several monthly reports referred to a data record that was being prepared that was to present a history of the storage and disposal of spent extraction solvent. The record was said to detail the accumulation of the present inventory along with “a history of the tanks in which it is stored and the burning process by which it is destroyed.” No such data record was located. A brief report on radioactive waste management at the Site first published in 1969, then issued as a revised document in 1972, said that 400,000 gal of solvent had been burned since February 1956. This amount probably represents burning over about a 16-year period (1956–1971). The text indicated

that the quantities stored and destroyed were shown in an attached figure, but the figure was not included in the copy that was found (Ice 1971).

Information on degraded solvent burning reported in many of the monthly progress reports was summarized as follows. In 1956, a burning rate of 80 lb d^{-1} in F-Area was reported. A total of 26,000 gal was burned and 55,000 gal remained to be disposed of at the end of the year. Airborne contamination was said to have been negligible (Du Pont 1974b). The removal of degraded solvent from the rerun facilities and transportation to the burial ground was mentioned in the 1956 monthly report because of problems from high activities in the unshielded truck and transport areas. During the month of May 1956, 830 gal of solvent was burned in 72 hours of operation at the average burning rate of 0.2 gal min^{-1}. The waste solvent inventory in the burial ground was said to be 70,000 gal (DuPont1956c). The June report states that routine burning continued and that the burning rate was increased from 50 to 250 gal d^{-1} by changing equipment. About 3500 gal was burned that month (June 1956), and a total of 5000 gal (35,000 lb) was reported to have been burned from January to June 1956 - (Du Pont 1956d). The July report indicated that the burning rate was increased to about 90 gal h^{-1}, and about 5300 gal was burned in July (Du Pont 1956b). The solvent being burned was said to have been in the burial tanks for about 1 year and was filtered through underground charcoal beds to reduce radioactivity. A May 1956 report (Du Pont 1956c) refers to solvent having been sent to the rerun station where it was stripped and washed before being sent to the burial ground for burning. A monthly report from 1957 stated that the total amount of solvent burned in 1956 was 31,700 gal (Du Pont 1957b). Some of the disagreement in values reported in different reports probably results from errors in reporting amounts sent to the burial grounds and amounts stored at the canyons or burial ground when compared to amounts actually burned.

In 1957, burning appeared to have been limited by rainy weather. A total of 12,600 gal was burned. In January 1957, a new type of burner was installed to test burning using a different fuel-to-air ratio. The burner was designed to spray the solvent at 8 gal h^{-1} into an air stream. The burner was being evaluated for smoke release and contamination of the surrounding area (Du Pont 1957b). In April 1957, the Separations Technology Section reported that 2200 gal had been burned so far that year and the inventory that needed to be burned was 59,000 gal (Du Pont 1957c).

Reports published in 1958 mention the periodic burning of waste degraded solvents, but no amounts were available. A weekly progress letter from the Separations Technology Section from December 1958 explained that solvent was being drawn off of the top of the storage tanks so that the high activity sediment was left in the tanks and not burned (Du Pont 1958).

No mention is made of solvent burning in 1959, 1960, or 1961. This probably reflects a change in the format of the reporting in the monthly reports rather than an absence of burning; however, it is unknown how much was burned during this period.

In 1962, 54,000 gal of low activity solvent was burned in the burial ground. In May 1962, 19,600 gal was burned during 1 week from May 17 through May 23. The June report explained that operating standards limited the radioactivity of the solvent that could be burned and most of the solvent in the storage tanks exceeded the limit and could not be burned (Du Pont 1962).

In 1964, as much as 7200 gal of spent solvent was burned each month during several months at the burial ground (Du Pont 1974b). Another monthly report said that from August 1955 through February 1964, 290,000 gal of spent solvent had been received at the burial ground, of which 170,000 gal had been disposed of by burning (Du Pont 1964b).

About 3000 gal of spent solvent was burned in January 1965. Other volumes reported to have been burned in 1965 were 5000 gal in February, 1800 gal in August, 9000 gal in November, and 7250 gal in December, which totaled 24,250 gal (Du Pont 1965). One separations area history reports that a total of 22,600 gal of waste solvent was burned in the burial ground in 1965 (Du Pont 1974b).

In the meeting minutes from a presentation by Albenesius, responses to questions from the audience included some interesting statements about solvent burning (Albenesius 1992). The speakers stated that 350,000 gal of solvent was disposed of by burning at the burial ground and that burning was stopped in 1972 because of air quality concerns (black smoke) rather than radiological concerns. Albenesius said, "they did burn solvent at night because people onsite were worrying about the black smoke produced." One of the presenters also said that someone mistakenly pumped much of a truckload of solvent down a well near the burial ground, mistaking it for a solvent tank. About 60 gal was pumped down the well, until the well overflowed. He also said that there were some spills associated with solvent burning and they are "they are well written up in a document produced by Elmer Wilhite" (Albenesius 1992). Several documents about the burial grounds authored by E. Wilhite were found, but we did not locate documents describing solvent burning or spills (Wilhite et al. 1989).

The monthly reports suggest that burning was not continuous and varied tremendously from month to month ranging from zero to 19,600 gal (in 1 week during May 1962). Solvent burning was discontinued in 1972. Obviously, burning rates reported for one time period cannot be applied to another time period. Taken together, the values in various reports suggest a typical solvent burning volume may have been about 25,000 gal y^{-1}, ranging from zero in later years, 12,600 gal in 1957, and 170,000 gal in 1964. A reasonable central estimate for the total amount of solvent burned over the 16 years solvents were burned is 400,000 gal or about 2.8×10^6 lb. The range that is implied by the very limited amount of monthly data available is about 320,000 to 650,000 gal or 2.2×10^6 to 4.4×10^6 lb.

Because monthly or annual values were available for 1956, 1957, 1962, 1964, and 1965 only, the total for 1956–1971 of 400,000 gal reported by Ice (1971), provides the best estimate during the 16-year period when solvents were burned. The amount burned averages to about 25,000 gal y^{-1}. Data from which to determine uncertainty are limited. The monthly estimates reported vary tremendously. More solvent was burned in the month of May 1962 than for the entire year in 1957. Ice (1971) may have had more information on which to base his estimate of 400,000 gal than is now available, but the uncertainty associated with the Ice (1971) estimate was not quantified or described.

