CHAPTER 16

RANKING AND SELECTION OF CHEMICALS OF CONCERN

ABSTRACT

This chapter describes the ranking method used to determine which chemicals were to be evaluated during Phase II of the Savannah River Site (SRS) dose reconstruction project. The method involved comparing amounts of chemicals that could have been released to the environment in a worse-case situation to those in air or water that would not be expected to cause adverse health effects. The comparison resulted in a ratio that indicated whether there was a sufficient quantity of a chemical onsite to have presented a hazard. From these ratios, we concluded that is was important to derive a source term that described how much, when, where, and in what form the following chemicals were released from the Site: arsenic, benzene, cadmium, chromium, coal and coal ash, hydrogen sulfide, hydrazine, lead, manganese, mercury, nickel, nitric acid, nitrogen dioxide, sulfur dioxide, and zinc. Chapters 17 and 18 describe the estimates of the amount of chemicals released to the air and surface water and the information used to develop them. Chapters 19 and 20 describe additional environmental and effluent monitoring information used to develop or support chemical release estimates.

PURPOSE

Thousands of chemicals have been used at the SRS over the years., We used a ranking method to determine which chemicals were important to evaluate for Phase II of the dose reconstruction study because they may have been discharged to the air or water in quantities that could have posed an offsite hazard.

We found documents and records that describe how chemicals were used, stored, purchased, and disposed of as a part of specific operations. We used essential materials lists, purchasing records, and inventories to try to determine what chemicals were onsite, when, and in what quantities. From this information, we developed a list of potential chemicals of concern and subjected the chemicals to a ranking exercise.

We determined a ratio for each chemical that compared an approximation of the amount of chemical that may have been in the environment to the concentration in water and air that was not expected to cause adverse health effects. To develop the ratios, we derived the amounts of chemicals that may have been in the environment from inventory amounts using conservative release fractions and air dispersion and water dilution factors. We used the term toxic levels of concern or toxicity values to refer to the threshold concentrations in water and air that were not expected to cause adverse health effects. The ratio indicates whether there was a sufficient quantity of a chemical onsite to have presented a hazard. The more toxic or carcinogenic a substance, the smaller the amount dispersed or released needed to exceed toxic levels of concern. These ratios involved several very conservative assumptions and represent a worse-case or upper-bound situation.

RANKING METHOD

Inventory Information

A list of potential chemicals of concern was compiled primarily from three sources: (1) a list of 34 essential materials in a *Survey of Effluent and Environmental Monitoring at the SRP*, from 1973 (Reinig et al. 1973), (2) the *Company Chemical Inventory (CCI) Report* compiled by Du Pont in the 1970s (Du Pont 1979), and (3) the 1994 *Chemical Information and Inventory System Database* of materials onsite (Information Systems Engineering 1994). The latter two inventories were developed to comply with U.S. Environmental Protection Agency (EPA) reporting and listing requirements and are both described in more detail in the Phase I Task 3 Report (Meyer et al. 1995) and below. In addition, we used lists of materials in safety analysis documents and other documents that described processes and operations. Materials listed in the SRS Ground Water Monitoring Program's quarterly report (Westinghouse 1994) as being found above levels of concern in groundwater were also included.

The May 1959 Monthly Progress Report from the Works Technical Department reported that in response to a request by the Atomic Energy Commission Division of Biology and Medicine, a survey of potentially hazardous materials used in bulk quantities at SRS was made. The survey was said to identify a total of 48 potentially hazardous materials on the plant. The monthly report stated that these survey results were issued as a report (Du Pont 1959). Tom Cavenaugh and the SRS Central Records staff conducted a search of the central records and the PINT database for the 1959 report during Phase I in 1994 when mention of the survey was first found in a monthly report. They were unable to find a report of the survey

Radiological Assessments Corporation (RAC) team members interviewed many former and current Site workers with knowledge of chemical usage, receipts, and records in Phases I and II. They agreed that purchasing records would not be useful and purchase order and related records would not have been retained far enough back in time to be useful. Some essential materials ledgers were found and were used to develop the list of chemicals of potential concern. Inventory amounts were all converted from pounds, tons, or grams per week or month to kilograms per year using 2000 lb ton^{-1}, 0.4536 lb kg^{-1}, 1000 g kg^{-1}, 12 mo y^{-1}, and 52 wk y^{-1} conversions.

The list of materials in the 1973 *Survey of Effluent and Environmental Monitoring at the SRP* included estimates of the amount of material used each month (Reinig et al. 1973). These estimates provided the largest amounts listed in any of the inventories found, for several materials.

Du Pont developed an index of chemicals at the SRS, called the *CCI Report* (Du Pont 1979), in the mid-1970s to comply with the Toxic Substances Control Act. The index was a list of about 400 chemicals that were present onsite. A printout of the index can be found in Appendix A of the Task 3 Report for Phase I (Meyer et al. 1995). The inventory cataloged each chemical by name; registration number; jurisdiction values (whether the material is in a published inventory, reportable, user exempt, etc.); quantity; and date the material was added and/or deleted from the inventory. Most of the chemicals were identified as a chemical synthesized at the Site, imported onsite, a process chemical, a support substance that does not end up in the commercial product, an intermediate chemical, a laboratory chemical, a nonwaste impurity, a waste by-product, or a research chemical. Quantities were given by letter designations corresponding to ranges of less than 454 kg; 454 to 4540 kg; 4540 to 45,400 kg; 45,400 to 454,000 kg; 454,000 to 4.54 million kg; 4.54 to 22.7 million kg; 22.7 to 45.4 million kg; 45.4 to 227 million kg; 227 to 454 million kg; over 454 million kg; and quantity not reported or reported under another synonym. For the ranking, the upper bound of the corresponding range was used as the inventory amounts for materials. ‘Quantity not reported’ was the most common entry. The Du Pont inventory contained quantity entries for only 65 chemicals, which accounted for about 15% of the chemicals listed. Of these, seven chemicals (copper, dioctyl phthalate, gadolinium nitrate, lead, mercury, nickel and nickel sulfate, and uranium) were listed as being present in quantities less than the quantities reported in the Chemical Information and Inventory System (CIIS) database. Amounts for five chemicals (cadmium, ceric ammonium nitrate, ferrous sulfamate, phosphoric acid, and potassium permanganate) in the Du Pont inventory were consistent with the CIIS database. Quantities of nine chemicals (hydrazine, hydrofluoric acid, hydrogen sulfide, hydroxylamine nitrate, hydroxylamine sulfate, manganese nitrate, napthalene, oxalic acid, and sodium hydroxide) were listed in the Du Pont database with quantities greater than CIIS database amounts. The 44 chemicals presented below were listed with quantities in the Du Pont database, but they were not included on the list to be ranked because, for various reasons, they are very unlikely to present an offsite hazard.

Acetylene
Aluminum
Aluminum nitrate
Aluminum sulfate
Ammonium sulfamate
Aquadag
Ascorbic acid
Calcium
Calcium fluoride
Several paints, thinners and primers
Calgon
Carbon
Calcium oxide
Dodecane
Ethylene glycol
Formic acid
Gelatin
Glucose
Helium
Iron
Methane
Nitrogen
Oxygen
Polyethyleneimine
Propane
Sodium aluminum silicate
Sodium carbonate
Sodium hypochloride
Sodium nitrate
Sodium nitrite
Sodium salicylate
Sodium sulfite
Steel
Sucrose
Urea

The CIIS database, maintained by Westinghouse SRS, is a comprehensive listing of all hazardous materials used or stored in the workplace. The database was designed to fulfill the requirements of Worker-Right-To-Know legislation and to help organize inventory data for EPA reporting requirements. It is an ORACLE relational database that runs on the VAX computer. Information in the database is derived from material safety data sheets (MSDSs) that are also stored in hard copy form in notebooks. The database is designed to be updated each year and to provide information for annual reports. The SRS CIIS database is not historical but contains materials currently inventoried onsite. It does not provide specific information on toxicity, use, monitoring information, or time periods of use.