The solvent was primarily n-parrafin, or kerosene, with tributyl phosphate. Burning of kerosene and tributyl phosphate probably resulted in emissions of carbon monoxide, carbon dioxide, water, nitrogen oxides, sulfur oxides, and trace amounts of metals. Some research on this has been done for crude oil burning in oil wells in Alaska and in Kuwait, and the EPA has established emission factors for burning of fuel oil and fuel distillates, given in lb/10^{12} BTU for metals.

The EPA AP-42 estimates that about 104 lb of total carbon compounds are released from burning 100 gal of fuel (EPA 1988). The BTU gal^{-1} value for No. 1 and No. 2 fuel oil ranges from 134,000 to 142,000. Table 17-66 summarizes the emissions factors for metals released from No. 6 fuel oil burning, the estimated releases assuming 400,000 gal of solvent was burned, and the maximum emission factors:

AP-42 lb released/10^{12} BTU × 142,000 BTU/gal × 400,000 gal burned = pounds released.

These values are conservative and very uncertain. Fuel oil is more crude than kerosene and the metal content of the solvent burned was likely to have been less than that of fuel oil. The amounts of nonradioactive materials released from solvent burning were much less than that released from the coal burning power plants. Because the combustion products of kerosene and tributylphosphate are not particularly hazardous, it seems that burning solvent in the burial ground area would not have produced sufficient quantities of criteria pollutants or metals to have resulted in concentrations of concern offsite.

Table 17-66. Emissions Estimated from the Number of Gallons Waste Solvent Burned at the SRS Burial Grounds (1956–1971)

Pollutant	AP-42 factor lb/10^{12} BTU	Estimated total release (lb)	Estimated total release (kg)
Arsenic	19–114	1–6	0.5–3
Beryllium	4.2	0.2	0.1
Cadmium	16–211	1–12	1.5–5
Chromium	21–128	1–7	5–3
Lead	28–194	2–11	1.5–5
Manganese	23–74	1–4	0.5–2
Mercury	1.4–32	0.08–2	0.04–0.8
Nickel	837–2330	47–132	22–60

Solvent releases to the air from the solvent extraction process H-Area and F-Area did not survive the screening process described in Chapter 16 and were not evaluated further, largely because the solvents are not very toxic and are less volatile than chlorinated solvents. The solvent extraction process was done in mixer-settler banks using tri-n-butyl phosphate (TBP or $[C_4H_9]_3PO_4$) in a kerosene solvent. Using the SRS safety analysis flow sheets, VOC emissions from these units were estimated by Radian using the EPA's AP-42 algorithm for organic liquid storage tanks. Solution volume and throughput data were derived from the dissolution solution feed rates in safety analysis flow sheets. Relative input and output streams for each mixer-settler unit were listed. Because temperatures in the canyon building were relatively constant, breathing losses of the tanks were assumed to be zero. The solvent feed loop was essentially a closed system. Degradation products of the extraction solvents include butanol, mono and dibutyl phosphate and butyl nitrate. Degraded solvent was replaced with fresh tributyl phosphate (TBP or $[C_4H_9]_3PO_4$) and n-paraffin. During times of greatest processing in the mid-1980s, amounts of TBP and the diluent (n-paraffin, kerosene, or n-dodecane, containing predominately 13 and 14-carbon n-paraffins, $C_{13}H_{28}$) fed to the contactors were used to calculate working losses for the solvent extraction process. The amounts totaled about 50 lb per contactor at maximum design capacity. Actual cycle times for extraction were not available, so the emission rate was calculated by averaging annual emissions over a continuous 24-hour period. This resulted in a very conservative estimate for the sum of the loss from each unit in the two cycles of 582.32 lb of total VOCs and 266 lb of TBP in 1985 (Radian 1993). This is a very small emission compared to

routine emissions from the use of gasoline and fuel and compared to the emissions of chlorinated solvents from M-Area.

The Operating Permit Application included emissions estimates from F-Area and H-Area waste tank purges for tributyl phosphate, n-paraffin, benzene, and mercury from 51 tanks (Westinghouse 1996a). Tributyl phosphate and n-paraffin do not present serious health hazards and source terms for these materials were not determined for this study.

The loss of degradation products was also calculated for the air emissions inventory. The maximum design capacity estimated totaled 3788 lb (1.9 ton) in 1985 for butanol and 6095 lb for butyl nitrate (Radian 1993). These chemicals were not included in the chemicals of concern because they are relatively nontoxic. Releases of this magnitude would not likely result in toxic concentrations at the Site boundary.

Uranium

Uranium in solution was discharged to the M-Area settling basin. Because chlorinated solvents in the waste contaminated groundwater, it is likely that uranium also could have entered the groundwater through this pathway. The DOE Environmental Survey team (DOE 1987) was concerned that the air stripper water and Liquid Effluent Treatment Facility water were potential sources of uranium contamination from M-Area. No other supporting documentation for this was found.

A series of engineering worksheets for air emissions inventory calculations done by Radian in 1992 included data on filter aid preparation in 313-M. A filter aid tank was installed in September 1985. Water previously sent to the settling basins was sent to the treatment facility after June 1985. An autoclave was used to pressure test slugs. A description of the autoclave waste treatment system said the purpose was to remove uranium dioxide solids from condensate in the autoclave collection sump. The sump water was mixed with filter aid and sent through the autoclave pressure filter, and the filtrate and the filter cake (as a slurry) were pumped to separate hold tanks. No volatile chemicals or dry solids were involved, but particulate emissions from the addition of filter aid to the top of the filter aid mix tank may have occurred. The tank has a vent with a fan exhausting to the outside of the building. The maximum, worst case emission estimates for natural uranium calculated for 313-M, DETF, CTF, and 340-M totaled 0.037 ton y^{-1} in 1985, 0.0665 ton y^{-1} in 1986, 0.0504 ton y^{-1} in 1987, 0.0212 ton y^{-1} in 1988, 0.012 ton y^{-1} in 1989, and 0.021 ton y^{-1} in 1990. More than one-half of the emissions were from the DEFT facility (Radian 1992a). Releases of uranium to the atmosphere are addressed in Chapter 4.4. Uranium releases may be best characterized by looking at uranium as a radionuclide that was routinely monitored. However, the toxicity of the uranium metal to the kidney may outweigh the carcinogenicity from radioactive decay. This should be considered in subsequent phases of the dose reconstruction study.

CONCLUSIONS

We found enough information to calculate the uncertainty associated with the release estimates for the chemicals presented in Table 17-67.

Table 17-67. Release Estimates and Uncertainty Ranges for Chemicals Released to the Air

Chemical	Median average annual release (ton y^{-1})	5^{th}–95^{th} percentile values on the median (ton y^{-1})
Coal ash	4200	2300–7100
Mercury	0.3	0.18–0.51
Nitrogen dioxide	6050	4320–8480
Sulfur dioxide	11000	8470–14400

Uncertainty calculations were not made for the chemicals listed in Table 17-68 because of a lack of information, but a range of releases was estimated.

Table 17-68. Range of Releases Estimates

Chemical	Range of release estimates (ton y^{-1})
Benzene	1.8–18
Lead	0.05–0.12
Manganese	0.07–1.9
Nickel	0.11–0.42
Nitric acid	30–150

Seven coal-fired steam plants have operated at the SRS. Burning coal released relatively large amounts of nitrogen dioxide and sulfur dioxide and contributed to the releases of arsenic, cadmium, chromium, lead, manganese, mercury, and nickel. After 1972, the SRS annual reports provided estimates of the amount of coal burned; the sulfur content of the coal; and emission estimates for sulfur dioxide, nitrogen dioxide, and particulates. About 500,000 tons of coal were burned each year from 1972 to the mid-1980s. We estimated the amount of coal burned in earlier years by assuming coal consumption was correlated to production by the reactors.

Not enough information is available to allow us to estimate releases of chromium from its use as a corrosion inhibitor in process and cooling water with reasonable certainty. Chromium releases from machining, construction, and maintenance operations probably ranged from 0.1–0.5 ton y^{-1} for most years. Cadmium releases from similar activities may have been about 0.19 ton y^{-1}. As much as 150 ton y^{-1} of hydrogen sulfide, much of which was released via a flare tower and was probably burned to sulfur dioxide, was released until 1982. After 1982, about 3.5 ton y^{-1} was released from the treatment of groundwater. Releases of hydrazine and emissions from the use, storage, and transport of gasoline and diesel fuels were evaluated. The release of pollutants from open burning was also described.

Almost all of the chlorinated solvents evaporated during use or after being discharged to surface water. Until 1979, waste solvent was released to the M-Area settling basin or to a stream called the Tim's Branch, where most evaporated. Trichloroethylene and tetrachloroethylene have also been released from air strippers used to remediate groundwater under M-Area. Release estimates for trichloroethylene, tetrachloroethylene, and trichloroethane are summarized in Table 17-69.

Table 17-69. Trichloroethylene, Tetrachloroethylene, and Trichloroethane Releases to the Air

Solvent	Source	Time period	Median	5^{th}–95^{th}% range (ton)
Trichloroethylene	M-Area use	1952–1970	1700 ton (average of 90 ton y^{-1} over 19 y)	1530–1900
	M-Area air strippers	1985–1990	70 ton (average of 12 ton y^{-1} over 6 y)	57–87
Tetrachloroethylene	M-Area use	1962–1975	4055 ton (average of 289 ton y^{-1} over 14 y)	3520–4675
	M-Area air strippers	1985–1992	30 ton (average of 3.8 ton y^{-1} over 8 y)	22–40
Trichloroethane	M-Area use	1979–1988	2200 ton (average of 220 ton y^{-1} over 10 y)	1780–2710

REFERENCES

ATSDR (Agency for Toxic Substances and Disease Registry). 1996. Toxicological Profiles. Atlanta, Georgia. OpenLit.

Albenesius, E.L. 1992. "SRS Burial Ground Operation from a Historical Perspective." Transcription of a presentation. WSRC-RP-92-349. SRS Phase II Database EIW199406212. February 14.

Allender, J.S. 1985. Memo to E.K. Dukes. Subject: Fuel Production Facility Calculation Bases for Stack Releases from Chemical Processes. FPF-86-171. SRS Phase II Database HAG1993110823. July 16.

Arnett, M.W., L.K. Karapatakis, and A.R. Mamatey. 1993. *Savannah River Site Environmental Report for 1992*. WSRC-TR-93-075. Westinghouse Savannah River Company. SRS Phase II Database MOL1993120610.

Argonne National Laboratory-West. 1973. Facility Waste Descriptions. Draft. Idaho National Engineering Laboratory. SRS Phase II Database KRM199810231. December 14.

Ashley, C. and C.C. Zeigler. 1973. *Environmental Monitoring at the Savannah River Plant, Annual Report–1972*. DPSPU-73-302. SRS Phase II Database MJC1994051716. August.

Ashley, C. and C.C. Zeigler. 1974. *Environmental Monitoring at the Savannah River Plant, Annual Report–1973*. DPSPU-74-302. SRS Phase II Database LWB1994032112. September.

Ashley, C. and C.C. Zeigler. 1975. *Environmental Monitoring at the Savannah River Plant, Annual Report–1974*. DPSPU-75-302. SRS Phase II Database LWB1994032113. August.

Ashley, C. and C.C. Zeigler. 1976. *Environmental Monitoring at the Savannah River Plant, Annual Report–1975*. DPSPU-76-302. SRS Phase II Database LWB1994021824. August.

Bebbington, W.P. 1990. *History of Du Pont at the Savannah River Plant*. Du Pont. Wilmington, Delaware. OpenLit.

Bradley, F. 1981. *Preliminary Scope of SRL Program for M-Area Groundwater and Process Effluent Cleanup*. DPST-81-970. SRS Phase II Database SKR199310077. December 31.

Brogdon, A.N. 1964. Memo to A.R. Boulogne. Subject: Radium-226 in Coal Ash. *Environmental Monitoring Memos*. From Carol Zeigler's personal files. SRS Phase II Database SKR1994020120. December 15.

ChemRisk. 1994. *Project Task 5 Report: Estimating Historical Emissions from Rocky Flats*. ChemRisk, A Division of McLaren/Hart. March. OpenLit.

Christensen, E.J. and C.K. Brendell. 1981. Technical Division, Savannah River Laboratory. Memo to E.B. Sheldon. Subject: Chlorinated Solvent Releases to M-Area Process Sewers. DPST-81-968. SRS Phase II Database MJC199405171. December 18.

Christensen, E.J. and D.E. Gordon, eds. 1983. *Technical Summary of Groundwater Quality Protection Program at Savannah River Plant. Volume I–Site Geohydrology, and Solid and Hazardous Wastes*. DPST-83-829, Vol. I. SRS Phase II Database SKR1993101316. December.