Two products were sought from the CIIS. Cheryl Hardy and John Harris, Westinghouse SRS Environmental Protection Department personnel, selectively extracted this information from the database. One product was a list of all of the chemicals in the database with a Chemical Abstract Service (CAS) number. The material name, CAS number, average amount, and number of hits (number of times the material is reported onsite) were printed for 1994. A list of about 4000 chemicals resulted. This list is printed in Phase I Task 3 report (Meyer et. al. 1995). The CIIS list appeared to be the most complete listing of chemicals. It seemed prudent to start with a comprehensive list and eliminate materials not of concern for dose reconstruction. Although some of the chemicals used onsite at one time may not have been stored onsite in 1994, many chemicals used historically were included in this large database. The second product was the result of several data extractions. The resulting database of chemicals was transferred to *Radiological Assessments Corporation* (*RAC)* on disk, converted to a FoxPro format, and incorporated into the *RAC* SRSCHEM database developed for Phase I. This database included information on the chemical name, manufacturer synonyms, symbols, quantities reported, and uses onsite.

The following fields were entered into FoxPro for about 30,000 records:

MSDS number
CAS number
Material name
Manufacturer
Form (liquid, gas, solid, or mixture)
Maximum amount (onsite in 1994)
Average amount (onsite in 1994)
Synonyms
Formula
EPA storage code

A	Above ground tank	H	Silo
B	Below ground tank	I	Fiberdrum
C	Tank in a building	J	Bag
D	Steel drum	K	Box
E	Plastic or nonmetallic drum	L	Cylinder
F	Can	M	Glass bottle
G	Carboy	N	Plastic bottle

Usage code

1	Import
2	Byproduct
3	Impurity
4	Reactant
5	Repackaged
6	Laboratory
7	Manufacturing aid
8	Processing aid
9	Other use.

The department, area, building, and room where the chemical was currently used or stored could have been extracted from the CIIS. However, because many of the release point locations were classified and the ‘area’ provided sufficient information about the location of the release, this information was not included to expedite the security review.

Several subsequent extractions of this database were conducted. One extraction targeted all chemicals on EPA lists and other lists including, Superfund Amendments and Reauthorization Act (SARA) Title III; Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); Resource Conservation and Recovery Act (RCRA), Toxic Substances Control Act (TSCA); and a list of reproductive hazards. The extractions excluded chemicals with no hazard rating (no acute toxicity, chronic toxicity, flammability or reproductive hazard). We made a second extraction of all chemicals in quantities greater than 50 lb. This, we felt, captured all of the chemicals that might be of concern based on toxicity and quantity. We then conducted a line-by-line review of the database to delete materials that were unlikely to present an offsite hazard, such as concrete, plastic materials, and solid building materials. Records that involved the following materials and/or synonyms for them were deleted:

Joy dishwashing
Glass cleaner
Glue
Paint
Welding rod
Toner
Saddle Soap
Mounting solutions
Weatherstrip
Adhesives
Resins
Cements
Lubricants
Insect repellents
Small volume cleaners
Steel
Cast iron
Deodorizers
Inert solids
Salts
Markers
Copier
Analytical standard
Correction fluid
Battery
Air freshener
Ink
GC column packing
Cutting oils
Polyurethane
Welding wire
Sealants
Oil absorbants
Spill absorbents
Abrasives
Pump oils
Art supplies
Acetylsalicylic acid
Sand and aggregate
Insulation
Crayons
Typewriter
Deep Woods Off
Ajax
Comet
Carpet
Crayons, pens
Mortar
Enamels
Shellacs
Salt solutions
Buffer solutions
Gaskets
Office supplies
Laboratory supplies
Grease
Tape
Solder and flux
Scintillation fluids
Lotions

We then reviewed the list of deleted items line-by-line and added back in items that could not be identified by name (for example ‘fuel additive number 13,’ or ‘accelerator SFA342’). A total of 168 materials were listed in the database by trade name and with insufficient manufacturer or synonym information to allow identification. A list of these was sent to Dick Reynolds, Manager of the Chemical Commodity Group at SRS, for further identification. The task of looking at these materials was assigned to Mark Lloyd, who provided synonym, carcinogenicity, or reproductive hazard (yes or no) information and the hazardous constituents of each material if known. Based on this information, trade name materials were deleted, retained as discrete materials, or combined with and listed under their most hazardous component.

The following groups of materials were removed from the list of chemicals of potential concern. The following materials contain noncarcinogenic components and relatively nontoxic components or ingredients:

Mod U Formula
CP 220 ChilWet
Cronwear Eagle
Apiezon Q Compound
Inhibitor 526C
Magicfloc 985N
Sediperse All
Polysperse Plus
Bycothane 300
Durapox Primer
Industrial Grade PVC solvent
Crimstar 30
Solucom Clear
Electrostatic solution
Mojave
Snapback
Corrosion Inhibitor GC Formula
Drewguard 315
Monosodium titinate slurry
Formed Molecular Sieve
CI Mastic
Paraffin Wax

The following are relatively nontoxic and are used as food additives, medicines, anesthetics:

Sodium nitrate
Potassium nitrate
Propylene glycol
Sodium sulfite
Hexane
Trisodium phosphate
Sodium phosphate
Ascorbic acid
Sodium nitrite
Polyethylene glycols
Phospholene
Fumaric acid
Boric acid
Sodium sulfite
Nitrous oxide

The following materials are used in office equipment, primarily copiers. Some of these materials contain usually less than 1% of formaldehyde, which is a carcinogen:

Cronar reducer
Cronolith liquid blender
Itek activator

The following materials contain components that are not chronic hazards, have relatively low acute toxicity, and are not carcinogenic:

Doubleteam
Alconox cleaner (sulfonate)
Cryosan (bleach)
Chloroethane
Calcium
Barium
Graphite
Paraffin
Chloride
Phosphate
Silver
Calcium hydroxide
DPD free Cl reagent (disodium phosphate)
Synthetic sludge
Exotherm (calcium chloride)
Sulfamic acid
Biphenyl
Cerium
Hydrogen peroxide
Oils and lubricants
Aluminum
Iron
Selenium
Silver nitrate
Butyl stearate

The following materials contain components that are not carcinogenic but are sensitizers or irritants:

Rynothane activator (diisocyanate)
Fortify (acrylic polymers 11–25%)
HitCZO Part A (diglycidyl resorcinal ether)
R process gum (<1% formaldehyde)
diethyl hexyl phosphoric acid
Duraskid
Phosphates
Lanthanum
Terphenyls
Polyethyleneamine
LTC accelerator
ChemTreat
Concresive liquid hardener (polyaminoamide)
Virchem 931 hardener
Scotchcast (vinylcyclohexanedioxide)
Diphenyl methane diisocyante
Cloro-m-cresol
Epon
Neodynium oxide
Polyphosphates
Erbium oxide
Saframine
CreteLease

The database contained many paints, paint thinners, and epoxies that may be hazardous in a liquid form but once dried would not be expected to pose an offsite hazard. These materials may have been stored in large amounts, but they were likely to have been used in relatively small amounts. Although resins and enamels may contain toxic components, they are generally used for coating and painting structures and equipment and would be found in a polymerized state or stored as active ingredients, separated in small quantities. Epoxy components known to be potent sensitizers in occupational settings were listed above as sensitizers.

In another data extraction, substances with maximum annual inventory amounts of less than 0.25 lb were deleted. This extraction eliminated the thousands of hazardous materials that were used in very small volumes, such as laboratory reagents, analytical standards, or samples. These materials would have been present and used in such small amounts that they would not pose an offsite hazard. The cut off of 0.25 lb was chosen from the results of an assessment of a hypothetical release of TCDD, the most potent carcinogen and developmental toxin ever evaluated by the EPA. The proposed cancer potency factor for TCDD yields a daily intake level corresponding to a 10^{-6} cancer risk level of 0.01 picograms per kilogram per day (pg/kg/day). In this assessment, we attempted to back calculate an amount that if released over a very short time, would be low enough not to be harmful. If 100 g (0.22 lb) of a chemical was released at one time and a conservative dispersion factor (χ/Q) of 10^{-5} sec m^{-3} was used, the resulting exposure would correspond to a maximum daily intake of about of 0.00065 pg/kg/day. This value is about 15 times less than the daily intake level for a 10^{-6} cancer risk. This justifies 0.25 lb as a very conservative cut off amount. For similar exercises, others have chosen 1 or 0.5 lb, which are also justifiable limits. Using 0.25 lb seemed to accomplish our goal of eliminating most of the chemicals used in very small amounts.

Again, the list of deleted materials was reviewed line-by-line and exceptionally potent carcinogens (such as some of the polyaromatic hydrocarbons and pesticides that were listed with inventory amounts of less than zero but were likely to have been used onsite in the past) were added back to the list. Many of the materials remaining on the list with inventory amounts of less than 0.25 lb were not derived from the CIIS database. They were taken from essential material lists or the list of groundwater contaminants of concern, so they were not eliminated as a result of this data extraction.