Clark, J.R. 1954. Memo to J.E. Cole. Subject: Community Vulnerability to Plant Hazards. DPW-54-547. SRS Phase II Database PDM199611084. September 9.

Cole, J.E. 1957. Letter to R.C. Blair. Subject: Community Vulnerability to Plant Hazards. SRS Phase II Database TFW1993081818. June 28.

Colven, T.J., G.M. Nichols, and T.H. Siddall. 1953. *TNX Evaporator Incident. Jan. 12, 1953*. Interim Tech. Report. DP-25. Du Pont. SRS Phase II Database KRM199810232. May 15.

Colven, W.P., L.F. Boone, J.G. Horvath, and R. Lorenz. 1987. *First Year Effectiveness of the M-Area Ground Water Remedial Action Program. September 1985–September 1986*. DPSP-87-26. SRS Phase II Database TFW199309292. February.

Colven, W.P., C.F. Muska, and J.B. Pickett. 1985. *M-Area Settling Basin and Vicinity, Draft.* Environmental Information Document. DPST-85-703. SRS Phase II Database GKH199403117. September.

Cummins, C.L., D.K. Martin, and J.L. Todd. 1990. *Savannah River Site Environmental Report for 1989. Annual Report for 1989. Volumes I and II.* WSRC-IM-90-60. Westinghouse Savannah River Company. SRS Phase II Database DWS1994122028.

Davis, H.A., D.K. Martin, and J.L. Todd. 1989. *Savannah River Site Environmental Report for 1988. Volume I, Text, Volume II, Figures and Data Tables*. WSRC-RP-89-59-1. Westinghouse Savannah River Company. SRS Phase II Database DWS1994122027.

Dodgen, M.S. and G.H. Sykes. 1971. *Suppression of Iodine-131 Releases. Test Conclusion No. 2-575*. DPSOX-7831. SRS Phase II Database SKR1994020457. June 15.

DOE (U.S. Department of Energy). 1982. *Environmental Assessment: Naval Reactor Fuel Materials Facility*. DOE/EA-0170. SRS Phase II Database TFW1993111521. March.

DOE. 1987. *Environmental Survey Preliminary Report for the Savannah River Plant, Aiken, South Carolina*. DOE/EH/OEV-10-P. Environment, Safety and Health Office of Environmental Audit. SRS Phase II Database EIW199309238. August.

DOE. 1988. *M-Area Hazardous Waste Management Facility, Post-Care Closure Care Permit, Ground Water Monitoring and Corrective Action Program, 2nd Quarter 1988 Report*. Conclusion No. 2-575. DPSP-88-172-3. SRS Phase II Database HRM1993083121.

Dukes, M.D. 1993. *SCDHEC Regulation No 62.5 Standard No. 2 and Standard No. 8 Compliance Modeling Input/Output Data.* ESH-ESS-93-0531. Westinghouse. SRS Phase II Database PDM199609173. September 29.

Du Pont. 1953. *Monthly Progress Report, February 1953.* DPSP-53-14-2-DV. Explosives Department. SRS Phase II Database EAS1994072210.

Du Pont. 1955. *Monthly Report of the Atomic Energy Division June 1955.* DPSP-55-14-6-DV. Explosives Department. SRS Phase II Database EAS199407224.

Du Pont. 1956a. *Control Weekly Report. July 2–9, 1956*. Savannah River Laboratory. SRS Phase II Database MJC1993051812.

Du Pont. 1956b. *Monthly Progress Report, July 1956*. DPSP-56-1-7-S-DV. Separations Technology Section. SRS Phase II Database HRM1994041923.

Du Pont. 1956c. *Monthly Report, May 1956, Production Supplement*. DPSP-56-1-5. SRS Phase II Database EIW1994101313.

Du Pont. 1956d. *Monthly Progress Report, June 1956.* DPSP-56-1-5. Works Technical Department. SRS Phase II Database EIW1994101314.

Du Pont. 1957a. *Monthly Progress Report, September 1957*. DPSP-57-1-9-S-DV. Works Technical Department. SRS Phase II Database EAS1994080211.

Du Pont. 1957b. *Monthly Progress Report, January 1957*. DPSP-57-1-1-S-DV. Separations Technology Section. SRS Phase II Database EIW1994101321.

Du Pont. 1957c. *Monthly Progress Report, April 1957*. DPSP-57-1-4-S-DV. Separations Technology Section. SRS Phase II Database EIW1994101324.

Du Pont. 1958. *Weekly Progress Letter, December 28, 1957–January 3, 1958.* DPSP-58-70-1. Separations Technology Section. SRS Phase II Database MJC1994042913.

Du Pont. 1959a**.** Shift Log Books and Special Work Permits, 1955–1958. Health Physics Section. SRS Phase II Database TFW1993072010.

Du Pont. 1959b. *Works Technical Monthly Report for June 1959*. DPSP-59-1-6. SRS Phase II Database EAS1994080220.

Du Pont. 1962. *Monthly Report, June 1962.* DPSP-62-1-6-S. Separations Technology Section. SRS Phase II Database MJC1994012434.

Du Pont. 1964a. *History of the Separations Areas. Calendar Year 1963*. "Waste Solvent Burning." DPSP-64-1241 DV. SRS Phase II Database HRM199407227. March 5.

Du Pont. 1964b. *Separations Technology Section Progress Report, March 1964*. DPSP-64-1-3-S. SRS Phase II Database MJC1994080232.

Du Pont. 1965. *Progress Report, January 1965*. DPSP-65-1-1. Works Technical Department. SRS Phase II Database EIW1994101473.

Du Pont. 1967. *Radiological Sciences Group Monthly Report, July*. DPST-67-1-7. Radiological Sciences Division, Savannah River Laboratory. SRS Phase II Database LWB1994011926. July.

Du Pont. 1970. *Works Technical Department Report for December 1970*. DPSP-70-1-12. SRS Phase II Database TFW1994101748.

Du Pont. 1971a. *January Monthly Report*. DPSP-71-1-1. Technical Works Department. SRS Phase II Database TFW1994101749.

Du Pont. 1971b. *Chemical Suppression of Nitrogen Oxides*. Test Authorization Form. DPSOX-7769. SRS Phase II Database HAG1994090120. March 8.