Inventory amounts were not available for all materials. Many materials in the CIIS database had a zero inventory amount. The staff at Westinghouse SRS who maintained the database in 1994 believed that the zero amounts on our ranking list were a result of less than 0.001 lb being reported and rounded to zero. Benzo(a)anthracene, benzo(a)pyrene, benzofluoranthene, benzoperylene, and chrysene were listed in the database with inventory quantities of zero or less than 0.001. These were probably used as analytical standards and were evaluated using a quantity of 0.001.

Gasoline and diesel fuels were added back to the list and were included in the ranking because they may have leaked from tanks into soil and groundwater. A large amount of developer was currently and has been historically used at the Site. Photographic developer was used in the Site’s photo labs to develop photos and x-rays of welds. Developer and toner were also used in all of the copy machines and in other equipment onsite and it may have been ordered in large quantities by some departments. It is unlikely that developer would have caused an offsite hazard, and entries totaling approximately 11,043 lb were deleted from the list. We also deleted many materials that contain small amounts of carcinogens or are carcinogens but were used in small quantities onsite. For example, we deleted Joy dishwashing liquid (which contains ethanol), upholstery cleaners containing chlorinated solvents, nickel-containing lubricants, roofing tars, chromium-containing corrosion preventatives used in small amounts (less than 2 lb), and formaldehyde-containing solutions used in small quantities. We also deleted EDTA and similar chelators from the list.

Although they present little or no chronic health hazard, several caustics (such as nitric acid, sulfuric acid, sodium hydroxide, and hydrochloric acid) were used and stored in very large quantities; therefore, we retained them on the list for the ranking. Other materials that generally present no chronic health hazard unless large amounts are ingested or they were used in quantities or ways that releases or transport offsite seems unlikely include waxes, Freons, antifreezes, diatomaceous earth, carbon monoxide, calcium carbonate, carbon, propane, and other inert and asphixiant gases. Fly ash, a large volume of which exists onsite, may have been stored outdoors and may have been subject to atmospheric dispersion or runoff into water; therefore, it was retained on the list. Because polyaromatic hydrocarbons and toxic metals may have been leached or contained in rainwater runoff from coal piles, coal inventories were also retained.

Although we used the initial data extractions for the CIIS from Phase I and the FoxPro database derived from the CIIS database was the starting point for the ranking, subsequent treatment of the list of chemicals differed. Therefore, the list of potential chemicals of concern in the Phase I Task 3 report (Meyer et al. 1995) is not the same as the list developed, with more care, in this phase of the study.

Toxicity Values

Toxicity values were obtained or derived from the EPA's 1995 HEAST Tables; 1995 National Ambient Air Quality Standards (NAAQS) in the Code of Federal Regulations, Part 50; the 1995 Integrated Risk and Information Systems (IRIS) Database; the Agency for Toxic Substances and Disease Registry's (ATSDR) Toxicity Profiles; and Workplace standards published by the American Conference of Governmental Industrial Hygienists (ACGIH) in 1994 and by the Occupational Safety and Health Administration (OSHA) or National Institute of Occupational Safety and Health (NIOSH) in 1994. The documents and databases used are listed in the references for this chapter. The toxicity values are listed in Appendix C3, Tables C3-1 and C3-2. We used the shaded values to calculate the ranking ratios.

The tables include a qualitative developmental effects designation (D) and reproductive effects designation (R). The number of Ds and Rs corresponds to potency or certainty of the information available. A chemical with a DDD or RRR designation is more potent or more positive human data were available for the chemical than for chemicals with a DD, RR, D, or R designations. The designations were determined from information obtained from a search of the Reprotext® Database, information found in ATSDR Toxicity Profiles, and data reported on developmental and reproductive hazards in the workplace in ACGIH (1994), NIOSH (1994), or Lewis (1993).

A carcinogenicity designation was listed for all of the chemicals that might be carcinogenic. In an effort to provide consistency, published EPA designations were used when available, followed by International Agency for Research on Cancer (IARC) designations, ACGIH categories, and any new information from the National Toxicology Program (NTP).

The EPA has evaluated many of the chemicals in Tables C3-1 and C3-2 for carcinogenicity and has assigned the chemical a designation based on the weight of evidence. There are five designations or groups:

Group A- Known human carcinogen. There is sufficient evidence from human epidemiological studies to support a causal association between the substance and cancer.

Group B - Probable human carcinogen. There is limited evidence of human carcinogenicity based on epidemiological studies but sufficient evidence of carcinogenicity based on animal studies.

Subgroups

B1 - Limited epidemiological but sufficient animal data

B2 - With sufficient animal data but inadequate or no data from human epidemiological studies.

Group C - Possible human carcinogen. There is limited evidence in animals and no human data.
Group D - Not classifiable, inadequate data or no data.
Group E - No evidence for carcinogenicity. Negative test results, usually in at least two animal species, or adequate negative epidemiological data.

Many of these chemicals have not been evaluated by the EPA and are classified as Group D because their carcinogenicity has not been adequately determined or are currently under evaluation. Some of the chemicals have not been tested for carcinogenicity.

The IARC has a similar ranking scheme. The scheme defines *sufficient evidence* as when a causal relationship has been demonstrated in humans; *limited evidence* as when there is causal relationship but chance, bias, or confounding factors cannot be discounted; *inadequate evidence* as when available studies cannot determine the carcinogenicity; and *evidence suggesting a lack of* when there are adequate studies that are negative. IARC groups chemicals into four groups:

Group 1 - Compounds are carcinogenic to humans.
Group 2 - Compounds cause cancer in animals.
  Subgroups
  2A - Probable carcinogen in humans. There is limited evidence of carcinogenicity in humans but sufficient evidence in animals and causal relationship is clear in multiple species or strains in independent experiments.
  2B - Possible carcinogens in humans. There is insufficient evidence in humans or animals.
Group 3 - Compounds are not classifiable. There is inadequate evidence and neither the presence nor absence of a carcinogenic effect can be demonstrated.
Group 4 - Compounds are probably not carcinogenic. There are adequate studies involving at least two species to suggest that the substance is not carcinogenic.

The ACGIH also has carcinogenicity designations for chemicals used in the workplace:

A1 - Confirmed human carcinogen
A2 - Suspected human carcinogen
A3 - Animal carcinogen
A4 - Not classifiable as a human carcinogen
A5 - Not suspected as a human carcinogen.

We also consulted reports published by the NTP of cancer bioassays that report ‘clear’ evidence, some evidence, equivocal evidence, no evidence, and inadequate evidence of carcinogenicity. If available, an EPA designation was listed. If an EPA designation was not available or was Group D, the IARC or ACGIH designation was entered. We listed several chemicals that are not yet designated by the EPA, IARC, ACGIH, or examined by the NTP but are mutagens or structurally resemble other carcinogens with the carcinogens in Table C3-2.

For noncarcinogens, we used a reference dose (RfD) for ingestion or a reference concentration (RfC) for inhalation. The RfC or RfD is defined by the EPA as a provisional estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a portion of a lifetime in the case of subchronic RfD or RfC or during a lifetime in the case of a chronic RfD or RfC (EPA 1995). When available, we used chronic RfCs in units of milligrams per cubic meter air for continuous exposure and chronic RfD values in units of milligrams per kilogram per day. The oral RfD was converted into a corresponding water concentration in milligrams per liter by the equation:

$$\text{mg / L in water} = \frac{\text{oral RfD in mg / kg / day} \times \text{70 kg}}{\text{2 L / day}} \tag{16-1}$$

which assumes a average human body weight of 70 kg and average water consumption of 2 L day^{-1}. The RfC, in milligrams per cubic meter or micrograms per cubic meter, corresponds to an ambient air concentration for continuous, 24 hr day^{-1} exposure.

For carcinogens, cancer potency factors, called slope factors, have been determined by the EPA for many environmental carcinogens. The slope factor is an upper-bound estimate. It is estimated using mathematical extrapolation models, most commonly the linearized multistage model that estimates the largest possible linear slope, within the 95% confidence limit. The EPA believes true cancer risk to humans is not likely to exceed this upper limit and is likely to be lower. The slope factor is expressed as risk per unit dose in units of risk per milligram/kilogram/day (EPA 1995).

Another useful value is the unit risk value, which is the risk per unit concentration. The unit risk for inhalation is the risk per concentration unit in air expressed as risk per micrograms per cubic meter. The unit risk for oral exposure is the risk per concentration unit in water expressed as risk per micrograms per liter. The unit risk is calculated by dividing the slope factor by the body weight of 70 kg and multiplying by an average breathing rate of 20 m^3 day^{-1} for air or 2 L day^{-1} average consumption for water (EPA 1995).

The risk-specific air or water concentrations can be estimated using the unit risk value at a given risk level. We choose to use a risk level of 1 in 100,000 or 10^{-5}. The concentration in air in micrograms per cubic meter corresponding to

$$\text{a lifetime cancer risk of } 10^{-5} = \frac{10^{-5}}{\text{unit risk per } \mu\text{g / m}^3} \ . \tag{16-2}$$

Risk-specific concentrations in drinking water can be estimated from the oral slope factor. The water concentration corresponding to an upper-bound increased lifetime cancer risk of 1 × 10^{-5} is calculated as

$$\text{the risk per mg/L in water} = \frac{10^{-5} \times 70\text{ kg}}{\text{slope factor (mg/kg/day)} \times \text{ 2 L/day}} \ . \tag{16-3}$$

These values are published in units of micrograms per cubic meter, milligrams per cubic meter, micrograms per liter, and milligrams per liter. There are 10^6 µg g^{-1}, 10^9 µg kg^{-1}, 10^3 mg g^{-1}, 10^6 mg kg^{-1}, and 10^3 µg mg^{-1}. Appropriate conversion factors were applied so that concentrations corresponding to a 10^{-5} risk level, drinking water standards, workplace standards, and other toxicity values could be compared in Tables C3-1 and C3-2.

The NAAQS are primary standards designed to protect public health. Six have been established to date. The NAAQS include an extensive database that has been rigorously reviewed. The primary NAAQS and the inhalation RfC have essentially the same function, and the EPA has stated that, except for lead, the NAAQS with annual averaging times can be used instead of the RfC.

The time weighted average (TWA) threshold limit value (TLV) established by the ACGIH or the permissible exposure limit (PEL) established by OSHA (in milligrams per cubic meter or fiber per cubic centimeter) were used when EPA toxicity values were not available. Because the TLVs are designed to protect healthy workers, these were divided by 10 to help account for the fact that some members of the general public (especially young children, elderly people, or people with preexisting health conditions) are more sensitive to the toxic effects of chemicals.

Drinking water standards (specifically the EPA maximum contaminant levels [MCLs]) were used if the RfD, oral slope factor or drinking water unit risk value was not available. We preferred to use the toxicity values in the order presented in Tables 16-1 and 16-2.

Table 16-1. Order of Preference for Carcinogens

Air	Water
10^{-5} unit risk	10^{-5} unit risk
RfC	RfD converted to a water concentration
NAAQS	MCL
TLV ÷ 10 or PEL ÷ 10	

Table 16-2. Order of Preference for Noncarcinogens

Air	Water
RfC	RfD converted to water concentration
NAAQS	MCL
TLV ÷ 10 or PEL ÷ 10	

Because they are more relevant to environmental contaminants, we first chose to use the EPA’s RfD or concentration, followed by unit risk values, NAAQS values, MCLs, then TLVs. In general, the concentrations corresponding to a risk level of 10^{-5} are the lowest concentrations of concern. However, in a case where the MCL, TLV/10, RfD, or RfC was lower, we used the lower, more stringent level to calculate the ranking ratios.

In some cases, a single toxicity value and combined inventory quantity was given to a group or class of compounds that contain a common element or component. Although different valence states of metals may vary tremendously in their toxicity, for the purposes of screening, the toxicity value we used was based on the toxicity or carcinogenicity of the most toxic or elemental form depending on the data available. For some materials, like manganese, sodium, and potassium compounds, more toxicity information is available on specific compounds, so we used it. We combined compounds of arsenic, cadmium, chromium, mercury, nickel, and tin for screening. For example, the chromium compounds include chromium metal; chromium oxide;

dichromic acid; lead chromate; potassium chromate; potassium dichromate; sodium chromate; sodium dichromate; chromium azo dye; chromic acids and salts (acetate, chloride, nitrates, sulfates); and ^{51}Cr. We used the toxicity values for carcinogen hexavalent chromium.

If both the anion and the cation of a compound are responsible for the toxicity, then we considered both. For example, zinc cyanide was included in both the zinc and cyanide inventory amounts, and we included both compounds in the ranking. Some metal salts (like mercuric nitrate) were used in large quantities, so we considered this compound separately from elemental mercury.

Many radionuclides, such as ^{51}Cr, are hazardous because of their radioactivity and chemical toxicity. Uranium, for example, is toxic to the kidney. Although uranium will be evaluated with the radionuclides of concern, for the purposes of this ranking we treated uranium as a toxic metal and assessed it using the RfD for kidney toxicity.

Isomers of tetrachloroethane, dichlorobenzene, dichloroethane, dichloroethylene, dimethylphenol, dinitrotoluene, dichlorophenol, chlorophenol, nitrophenol, trichlorobenzene, trichloroethane, tetrachloroethane, and trichlorophenol were summed, and we used the toxicity value for the most toxic or carcinogenic isomer. All of the inventories for various arochlors and polychlorinated biphenyls (PCBs) were summed and the toxicity values for arochlor 1260 were used for the PCBs.

We included chemicals used at the Naval Fuel Facility in the ranking. The names of these materials are classified; however, the materials of concern were not unique to the Naval Fuels Facility and were already included on one or more of the Site inventories.

Ranking Ratio Calculation

Using inventory amounts and toxicity values described above, we calculated ranking ratios for 170 chemicals in Tables C3-1 and C3-2. Initially, we did not calculate ranking ratios for 12 chemicals, primarily pesticides, for which there was no inventory amount or for which there was an inventory amount that seemed far too small. An effort was made in April 1996 to actively solicit information on inventory amounts from former and current Site employees who might have knowledge of chemical usage, purchase, storage, disposal, or other relevant operations onsite. A letter was sent to 118 individuals by post or electronic mail, and 18 individuals responded. Several respondents agreed that some of the pesticides listed may have been used onsite in the 1960s and 1970s; however, we did not obtain new or different inventories for any of the chemicals.

No published toxicity values could be obtained for 11 chemicals. We looked at the MSDSs for these chemicals in the SRS files and sought toxicity testing data and structure activity information for these compounds to determine air and water concentrations of potential concern. Because better toxicity values have not been determined, we used LD50 divided by 100,000 (Layton et al. 1987) as a toxicity value.

Some chemicals (for example, dichlorodifluoromethane and sulfur oxides) are only a concern if released to the air and inhaled. We did not calculated ratios for water for these types of chemicals. We did not calculate air ratios for chemicals, such as dichlorobenzidine and chlorophenol, because toxicity values have only been determined for consumption of water.

We calculated the ranking ratio for materials released to air using the following equation:

$$\text{air ratio} = \frac{Q_a\,(\text{kg}/\text{s}) \times \chi/Q\,(\text{s}/\text{m}^3) \times 10^9\,(\mu\text{g}/\text{kg})}{\text{Tox}_a\,(\mu\text{g}/\text{m}^3)} \tag{16-4}$$

where

Tox_a= air concentration that corresponds to a level of concern. The preferred toxicity values used are described on page 14.

χ/Q = atmospheric dispersion factor. The average χ/Q, based on tritium monitoring done in 1990, for onsite locations of 5.4×10^{-8} s m^{-3} (Cummins et al. 1991), was used

Q_a = the release rate

$$Q_a\,(\text{kg}/\text{s}) = \frac{I\,(\text{kg}) \times RF_a}{3.16 \times 10^7\ \text{s}/\text{year}}$$

where I = annual inventory amount in kg and Rf_a = the release fraction.

Release fractions account for the fact that some materials may be released in total (like volatile solvents or gases that are put out the stacks) and others (like solids) will not all be released. We chose to conservatively assume, for this first screening, that 100% of the inventory was used. Although more material is usually stored than is used, it is reasonable to assume that it all was used and the entire annual inventory was subject to release each year.

We assigned release fractions according to the volatility of the compound (that is, how readily it evaporates). For materials released to the air, we chose a release fraction (RF_a) of 1.0 for volatile liquids and 0.005 for nonvolatile liquids and solids. It is likely that workers would have made some effort to conserve reagents, keep lids on solvent baths, and prevent spills and leaks of volatile substances. However, for the purposes of this ranking, we assumed that all of the volatile material inventoried was eventually released to the atmosphere and we used the conservative release fraction of 1 (signifying 100% of the inventory quality was released).