Du Pont. 1972a. *Savannah River Laboratory Monthly Report–February 1972*. DP-72-1-2. Savannah River Laboratory. SRS Phase II Database TFW1994101762.

Du Pont. 1972b. *Savannah River Plant History for the Raw Materials Area for July 1954 through December* 1972. DPSP-55-454-3. SRS Phase II Database EIW1993081812.

Du Pont. 1973a. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1972*. DPSPU-73-30-1. SRS Phase II Database MJC1993121335.

Du Pont. 1973b. *Environmental Activities and Programs at the SRP*. DPST-73-436. SRS Phase II Database MJC1993121410. September.

Du Pont. 1974a. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1973*. DPSPU-74-30-1. SRS Phase II Database MJC1993121336.

Du Pont. 1974b. *Savannah River Plant History - Separations Area July 1954 through December 1972*. DPSP-55-454-2. SRS Phase II Database EIW1993081811.

Du Pont. 1975. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1974*. DPSPU-75-30-1. SRS Phase II Database MJC1993121337.

Du Pont. 1976. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1975*. DPSPU-76-30-1. SRS Phase II Database MJC1993121338.

Du Pont. 1977a. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1976*. DPSPU-77-30-1. SRS Phase II Database MJC1993121339.

Du Pont. 1977b. *Works Technical Monthly Report for April 1977*. DPSP-77-1-4-DV. SRS Phase II Database SVK199410074.

Du Pont. 1978. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1977*. DPSPU-78-30-1. SRS Phase II Database MJC1993121340.

Du Pont. 1979. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1978*. DPSPU-79-30-1. SRS Phase II Database MJC199405176.

Du Pont. 1980. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1979*. DPSPU-80-30-1. SRS Phase II Database MJC199405177.

Du Pont. 1981. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1980*. DPSPU-81-30-1. SRS Phase II Database MJC199405178.

Du Pont. 1982a. Separations Department Essential Material Ledger April 1982. DPSP-82-1043. SRS Phase II Database PDM199611081.

Du Pont. 1982b. Fact Sheet. Subject: Nonradiological Contamination of Ground Water. SRS Phase II Database MJC199409086. September 21.

Du Pont. 1983. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1982*. DPSPU-83-30-1. SRS Phase II Database DWS199401118.

Du Pont. 1984. *Environmental Monitoring in the Vicinity of the Savannah River Plant, Annual Report-1983*. DPSPU-84-30-1. SRS Phase II Database MJC1994051710.

Durant, W.S. 1978. *Adverse Experiences with Nitric Acid at the SRS, Rev. 1*. WSRC-TR-91-22. SRS Phase II Database MOL199405096.

Ebra, M.A. and J.R. Wiley. 1984. *Mercury Removal and Recycle from 200-Areas Waste Streams*. DPST-84-487, Revision 2. SRS Phase II Database KRM199810233.

Eisenbud M. and H.G. Petrow. 1964. "Radioactivity in the Atmospheric Effluents of Power Plants that use Fossil Fuels." *Science* 144: 228–229. April 17. OpenLit.

Ellett, J.D. 1960. Letter to R.C. Blair and Incident Report. Subject: Unusual Incident Major Gas Release and Fire–400 Area. Reported by L.M. Pope. SRS Phase II Database TFW1994090619. April 13.

EPA (U.S. Environmental Protection Agency) 1988. *Compilation of Air Pollutant Emission Factors. Volume 1: Stationary Point and Area Sources. 4th edition*. AP-42. Research Triangle Park, North Carolina. OpenLit.

Evans, D.W. and J.P. Giesey, Jr. 1978. "Trace Metal Concentrations in a Stream-Swamp System Receiving Coal Ash Effluent." In *Ecology and Coal Resource Development*. Edited by K.K. Wali. 2: 782–790. SRS Phase II Database PDM1997022410.

Evans, D.E., J.G. Wiener, and J.H. Horton. 1980. "Trace Element Inputs from a Coal Burning Power Plant to Adjacent Terrestrial and Aquatic Environments." *APCA Journal* 30 (5). SRS Phase II Database PDM1997022414.

Faugl, T. 1996a. Environmental Protection Department, Westinghouse Savannah River Company. Communication with P.D. McGavran, Consultant to *Radiological Assessments Corporation*. Subject: AIRS Database Run. SRS Phase II Database PDM199711111.

Faugl, T. 1996b. *Benzene Emissions (Controlled) for 1985, 1987 and 1990.* AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company. SRS Phase II Database PDM199611048.

Faugl, T. 1996c. *Cadmium Emissions (Controlled) for 1985, 1987 and 1990*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company. SRS Phase II Database PDM199611043.

Faugl, T. 1996d. *Chromium Emissions (Controlled) for 1985, 1987 and 1990*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company. SRS Phase II Database PDM199611042.

Faugl, T. 1996e. *AIRS Database Information on Mercury Emissions for 1995.* SRS Phase II Database PDM199611073.

Faugl, T. 1996f. *Manganese Emissions (Controlled) for 1985, 1987 and 1990*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company SRS Phase II Database PDM1997022418.

Faugl, T. 1996g. *Lead Emissions (Controlled) for 1985, 1987 and 1990*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company SRS Phase II Database PDM199611044.

Faugl, T. 1996h. *AIRS Database Information on Mercury Emissions for 1985, 1987 and 1990.* SRS Phase II Database PDM199611041.

Faugl, T. 1996i. *Nickel Emissions (Controlled) for 1985, 1987 and 1990.* AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company SRS Phase II Database PDM199611045.

Faugl, T. 1996j. *Nitric Acid Emissions (Controlled) for 1985, 1987 and 1990*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company SRS Phase II Database PDM199611046.

Faugl, T. 1996k. *Oxides of Nitrogen Emissions (Controlled) for 1985, 1987 and 1990*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company SRS Phase II Database PDM199611047.

Faugl, T. 1996l. *Trichloroethylene Emissions (Controlled) for 1985, 1987, 1990, 1992 and 1994*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company. SRS Phase II Database PDM1997022416.

Faugl, T. 1996m. *Tetrachloroethylene Emissions (Controlled) for 1985, 1987, 1990, 1992 and 1994*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company SRS Phase II Database PDM1997022417.

Faugl, T. 1996n. *Sulfur Compound Emissions (Controlled) for 1985, 1987, 1990, 1992 and 1994*. AIRS Database. Environmental Protection Department, Westinghouse Savannah River Company SRS Phase II Database PDM1997022415.