The ranking ratio for materials released to water was calculated using the following equation:

$$\text{ratio}_w = \frac{Q_w\ (\text{kg/s}) \times 10^6\ \text{mg/kg}}{\text{DF}\,(\text{L/s}) \times \text{Tox}_w\ (\text{mg/L})} \tag{16-5}$$

where

Tox_w = water concentration that corresponds to a level of concern. The preferred toxicity values used are described on page 14.

DF = the dilution due to flow of the river. We assumed that the Savannah River is the surface water of concern and that it was used for drinking water (untreated). Other activities, such as fishing, boating, swimming, etc., will be considered in later phases of this work. The 1990 *SRS Environmental Report* includes a plot of the flow rate of the Savannah River for 1980–1990. The median value corresponds to a DF of 2.55×10^5 L s^{-1} (Cummins et al. 1991).

Qw = the release rate.

$$Q_w \text{ (kg / s)} = \frac{\text{I (kg)} \times \text{RF}_w}{3.16 \times 10^7 \text{ s / year}}$$

We used the release fractions (RF_W) 0.02 for volatile liquids, which would tend to evaporate out of the water, and 0.1 for nonvolatile liquids and solids.

To compare among values, we converted all of the concentrations corresponding to 10^{-5} risk levels, MCLs, TLVs, and NAAQS to units of milligrams per cubic meter or milligrams per liter in the tables. In summary,

$$\text{air ratio} = \frac{\text{I (kg)} \times \text{RF} \times 5.4 \times 10^{-8} \text{ s/m}^3 \times 10^6 \text{ mg/kg} \div \text{toxicity value mg/m}^3}{3.16 \times 10^7} . \tag{16-6}$$

If all the toxicity values are in units of milligrams, then the two ranking ratio equations can be summarized as

$$\text{ratio air} = \frac{\text{inventory amount in kg} \times \text{release fraction} \times 1.7 \times 10^{-9}}{\text{Tox}_a} \tag{16-7}$$

$$\text{ratio water} = \frac{\text{inventory amount in kg} \times \text{release fraction} \times 1.24 \times 10^{-7}}{\text{Tox}_w} . \tag{16-8}$$

Ranking Results

Tables C3-1 and C3-2 in Appendix C3 list the resulting ranking ratios for 166 chemicals. Ratios could not be determined for methyl bromide and methyl chloride (two chemicals detected in groundwater but not used onsite and for which there was no inventory) and ozone, an air pollutant produced as a byproduct for which there is no inventory. Materials with the highest ratios are listed in Tables 16-3 through 16-6.

Table 16-3. Chemicals with Ranking Ratios > 1.0

Chemical	Ranking ratio	Ratio
Coal	254	Water
Hydrazine	36.7	Air
Uranium	1.87	Water
Gasoline	1.77	Water
Hydrazine mononitrate	1.26	Air

Table 16-4. Chemicals with Ranking Ratios < 1.0 but > 0.1

Chemical	Ranking ratio	Ratio
Tetrachloroethylene	2.29×10^{-1}	Water
Hydroxylamine sulfate	1.10×10^{-1}	Water

Table 16-5. Chemicals with Ranking Ratios < 0.1 but > 0.01

Chemical	Ranking ratio	Ratio
Benzene	1.04×10^{-2}	Air
Nickel compounds	1.20×10^{-2}	Water
Mercury	1.21×10^{-2}	Water
Sulfuric acid	1.32×10^{-2}	Air
Trichloroethane	1.54×10^{-2}	Air
Chromium compounds	2.32×10^{-2}	Water
Lead compounds	3.25×10^{-2}	Water
Mercuric nitrate	3.53×10^{-2}	Water
Asbestos	9.40×10^{-2}	Air

Table 16-6. Chemicals with Ranking Ratios < 0.01 but > 0.001

Chemical	Ranking ratio	Ratio
Zinc compounds	1.03×10^{-3}	Water
Manganous nitrate	1.28×10^{-3}	Air
Copper compounds	1.35×10^{-3}	Water
Nitric acid	1.48×10^{-3}	Air
Aldrin	2.48×10^{-3}	Water
Cadmium	2.52×10^{-3}	Water
Hexanol	3.44×10^{-3}	Air
Chlorine	3.95×10^{-3}	Air
Gadolinium nitrate	4.27×10^{-3}	Air
Coal tar	4.45×10^{-3}	Water

In addition, we found no inventory amount or the inventory amount seemed far too small, for 19 chemicals:

Aldrin
Chloromethane
Endosulfan
Heptachlor
Toxaphene
Chloroethane
PCBs
Carbon tetrachloride
DDT
Endrin
Hydroxyquinoline
Trichlorophenol (2,4,5-T)
DDT
Chloroethane
Dieldrin
Chlordane
Lindane
Velpar-L
Chloromethane

Because many hazardous, persistent pesticides (like DDT) have been banned for some time, we might expect little or no inventory amounts although these materials may have been used in the past. We found little mention of these materials in the periodic reports. We compiled recent monitoring study results to see if they could help us quantify some of the pesticides of concern. Although we will could not determine an inventory amount for many of these pesticides and many could not be adequately evaluated in the ranking, it seemed inappropriate to simply dismiss these pesticides at this early stage of the ranking simply because of a lack of inventory.

Limitations of the Ranking

This approach to ranking chemicals of concern has several limitations that are important to recognize. The amount of material listed on an inventory is not necessarily related to the amount that was discharged out a stack as a result of a process. For example, nitrogen dioxide stored in tanks or cylinders onsite is in no way related to the amount of nitrogen dioxide produced by a process and discharged to the environment. A careful examination of processes and materials that may have been produced and released at certain points of an operation will be another important part of this work.

Another problem is that the CIIS database contains the inventory for 1994. The amounts onsite now may be more or less than when facilities at the plant were in full operation. We compared the amounts in the 1994 CIIS database and the Du Pont Index from the 1970s, and noted differences. We used the largest amounts (usually those in the listing from 1973 or the upper value from the range in the Du Pont database). It is unfortunate that we could not locate additional inventories from the 1950s, 1960s, and early 1970s.

One of the most significant problems with this approach is a lack of information. Information on inventory amounts and toxicity is missing for many of the materials. Often, toxicity values are available for inhalation or ingestion but not both pathways. Information on reproductive and developmental effects is not available for most of the materials. Eleven materials have no published toxicity values, so we used a very conservative and uncertain value of the lowest LD50 value reported (usually an oral LD50 in rodents or rabbits) divided by 100,000 (Layton et al. 1987). For several materials on which no toxicity testing has been done, we used values derived for similar compounds.

Second Stage of the Ranking

After the ranking ratios were calculated, it was obvious that the ratios alone could not adequately be used to prioritize chemicals of concern. The conservative assumptions used created unrealistic scenarios for many of the chemicals that had ranking ratios greater than 10^{-3}.

The next step was to further evaluate the chemicals identified in the ranking by considering environmental fate and transport characteristics, information on chemical use at the plant; and release potential. We also assessed the chemicals based on the physical and chemical properties relevant to their behavior in the environment, such as water solubility, volatility, susceptibility to biodegradation and chemical breakdown, and mobility. These properties can be very important to environmental behavior. For example, highly water-soluble compounds are generally less likely to adsorb to soils and sediments, more likely to remain in the water, more biodegradable, and less likely to volatilize from water. The octanol-water partition coefficient, K_{ow}, is a measure of the degree to which an organic material will preferentially dissolve in octanol compared to water. The greater the K_{ow}, the greater the tendency for the material to partition from water to a more organic phase.

Some chemicals, for example titanium tetrachloride, break down so rapidly that environmental exposure for people living offsite from this chemical is unlikely. Other chemicals, for example asbestos, were used in building materials and were not subject to storage in large amounts, leakage, spillage, or routine release.

Chemicals with ranking ratios greater than 10^{-3} are evaluated further in the following paragraphs.

Alcohols

Large amounts of ethanol and hexanol and smaller amounts of propanol, ethoxyethanol, and other alcohols were used for cleaning and as part of processes at the SRS. The ranking ratios for these compounds were very low. The highest ratio was for hexanol, with an air ratio of 3.4×10^{-3}. Because toxicity information on hexyl alcohol was limited, it was ranked using the very conservative LD50/100,000 value. Hexanol is a volatile skin and eye irritant that appears to cause liver toxicity and other toxic effects similar to those caused by other alcohols. The availability of documentation specific for this alcohol limited our ability to develop a source term. It is likely subject to biodegradation and has fate and transport characteristics similar to other alcohols. Emission estimates in the 1985, 1987, and 1990 Air Emissions Inventory are low, and significant offsite concentrations would not be expected. Therefore, we did not develop a source term for this chemical.