Fisk, P.L. and W.S. Durant. 1987. *Safety Analysis, 200-Area Savannah River Plant. Separations Area Operations Building 211H, Outside Facilities*. DPSTSA-200-10. Suppl 11. SRS Phase II Database MOL199405092. December.

Franklin, M.G. 1985. Memo to J.G. McKibbin. Subject: Mercury Emissions Monitoring of 292-H Stack. WSRC-RP-90-182-251. SRS Phase II Database DWS1993092312. August 21.

Garvin, R.A. 1996. Retired D-Area Power Plant Engineer. Personal communication with P.D. McGavran, Consultant to *Radiological Assessments Corporation*. Subject: Power Plant Operations. SRS Phase II Database Interview 6.

Gary, S. 1996. Westinghouse. Communication with P.D. McGavran, Consultant to *Radiological Assessments Corporation*. Subject: Raw Materials Area. SRS Phase II Database Interview 7. February.

Gordon, D.E. 1982. *Preliminary Technical Data Summary: M-Area Groundwater Cleanup Facility*. DPSTD-82-69. Du Pont. SRS Phase II Database HAG1994061623. October.

Graham, R.F., W.T. McDuffee, and D.J. Wilkes. 1987. *Savannah River Plant Spill Prevention Control and Countermeasures Plan.* DPSP-87-1083. SRS Phase II Database PDM199710025.

Hale, W.H. 1973. Memo to J.A. Porter. Subject: Fate of Mercury in the Burial Ground. DPST-73-457. SRS Phase II Database TFW1994061014. October 8.

Hardt, H.A. 1970. Du Pont interoffice memorandum to K.W. Millett. Subject: Control of Industrial Wastes in Raw Materials Area. SRS Phase II Database TFW1994061019. October 30.

Hardt, H.A. 1971. Memoradum attached to Monier, J.A. Jr. 1970. Memo. Subject: Chemical Waste Discharges- 300 Area. SRS Phase II Database TFW1994061041.

Harper, J.A. and J.J. Croley. 1976. *Summary of SRP Industrial Hygiene Activities 1975*. DPSPU-76-276. Du Pont. SRS Phase II Database LWB1994021823.

Haywood, J.E. 1980. Memo and final report to T. Hendrick. Subject: H2S Leak Incident and GS Plant Incident. SRS Phase II Database HRM199401069.

Herbst, A.K. 1979. *Mercury Concentrations in the Effluent Streams of the Idaho Chemical Processing Plant*. M.S. Thesis. University of Idaho, Moscow, Idaho. INEEL Task Order 1. Database PDM1997080617.

Horton, J.H. 1962. Savannah River Plant, Du Pont. Memo to W. L. Marter. Subject: Ground Water Monitoring at the 200 Area Seepage Basins. SRS Phase II Database TFW199406102. April 9.

Horton, J.H. 1973. Memo to B.C. Rusche. Subject: Mercury in the 643-G Burial Ground. DPST-73-480. SRS Phase II Database GKH1994031124. December 6.

Horton, J.H. 1974a. Memo to B.C. Rusche. Subject: SRL-SRP Mercury Monitoring Program. DPST-74-389. SRS Phase II Database SKR1994020134. June 11.

Horton, J.H. 1974b. Technical Division, Savannah River Laboratory. Memorandum to B.C. Rusche. Subject: Mercury in the Separations Areas Seepage Basins. DPST-74-231. SRS Phase II Database GKH1994031125. January 30.

Horton, J.H. and G.A. Carothers. 1974. Memo to B.C. Rusche. Subject: Nitrate in the Separations Area Seepage Basins. SRS Phase II Database GKH1994031126 and JMW1996011111. March 22.

Howard, P.H. 1990. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Lewis Publishers, Inc. Chelsea, Michigan. OpenLit.

Ice, C.H. 1971. *Management of Radioactive Waste at the SRP*. DPST-69-310-DV. SRS Phase II Database HRM1994081914. July.

Ice, C.H. 1973. Letter to N. Stetson. Subject: Mercury in Bass from Skinface Pond. SRS Phase II Database TFW1994061060. August 7.

Jewell, C.E. 1990. Westinghouse. Memos to G.F. Stejskal and K.B. Broom. Subject: Remediated Spills Requiring Documentation. SRS Phase II Database TFW199406141. March 6.

Johnson, D.R. 1983. *Mercury Inventory Record for Tritium Facilities*. Letter to O. M. Morris. Tritium Facilities Separation Technical Memo No. 438. Du Pont. SRS Phase II Database HJM2001031504. August 29.

Johnson, J.E. 1966. *Fish Kill in Steel Creek Swamp*. From Carrol Zeigler's personal files. SRS Phase II Database SKR1994020120. February 15.

Johnson, J.E. 1968. Memo to S.R. Smith. Subject: Analysis of 300-M Weir Sample. SRS Phase II Database PDM199811221. January 5.

Johnson, J.E. 1978. Handwritten Meeting Record to S.P. Tucker and C. Ashley. Subject: Meeting of Raw Materials, Raw Materials Technology, and Health Physics Section representatives held February 13, 1978, to discuss the measurement of liquid releases from the M-Area facilities. SRS Phase II Database MJC1996011011.

Karoly, W.J. 1985. Du Pont. Memo to D.A. Stevenson. Subject: Biological Monitoring for Nonradioactive Chemicals in the 200-H Areas. SRS Phase II Database HG 199304083. April 30.

Krolewski, J.F. and D.A. Webber. 1985. *Consolidated Incineration Facility for Radioactive and Hazardous Waste.* DPSP-85-1157. SRS Phase II Database TFW1994061618. December 23.

Kvartek, E.J., W.H. Carlton, M. Denham, L. Eldridge, M.C. Newman, and A.L. Boni. 1994. *Assessment of Mercury in the Savannah River Site Environment.* WSRC-TR-94-0218 ET. Westinghouse. SRS Phase II Database HRM199502132. September.

Looney, B.B. 1984. Memo to D.E. Gordon. Subject: Quantification of the Redeposition of Chlorinated Organics Downwind of the A/M Area Groundwater Strippers. DPST-84-683. SRS Phase II Database SKR1993093011. August 22.