Aldrin

Aldrin is a particularly toxic chemical for which we have no reasonable SRS inventory and usage information. In general, in the U.S., it was used as an agricultural pesticide until 1970 and for termites until 1987. Aldrin and its toxic breakdown product, dieldrin, are very persistent, not soluble in water, and tend to bioaccumulate. Further evaluation of this chemical was not possible because documentation on its use was not found.

Asbestos

Asbestos is a known human carcinogen. It causes lung cancer and lung disease. Asbestos insulation was used extensively in the 1950s, when many facilities at the SRS were initially constructed. Asbestos materials can be found in roofing, pipe, and vessel insulation; building insulation; gaskets; packing; siding; and other building materials. The materials have been removed as they deteriorate or as renovations, maintenance, and repairs have been done. Worker protection has necessitated that asbestos controls be in place during all removal operations (DOE 1987).

More than 80,000 linear feet of asbestos-containing materials were reported to have been removed in 1984. Nonradioactive asbestos has been disposed of in a separate trench in the sanitary landfill. Radioactive asbestos was buried in the Solid Waste Disposal Facility (formerly referred to as the Radioactive Waste Burial Grounds). An asbestos disposal site in C-Area was closed and capped in 1984 (DOE 1987).

Although a concern for workers onsite, asbestos has not been considered an environmental contaminant and has not been a concern for offsite exposure. In 1967, asbestos concentrations in air at several plant locations were measured. The maximum concentration was “1 million particles per cubic foot,” which was said to have been one-fifth of the TLV for workers at that time (Du Pont 1967). No facility has listed asbestos as an emission for the Air Emissions Inventory (Faugl 1996). We did not evaluated asbestos further because it is primarily found in building materials that are resistant to environmental transport unless seriously degraded or the building is demolished. If a building is imploded, exploded, or demolished all at once, the asbestos would be released to the air and would be subject to resuspension with time unless precautions were taken to contain it. It is likely that most of the buildings containing asbestos materials have been remediated or destroyed in the last decade, when awareness of asbestos hazardous was high and precautions were taken to protect workers and limit dispersion of asbestos fibers. For the purposes of the conservative stage one ranking, if all of the asbestos reported onsite was released to the air, concentrations about 100 times the level of concern could have been reached. This is a very unreasonable scenario, however, because most of the asbestos onsite is in insulation and building materials. Asbestos has not been subject to storage in large amounts, leakage, spillage, or routine release to the environment; therefore, we did not estimate a source term for asbestos.

Benzene

Benzene is a very volatile, slightly water-soluble chemical used in the past as a solvent. It is a contaminant of several other materials used at the SRS, including gasoline. Chemical degradation, primarily reaction with hydroxyl radicals, limits the persistence of benzene in air to a few days or even a few hours. Benzene released to soil and water is subject to biodegradation, photooxidation, and volatilization. The half-life in surface water has been estimated to be about 17 days for photolysis. Biodegradation half-lives are estimated to be about 8 to 16 days in surface water and about 30 days in groundwater. Although a large volume of benzene is released to the environment from a variety of sources, environmental levels are generally low because of rapid removal and degradation. The Log K_{ow} is 2.15. Benzene is considered highly mobile in soil and water, but it will adsorb to organic matter in soil. Benzene does not bioconcentrate, and it is a known human carcinogen. Because large amounts of petroleum products were used at the SRS, we investigated environmental monitoring information and releases of benzene further.

Chlorine

Chlorine is a severely irritating gas that is also more of a hazard in the workplace than an environmental contaminant of concern. Chlorine is reactive and would not be expected to persist in the environment as an irritating gas. It is not a carcinogen or chronic toxicant and would not be likely to have caused health effects offsite unless released in very large quantities at one time. Therefore, chlorine was not included in the chemicals to be considered further.

Coal

Coal is primarily carbon containing varying amounts of toxic or carcinogenic metals, sulfur, and other contaminants. Coal is regulated in the workplace as a nuisance dust (Lewis 1993). Although the ranking ratio is high, coal should not be the first priority in evaluating source terms for chemicals because of the ultraconservative ranking assumptions applied. For the purposes of consistency in the ranking exercise, it was assumed that all the coal piles were discharged to the Savannah River and that the toxicity value for the entire pile was that of benzo(a) pyrene, with an MCL of 0.002 mg L^{-1}. This led to a ranking ratio of 254. If the entire store was evaluated using the MCL of 0.005 mg L^{-1} for benzene, another carcinogenic component, the ranking ratio would be 101. It is unreasonable to treat the entire coal inventory as if it were carcinogenic aromatic hydrocarbon or benzene. We could conservatively estimate that coal tar and coal tar creosote material could contain as much as 3% aromatic hydrocarbons (Gosselin et al. 1984) and as much as 10% benzene (ATSDR 1995). If the inventory amount is reduced by these percentages, the resulting ranking ratios are 7.6 for benzo(a)pyrene and 10.1 for benzene. It is also unreasonable to assume that all of the coal inventory was discharged into the river. We know the piles remain onsite, but we do not have an estimate of the amount of material that left the pile in runoff or leachate. A preliminary evaluation of the runoff history, means taken to prevent runoff, and the results of environmental sampling around the coal piles was worthwhile for this phase of the study. We also evaluated coal ash.

Coal Tar

Coal tar and coal pitch are volatiles formed during the distillation of coal, and they contain carcinogenic polyaromatic hydrocarbons like pyrene, benzo(a)pyrene and chrysene, benzene, and phenol. If stores of coal tar were not contained, they could be subject to rainwater runoff and leaching, and they could contaminate surrounding soil, surface waters, and underlying groundwater. We investigated this material as a part of the qualitative evaluation of coal stores.

Freons

Chlorinated, fluorinated hydrocarbons, also called Freon (a registered trademark of Du Pont), are clear, colorless, noncombustible liquids. Perhaps best known for their use as refrigerants, they were also used at the Site for cleaning, degreasing, and as decontamination solutions. Freons were used in solvent degreasers, especially after 1988. Freon was also used as a coolant during operation of saws and lathes in M-Area. About 530 gal y^{-1} was used during the peak production times of 1985–1988. All of this was probably released to the atmosphere (Radian 1992). Freon was also released from heating, ventilation, and air-conditioning equipment.

Freon vapors are four to five times heavier than air and tend to accumulate in tanks, pits, sumps, and other low places; therefore, inhalation of concentrated vapors can be an occupational hazard (Haynes and Stoddard 1984). In a 1975 industrial hygiene summary report, mention is made of 800 gal of Genetron 11 being removed from a refrigeration unit and disposed of. The Du Pont Freon Products division memo informed SRS staff that the company had “no method or requirement for chemically changing these materials into other substances that would be more acceptable for release to the environment the recommendation (and practice) is to remove the material to a remote area and allow it to evaporate” (Harper and Croley 1976). Although release of these compounds to the environment is recognized to contribute to ozone depletion, it is very unlikely these materials would have presented a health hazard offsite; therefore, we did not determine releases of Freon.

Gadolinium Nitrate

Because toxicity information on this chemical is limited, we ranked gadolinium nitrate using the very conservative LD50/100,000 value reported in the MSDS. Gadolinium nitrate is described as a severe irritant and no chronic health effects are known. It is a relatively stable material, but environmental fate and transport of this material has not been studied. It is likely that precautions were taken to conserve this material and large releases were probably uncommon. The unavailability of documentation specific for this material would have seriously limited our ability to develop a source term; therefore, we did not evaluate gadolinium nitrate further.

Gasoline and Other Fuels

Gasoline is a complex mixture of hydrocarbons containing small amounts of benzene, toluene, xylene, 1,3-butadiene, and sometimes lead. Gasoline may have been released to the air or water and it may have seeped into groundwater from leaking storage tanks, pipelines, or as a result of spills. For the purposes of the ranking, we assumed all gasoline stores spilled into the river or discharged into the air, and the entire amount was ranked using the drinking water standard for a carcinogenic component, benzene.