Looney, B.B., J.B. Pickett, C.M. King, W.G. Holmes, W.F. Johnson, and J.A. Smith. 1987. *Selection of Chemical Constituents and Estimation of Inventories for Environmental Analysis of Savannah River Plant Waste Sites*. Environmental Information Document. DPST-86-291. Du Pont. SRS Phase II Database MOL199307146 and DWS1993092222.

Looney, B.B., T.C. Hazen, D.S. Kaback, and C.A. Eddy. 1991. *Full Scale Field Test of the In Situ Air Stripping Process at the Savannah River Integrated Demonstration Test Site*. WSRC-RD-91-22. Westinghouse Savannah River Company. SRS Phase II Database MOL199401113. June 29.

Lorenz, R. 1998. Environmental Protection Department. Personal Communication with Pat McGavran, Consultant to *Radiological Assessments Corporation*. Subject: M-Area Operations. SRS Phase II Database Interview 12.

Lower, M.W. 1983. Memo to T.V. Crawford. Subject: SRL Seepage Basins: History and Regulatory Implications of Closure. DPST-83-836. SRS Phase II Database TFW199310079. September 1.

Martens, R.I., R.M. Girdler, and E.T. Cook, Jr. 1959. Memo to L.C. Perry. Subject: Weekly Progress Letter-Separations Technology. October 10–16, 1959. DPSP-59-70-42. SRS Phase II Database KRM1994041164. October 22.

Mauderly, J.L. 1995. "Diesel Exhaust." In *Environmental Toxicants.* Edited by M. Lippman. New York: Van Nostrand Rienhold. OpenLit.

McGavran, P.D., K.R. Meyer, P.G. Voillequé, M. Dreicer, and J.E. Till. 1996. *An Analysis of Historical Source Term Estimates for Carbon Tetrachloride from the Rocky Flats Plant*. *Radiological Assessments Corporation*. CDPHE-RFP-1996. March. OpenLit.

McKibben, J.M. 1976. *Explosion and Fire in the Uranium Trioxide Production Facilities at the Savannah River Plant on February 12, 1975*. DPSPU-76-11-1. Du Pont. SRS Phase II Database LWB1994021820. October.

Merz, G.F. 1982. Du Pont. Memo to R.S. Swingle. Subject: M-Area Effluent and Groundwater Cleanup. Du Pont RMM-32. SRS Phase II Database MJC1993101946. March 5.

Mikol, S.C., L.T. Burckhalter, J.L. Todd, and D.K. Martin. 1988. *Savannah River Plant Environmental Report, Annual Report for 1987. Volume I, Text.* DPSPU-88-30-1. Health Protection Department, Savannah River Plant. SRS Phase II Database EIW199310211.

Monier, J.A. Jr. 1970. Memo. Subject: Chemical Waste Discharges—300 Area.. SRS Phase II Database TFW1994061041.

Monier, J.A. and W.P. Bebbington. 1970. Memo to J.D. Ellett. Subject. Disposal of Miscellaneous Nonradioactive Wastes at the SRP. SRS Phase II Database HAG199409025. August 10.

NIOSH (National Institute of Occupational Safety and Health). 1994. *Pocket Guide to Chemical Hazards.* Cincinnati, Ohio. OpenLit.

Orebaugh, E.G. and W.H. Hale, Jr. 1976. *Dispersion Study of Buried Elemental Mercury*. DP-1401. Du Pont. SRS Phase II Database PDM199611087.

Pelfrey, J.R. 1987. *Technical Manual: Target Slug Fabrication (Building 313-M)*. DPST-M-313. Du Pont. SRS Phase II Database PDM199506131. April.

Pickett, C.F., Campbell, T.G. and W.E Harris. 1989. *Mercury Requirement for Separations Area Processes.* Letter to J. S. Evans. OPS-STH-890145. Westinghouse. SRS Phase II Database HJM2001031502. November.

Pickett, C.F. 1996. H-Area Engineer. Personal Communication with Pat McGavran, Consultant to *Radiological Assessments Corporation*. Subject: H-Area Operations. SRS Phase II Database Interview 17.

Pickett, C.F. 1997. *221-H* Processing *History* 1966–1989. SRS Phase II Database HRM199704161.

Pickett, J.B., W.P. Colven, and H.W. Bledsoe. 1987. *M-Area Settling Basin and Vicinity*. Environmental Information Document. DPST-85-703. Du Pont. SRS Phase II Database GKH199403117. March.

Pickett, J.B. 1990. Memo to W.L. McDowell. Subject: Heavy Metal Contamination in Tims Branch Sediments. OPS-RMT-90-XXXX. Westinghouse. SRS Phase II Database PDM199610032. June 25.

Radian (Radian Corporation). 1992a. *SRS M-Area Air Emission Inventory Calculations Procedures Notebook.* Prepared for Westinghouse. SRS Phase II Database PDM199710013. November.

Radian. 1992b. *Savannah River Site K-Area Air Emission Inventory Calculation Procedures Notebook.* Prepared for Westinghouse. SRS Phase II Database PDM199710012. November 13.

Radian. 1993. *SRS H-Area Air Emission Inventory Calculations Procedures Notebook.* Prepared for Westinghouse. SRS Phase II Database PDM199611071. March 22.

Reinig, W.C., H.E. Hoy, W.T. Jacobsen, H.A. McClearen, and I.S. St. John. 1973. *Survey of Effluent and Environmental Monitoring at the Savannah River Plant.* DPST-73-293. SRS Phase II Database MJC199312148. June.

Reinig, W.C. 1989. Letter to S.R. Wright. *Action Plan for the Resolution of Findings in the DOE-HQ Environmnetal Survey of SRS*. ESH-EPB-890039. Westinghouse. SRS Phase II Database HJM2001031503. August.

Rodgurs**,** J.H., D.S. Cherry, and R.K. Guthrie. 1978. "Cycling of Elements In Duckweed In an Ash Settling Basin and Swamp Drainage System." *Water Research* 12: 765–770. SRS Phase II Database PDM199702245.

Rusche, B.C. 1973. *Compilation of Environmental Activities and Programs at the Savannah River Plant*. DPST-73-318. SRS Phase II Database MJC199312149. May 2.

Schmitz. 1989. *Tritium Facilities Mercury Inventory*. OPS-TPD-890413. OpenLit.

Sheldon E.B. 1996. Retired engineer from the Separations Areas. Communication with P. McGavran. Consultant to *Radiological Assessments Corporation*. Subject: Chemical Releases from Separations Areas. October 1996. SRS Phase II Database Interview 21.