The composition of gasoline varies tremendously. Compositional data studies sponsored by the American Petroleum Institute found the benzene content of gasoline mixtures were as high as 2% (ATSDR 1994). The IARC estimated that gasoline typically contains 0.5 to 2.5% by volume benzene (ATSDR 1994) or as high as 3.2% by weight. Benzene, ethylbenzene, and other aromatics related to benzene (like toluene and xylene) may make up as much as 30.5% by weight of a gasoline mixture (ATSDR 1994). Measurements of the amount of benzene versus total hydrocarbons gasoline released to the atmosphere vary greatly when tanks are vented, gasoline is pumped, or storage tanks are excavated. However, measurements do suggest benzene vapors could account for nearly 10% of the gasoline vapors under certain conditions of discharge. Studies have shown that benzene concentrations in air are highest during refueling operations. Studies on service station attendants suggest that the gasoline in the air they breathed averaged about 0.25% benzene. Taken together, these studies suggest an upper-bound estimate of 30% for the percentage of benzene in gasoline or gasoline vapors. Using the toxicity values for benzene and 30%, the inventory amount results in a ranking ratio of 0.531 for gasoline.

Gasoline is very volatile and does not dissolve readily in water. Most of the hazardous components of gasoline are broken down in a number of hours to weeks after their release. The Log K_{ow} for gasoline ranges from 2.13–4.87. Most chemicals in gasoline do not bioaccumulate. After it is released to the environment, gasoline is not transported as a mixture. The components of the mixture selectively partition into different environmental media according to their individual chemical and physical properties. The compounds of greatest health concern, like benzene, are water-soluble and are transported in groundwater, surface water, and through soils. These compounds are also subject to photochemical oxidation in air and have half-lives on the order of one or several days. They are also subject to biodegradation in water and volatilization, photooxidation, and biodegradation in soil. Although gasoline has caused liver and kidney tumors in animal studies, there is no evidence that gasoline causes cancer in humans. We did not find documentation, interview notes, or other evidence of leaks, spills, and large releases of gasoline that may have traveled offsite; therefore, we did not determine a source term estimate for gasoline released to surface water.

Hydrazine

Hydrazine is a reactive, flammable liquid used as a reducing agent for nuclear fuel reprocessing. It has also been used as an intermediate in the production of agricultural and industrial chemicals, as rocket fuel, and as a medication for sickle cell disease and cancer. Hydrazine has a relatively low vapor pressure and is soluble in water. Hydrazine could have been released to air, water, or soil. This chemical rapidly degrades in most environmental media by oxidation and biodegradation. Hydrazine in air is quickly destroyed by chemical reaction within minutes or hours, depending on the concentration of ozone and hydroxyl radicals in the air. Most hydrazine in air would be expected to have degraded within several hours of its release. Hydrazine released to water and soil can become dissolved in water or bind to soil. Hydrazine can sorb onto clay soils. The Log K_{ow} is –3.08. Hydrazine is subject to oxidation and biodegradation, and most of the hydrazine in water and soil would be expected to be gone within a few weeks. Hydrazine does not tend to biomagnify up the food chain. The potential for hydrazine to have been transported offsite is limited by its rapid degradation. Hydrazine causes several types of tumors in animals and is classified as a probable human carcinogen by the EPA (ATSDR 1994). We reviewed the use, storage, release history, and environmental monitoring results for hydrazine and hydrazine mononitrate.

Hydroxylamine Sulfate

Hydroxylamine sulfate is a white crystalline material that is very corrosive and can cause severe burns, ulceration, and sensitization reactions. There is a lack of toxicity information for this material, which is listed as being used in relatively large amounts in the 1970s Du Pont Index. The ranking ratio for hydroxylamine sulfate is comparatively large because we used the upper value of the range reported in the Du Pont inventory and the high LD50/100,000 value to calculate it. The LD50 was derived from data on mice given hydroxylamine sulfate i.p. and reflects the corrosive, irritant effects rather than any chronic effects. Although specific environmental fate data on this chemical are also lacking, it is a reactive chemical and would not be expected to persist in the environment. Based on this and the extreme conservatism of the toxicity values, we did not develop a source term for hydroxylamine sulfate.

Manganese

Manganese was evaluated using the EPA’s RfC value, which is quite conservative, with an uncertainty factor of 900 to account for a lack of toxicity data. Available monitoring data and source term information were examined, but the lack of documentation specific to this material limited our ability to develop a source term. We reviewed and evaluated monitoring and usage data on manganese compounds to the extent possible.

Mercury

The physical and chemical characteristics of metals that influence their behavior in the environment include solubility, oxidation state, and tendency toward sorption on materials in soils and sediments. Mercury exists in the elemental form (a volatile liquid), in the +1 and +2 oxidation states, and as organic mercury. Mercury sorbs strongly to organic material and oxides and tends to accumulate in sediments. Microorganisms in sediments can convert mercury to methymercury, which bioaccumulates. Mercury and methylmercury are very potent neurological toxins. The inventory amounts used for the ranking may not include mercury in pumps that was disposed of by burial through the years. We further evaluated discharges of mercury to the air and water and evaluated mercuric nitrate along with elemental mercury.

Other Metals

Chromium, lead, and nickel had ranking ratios for water that were greater than 10^{-2}. Zinc, copper, and cadmium compounds had ranking ratios for water that were greater than 10^{-3}. These metals are toxic, and chromium, nickel, and cadmium are carcinogenic. Lead is a potent developmental neurological toxin.

We used combined inventories of small metal stores all over the Site and numerous metal-containing compounds like rust and corrosion inhibitors that were used and stored in relatively small amounts to obtain the ratio. Many of these materials were primarily found in solid form, like sheeting, bricks, pellets and pipes. Especially large amounts of lead shielding, and lead pellets were used at the SRS. These materials were relatively resistant to environmental transport and were not likely to have been subject to resuspension in air or leaching into surface or groundwater. For the purposes of ranking, we assumed that all stores of these materials were placed in the Savannah River. This is especially unreasonable because these materials were not stored in large piles or tanks but were used all over the Site in many different facilities, in small and large amounts, and in many forms.

The mobility of all of the metals depends on soil and water chemistry and pH. For example, cadmium usually occurs as the Cd^{+2} ion at pH levels less than 8 or quite commonly as cadmium sulfate. Cadmium will adsorb to soils and sediments by cation exchange. Chromium occurs in the +3 or +6 oxidation state in water. Cr(III) is insoluble and readily absorbs to metal oxides in soils. Cr(VI) is soluble and is more mobile in the environment.

We compiled environmental monitoring data and information useful for source term determination for arsenic, cadmium, chromium, lead, manganese, mercury, nickel, and zinc. These metals were released into surface water from their use as cooling water treatment chemicals, during surface water runoff from coal and ash piles, and as a component of process waste in M-Area, F-Area, and H-Area.

Nitric Acid

Nitric acid is a caustic, severely irritating compound that is more of a workplace hazard than an environmental contaminant of concern. It is subject to rapid degradation. It is not a carcinogen or chronic toxicant and would not likely have caused health effects offsite unless released in very large quantities at one time. We compiled releases of nitric acid fumes and further evaluated nitrates and nitrogen dioxide, which are chemicals associated with the use of nitric acid.

Sulfuric Acid

Large amounts of sulfuric acid were used onsite, and several spills of sulfuric acid to Site streams occurred. Sulfuric acid is a caustic, corrosive material that would not be expected to persist in the environment. We noted documentation of sulfuric acid releases, but it did not seem necessary to develop a source term for this material because transport of hazardous amounts offsite would have been limited by its rapid degradation or conversion into other materials.

Tetrachloroethylene

Tetrachloroethylene is a volatile liquid used as a solvent, cleaner, and vapor degreaser. Tetrachloroethylene is slightly water-soluble, and tetrachloroethylene released to surface water would be expected to rapidly evaporate into the air. Tetrachloroethylene also evaporates from soil, but it can easily travel through soil into groundwater. The Log K_{ow} is 3.40. Tetrachloroethylene in air is photochemically degraded. The half-life in air has been estimated to be 3 to 4 months, while degradation in water is much slower. Tetrachloroethylene is subject to biodegradation, but it can persist in soils and groundwater for decades. Tetrachloroethylene has a very low tendency to bioaccumulate. Tetrachloroethylene has caused cancer in animal studies, but it has not been shown to cause cancer in humans. The ranking ratio for tetrachloroethylene in water was quite high because the drinking water standard for this chemical is quite protective. It is likely that most of the tetrachloroethylene used onsite was released into the atmosphere. We evaluated the discharge of this solvent and others to M-Area sewers, into groundwater, and into the air; however, the priority assigned to tetrachloroethylene was not as high as the water ranking ratio might suggest.

Trichloroethylene

Like tetrachloroethylene, trichloroethylene was used as a solvent and cleaner. Trichloroethylene released to surface water would be expected to rapidly evaporate into the air. Trichloroethylene also evaporates from soil, but it can easily travel through soil into groundwater. Large amounts of trichloroethylene were used in M-Area, and we further evaluated discharges to M-Area sewers, into groundwater, and into the air.

Trichloroethane

Trichloroethane is a volatile cleaner and solvent that was released to the air and to M-Area process sewers. It dissolves slightly in water and would be expected to evaporate rapidly from soil and water. Once in the air, it is estimated to persist for about 6 years. Trichloroethane is thought to be important in reducing the stratospheric ozone layer. Trichloroethane in soil and water is also subject to biodegradation. An estimated half-life for degradation in groundwater is about 10 months. Trichloroethane does not bioaccumulate. 1,1,1-Trichloroethane is not carcinogenic, and the likelihood that environmental exposure would cause significant health effects is low. 1,1,2-Trichloroethane has caused cancer in some animal studies, but it has not been shown to cause cancer in humans. For the purposes of the screening, we combined different isomers of trichloroethane and calculated a ranking ratio using the more conservative toxicity values for the carcinogenic isomer. We further evaluated discharge of this solvent and others to M-Area sewers and into groundwater and the air.

Uranium

Uranium is a radioactive metal that can cause cancer and kidney disease. In general, uranium releases were reported in curies rather than kilograms or pounds of material. Uranium is one of the radioactive materials being evaluated and we developed a source term for it. Understanding the kidney toxicity of uranium may be an important step in later phases of the project when health risks will be determined.

Other Chemicals of Potential Interest

There are several chemicals that, as a result of the screening, were not evaluated further but are of public interest. A discussion of these chemicals follows.

Anthracene. Anthracene is a polycyclic aromatic hydrocarbon. Unlike similar aromatic hydrocarbons, anthracene is not carcinogenic. Benzanthracene and other similar carcinogenic compounds have been listed in essential materials ledgers, but how they were used was unclear. Benzo(a) anthracene, benzo(a)pyrene, benzofluoranthene, benzoperylene, and chrysene were listed in the 1994 SRS CIIS database with inventory quantities of zero or less than 0.001 lb, which is consistent with use as an analytical standard or laboratory reagent. A September 1953 monthly progress report for the Works Technical Department mentioned that assistance had been given to the instrument department concerning the use of anthracene in relatively large quantities to coat tubes in building 773-A. The Works Technical Department recommended that this be done in a hood, using protective clothing and a respirator, and special attention be given to personal clean up after each job (Du Pont 1953).

Carbon Tetrachloride. An inventory amount for carbon tetrachloride was not given in the CIIS database. The inventory amount in the CIIS database would not have been particularly useful for estimating quantities of carbon tetrachloride used in the past because it is likely that use of this chemical as a solvent was phased out. As at other U.S. Department of Energy facilities, it is likely carbon tetrachloride was replaced with less toxic solvents, such as tetrachloroethylene, trichloroethylene, and trichloroethane. Very large amounts of carbon tetrachloride were used at the Rocky Flats Plants in Colorado. However, no documentation has been found to support the use of large amounts of carbon tetrachloride at the SRS. It seems that tetrachloroethylene, trichloroethylene, and trichloroethane were the solvents used in M-Area to clean materials such as targets and cans. Recent RCRA and CERCLA monitoring data have detected carbon tetrachloride in groundwater but not in quantities suggesting a significant use in the past. Carbon tetrachloride was not reported in the 1974 inventory. Based on an apparent lack of inventory, we did not evaluate carbon tetrachloride further.

Fluoride. Hydrogen fluoride was released from the JB-Line stack in F-Area (Reinig et al. 1973). Fluoride was also a component of liquid waste from the separations area processes. Potassium fluoride was used in the frames process to isolate ^{238}Pu. A 1988 summary of separations activities reported that 59 lb of fluoride was discharged to the seepage basins without evaporating because of corrosion problems with evaporators. This amount was said to represent the maximum annual amount that would have been discharged during 1 year from one separations plant (Du Pont 1988).

Fluorides are ubiquitous in food and water. Human exposure to toxic amounts of fluorine and hydrogen fluoride is unlikely outside of an occupational setting. Fluoride is highly electronegative and reacts vigorously with other compounds. Fluoride, fluorine, and hydrofluoric acid released into soil or surface waters would rapidly react to form fluoride salts. Fluorides discharged to the seepage basins have been retained by the soil.

Hydrofluoric acid was spilled on the grounds west of central shops sometime before 1970. Monitoring wells have been installed in the area. Contaminated groundwater has not moved offsite (Christensen and Gordon 1983), and it is not likely to move offsite in the near future because the central shops are centrally located. A hydrofluoric acid solution has been used in the 773-A glass shop, which makes glassware used at the Savannah River Technology Center. The 1996 Operating Permit Application described the releases as being exhausted from two small stacks. The application considered the releases to air to be very small (Westinghouse 1996). A 1987 annual environmental report describing ambient air quality monitoring onsite and offsite said that gaseous fluorides were not monitored because the potential release was insignificant compared to the standard (Mikol et al. 1988). We did not evaluate fluorides further.

Scintillation Fluids. Scintillation fluids are photofluoric compounds and surfactants in organic solvents, such as xylene, toluene, dioxane, napthalene, or trimethylbenzene solutions. An annual waste generation rate for scintillation fluids used to analyze samples for radioactivity was estimated to be about 200 gal y^{-1} (Smithwick 1984). Liquid scintillation solutions have been buried at the Radioactive Waste Burial Grounds since 1965. As of 1984, the amount sent to the burial grounds was estimated to total 10,000 gal, most of which had been used for tritium analysis. The solutions were buried in plastic or glass vials in containers with absorbent material. After 1987, all liquid scintillation solutions were supposed to be incinerated (DOE 1987). There is no evidence that these fluids traveled offsite; therefore, we did not evaluate them further.

CONCLUSIONS

Based on the ranking results and the discussion above, we concluded at the beginning of Phase II of the project that a source term should be developed for the following chemicals:

Benzene
Coal
Coal Ash
Hydrazine
Gasoline
Mercury and mercuric nitrate
Nitric acid
Trichloroethylene
Tetrachloroethylene
Trichloroethane

We concluded the following metals should also be evaluated:

Arsenic
Chromium
Manganese
Nickel
Cadmium
Lead
Uranium
Zinc

A source term was estimated for chromium, cadmium, and lead releases to air and nickel releases to Site streams. We did not find enough information to estimate a source term with reasonable certainty for arsenic in coal and ash pile runoff; chromium releases to surface water; or nickel, zinc, and arsenic releases to air. We compiled monitoring data for these metals and described releases using all available information. Information on gasoline, coal, and ash storage, use, transport, and disposal was reviewed and summarized. We made release estimates for benzene and toxic components of metals in coal and ash and releases of toxic metals and other pollutants from coal burning. In addition, we developed source terms for nitrogen dioxide, sulfur dioxide, ash particulates, and hydrogen sulfide. The SRS operations had the potential to release large amounts of these pollutants into the air.

The following chemicals may have been released, but additional analyses were impossible because of a lack of available inventory or toxicity information:

Aldrin/dieldrin
Chloromethane
Endosulfan
Heptachlor
Lindane
Trichlorophenol (2,4,5-T)
Chloroethane
DDT
Endrin
Hydroxyquinoline
Toxaphene
PCBs (polychlorinated biphenyls, arochlors)

An inventory for these chemicals was not reported in 1974 or 1994. Chloroethane and chloromethane have been detected in onsite groundwater. There is no amount listed in the inventory for PCBs, but PCBs have undoubtedly been used in electrical equipment onsite, and some of this equipment was likely to have been buried in onsite waste areas. The *RAC* researchers reviewing monthly reports and other documents for Phase II of the dose reconstruction study were given a list of these compounds and asked to flag any information regarding their use, release, monitoring. or disposal. All of this documentation was reviewed and used to develop a source term estimate for as many of these chemicals as possible. The lack of documentation for some of the chemicals seriously limited our ability to develop a source term for them. However, where a release estimate could not be calculated, a qualitative evaluation of the use and potential release of the compound was conducted and the resulting characterization is provided in Chapters 17 and 18. Environmental monitoring for chemicals is addressed in Chapters 19 and 20.

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