Smith, S. 1996. Power Department, Savannah River Site. Personal communication with P.D. McGavran, Consultant to *Radiological Assessments Corporation*. Subject: Powerhouse History and Operations. SRS Phase II Database Interview 25.

Smithwick, G.A. 1984. *Information on Department of Energy Mixed Wastes, Mixed Hazardous Waste Stream Generated at the SRP*. DOE-03330. SRS Phase II Database SVK1994091423. August 23.

Specht, W.L. 1991. Transcript of a Presentation: "Tims Branch Heavy Metal Inventory and Hazard Evaluation of Sediments." Savannah River Laboratory. Environmental Sciences Section. SRS Phase II Database PDM199610031.

Specht, W.L., J.B. Pickett, C.F. Muska, W.M. Starkel, M. Griffin, K.E. Trapp, and A.E. Hadden. 1987. *Biological and Chemical Assessment of M-Area Process Discharge to Tims Branch June 1985–December 1986*. DPSP-87-1115. SRS Phase II Database SKR199310011. August.

Thompson, G.H and W.H. Hale. 1972. *Safety Analyses of the Iodine Test Facility for Building 221-H*. DPST-72-549. SRS Phase II Database HAG1993060211.

Villa, E. 1997. F-Area Engineer. Personal Communication with Pat McGavran, Consultant to *Radiological Assessments Corporation*. Subject: F-Area Operations and Stack releases. SRS Phase II Database Interview 28.

Westinghouse. (Westinghouse Savannah River Company). 1983. *Essential Materials Transaction Report.* 12/82–12/83. Raw Materials Department. SRS Phase II Database PDM199609301.

Westinghouse. 1984. *Essential Materials Transaction Report.* 1/84–12/84. Raw Materials Department. SRS Phase II Database PDM199609302.

Westinghouse. 1985. *Essential Materials Transaction Report.* 1/85–12/85. Raw Materials Department. SRS Phase II Database PDM199609303.

Westinghouse. 1986a. *Essential Materials Transaction Report.* 1/86–11/86. Raw Materials Department. SRS Phase II Database PDM199609304.

Westinghouse 1986b. *300-Area Essential Materials Control Ledger*. 12/84–11/86. SRS Phase II Database PDM199609308.

Westinghouse. 1987a. *Essential Materials Transaction Report.* 1/87–4/87. Raw Materials Department. SRS Phase II Database PDM199609305.

Westinghouse. 1987b. Essential Material Control Sheets from 200-Areas from 1/86 to 12/87. SRS Phase II Database PDM199610011.

Westinghouse. 1989. *300-Area Essential Materials Control Ledger*. 6/75–2/89. SRS Phase II Database PDM199609307.

Westinghouse. 1992. *RCRA Facility Investigation CERCLA Remedial Investigation Workplan* Summaries. WSRC-IM-92-117. SRS Phase II Database MOL199307144. October.

Westinghouse. 1993a. *SRS Standard 8 Modeling Report.* ESH-ESS-93-0531. SRS Phase II Database PDM199609173. September 29.

Westinghouse. 1993b. Separations Waste Sludge Spreadsheet. WSRC-TR-93-135, Rev. 1. SRS Phase II Database HRM199704163. July 28.

Westinghouse. 1996a. *Part 70 Operating Permit Application. Submitted to the South Carolina Department of Health and Environmental Control, Bureau of Air Quality. Volumes I-XIX*. SRS Phase II Database PDM199710023.

Westinghouse. 1996b. Toxic Release Inventory (TRI) Summary Table, 1987–1995. SRS Phase II Database PDM199609172.

Westinghouse 1996c. *Part 70 Permit Application (U) SRS Volume X, Book 1 of 5. 1985–1995. Emissions Unit Narrative for H-Canyon.* SRS Phase II Database PDM199611072.

Westinghouse. 1997a. *Savannah River Site Best Management Practices Plan.* WSRC-IM-90-49, Revision 3. SRS Phase II Database PDM199710024. April.

Westinghouse. 1997b. *Spill Prevention Control and Countermeasures Plan*. WSRC-IM-90-48. SRS Phase II Database PDM199710026.

Westinghouse. 1997c. *SRS Title V Part 70 Operating Permit Application Amendment Number 3.* ESH-97-0370. SRS Phase II Database PDM199710027.

Willis, H.S. 1997. Power Department, Savannah River Site. Communication with P.D. McGavran, Consultant to *Radiological Assessments Corporation*. Subject: SRS Power Plants. SRS Phase II Database Interview 29.

Weiner, J.G. 1979. "Aerial Inputs of Cadmium, Copper, Lead and Manganese into a Freshwater Pond in the Vicinity of a Coal-Fired Power Plant." *Water, Air, and Soil Pollution* 12: 343–353. SRS Phase II Database HAG199506149.

Weiner J.G. and J.P. Giesey, Jr. 1979. "Concentrations of Cd, Cu, Mn, Pb, and Zn In Fishes In a Highly Organic Softwater Pond." *Journal of the Fisheries Research Board of Canada* 36: 270–279. SRS Phase II Database HAG199506147.

Wilhite, E., J. Cook, and W. McDonnell. 1989. *Low Level Radioactive Waste Disposal at the SRP*. DP-MS-88-160. SRS Phase II Database HRM199309025.

Zeigler, C.C., I.B. Lawrimore, and W.E. O'Rear. 1985. *Environmental Monitoring at the Savannah River Plant, Annual Report 1984*. DPSPU-85-302. Health Protection Department, Savannah River Plant, Du Pont. SRS Phase II Database MJC1994051722. June.

Zeigler, C.C., I.B. Lawrimore, E.M. Heath, and J.E. Till. 1986. *Savannah River Plant Environmental Report, Annual Report for 1985. Volume I, Text*. DPSPU-86-30-1. Health Protection Department, Savannah River Plant, Du Pont. SRS Phase II Database EIW1993082022.

Zeigler, C.C., E.M. Heath, L.B. Taus, J.L. Todd, and J.E. Till. 1987. *Savannah River Plant Environmental Report, Annual Report for 1986. Volume I, Text, Volume II, Figures and Data Tables*. DPSPU-87-30-1. Health Protection Department, Savannah River Plant, Du Pont. SRS Phase II Database EIW1993091417.