3.0 ROUTINE AIRBORNE EMISSIONS OF NONRADIOACTIVE MATERIALS

The preceding sections of this report have focussed on the radioactive materials of concern and the extensive airborne effluent monitoring program that has been in operation to quantify the release of these materials. As part of initial project efforts, materials of concern were identified based on their potential to cause off-site health impacts (ChemRisk 1991a, 1991b, 1992). These materials include both radioactive and nonradioactive materials. The nonradioactive materials of concern that were identified as warranting the development of emission estimates for routine release include:

- Beryllium
- Carbon Tetrachloride
- Chloroform
- Methylene Chloride
- Tetrachloroethylene
- 1,1,1-Trichloroethane
- Trichloroethylene

With the exception of beryllium, all of these materials are organic solvents that are liquids with relatively high vapor pressures, so that they will readily volatilize in air. Beryllium is a metallic element that is commonly found in solid form.

A beryllium effluent monitoring program was routinely conducted throughout most of the plant's operating history. However, there was no routine sampling of the organic solvents of concern. The following sections review the beryllium sampling program, provide a summary of the beryllium emission estimates, and also describe the approach to estimating emissions of each of the organic solvents based on available data and information.

3.1 Beryllium

The history of beryllium use at Rocky Flats has been summarized in the Tasks 3 and 4 report (ChemRisk, 1992). Beryllium has nearly always been present at Rocky Flats, but it was not actually used in full-scale production operations until 1958. Beryllium operations were not part of the manufacturing process in the first years of plant operation, but beryllium was being handled by the production engineering group in preparation for application to a new weapons concept. These early beryllium operations took place in Building 444 in preparation for regular pit production, which began in 1958. Beryllium manufacturing operations in Building 444 included casting (foundry), cutting, heat-treating, rolling, and machining. Beryllium foundry operations ceased in 1975.

Historically, beryllium has been present and monitored in a number of plant buildings. Some of these other buildings include the "B" side of Building 883, which in 1964 was converted to beryllium rolling and forming operations. In 1970, Building 865 began operations, serving as a research and development facility primarily for the manufacturing processes using uranium and beryllium. Recent-day uses of beryllium documented in Air Pollution Emission Notice reports from the late 1980s also include vapor deposition to coat metal parts in Building 705.

The Tasks 3 and 4 report described the nature of the ventilation systems used to control beryllium emissions. When manufacturing started in 1958, the system consisted of "Aero-Tech" cyclone separator units (to remove the larger particles from the exhaust stream) exhausting to the main building exhaust serving the uranium operations, which was subject to HEPA filtration. Upgrades in 1964 and 1974 improved on the cyclone separator units, and in 1986 Building 444 exhaust filtration was upgraded to include two stages of HEPA filtration.

Beryllium has been monitored in plant exhaust systems since at least 1960. It is currently monitored in 50 vents, although it is actually processed in only six of the associated areas according to plant reports (EG&G, 1990). According to the 1980 Final Environmental Impact Statement (USDOE, 1980), beryllium was among eleven elements analyzed by atomic absorption in waterborne effluents.

As a metallic element present in particulate form in airborne plant effluents, beryllium is the only nonradioactive material of concern in this study that would have been controlled by HEPA filtration that was installed at the plant for the purpose of controlling radioactive effluents. While some concerns have been raised about the control of beryllium in workroom air, virtually all airborne effluents discharged from plant facilities that processed beryllium were subject to HEPA filtration. One exception may have been Building 441 during the early 1960s. An industrial hygiene report from 1963 suggests that beryllium discharges from Building 441 were relatively high and recommended that exhaust hood filters be installed in the system (Hammond, 1963). Exhaust hood filters were not installed in Building 441 until sometime in 1964. The beryllium effluent monitoring data for Building 441 reflect the effect of increased filtration in reduced emissions. Interviewees have indicated that Building 441 housed a beryllium analytical laboratory. The following sections describe the plant program for monitoring beryllium in airborne plant effluents and summarize the emission data generated as a result of that program.

3.1.1 Historical Effluent Sampling and Analytic Practices — Beryllium

The beryllium monitoring program was the responsibility of the industrial hygiene group at Rocky Flats. The records searches for this study identified few documents pertaining to beryllium sampling and analysis, particularly for the 1950s and 1960s. A Rocky Flats retiree indicated that information relating to beryllium sampling was summarized in the industrial hygiene monthly progress reports;

however, a comprehensive source of these documents could not be located. While it has been reported that Rocky Flats operated a beryllium sampling program during the 1950s, no documentation of such a program or sampling data have been located for this period.

The sampling practices for beryllium are reported to be very similar to those employed for radionuclides, which is logical given the similarity in the physical characteristics of the beryllium, plutonium, and uranium effluents. The sampling system for each of these materials must be able to collect very small metal particles remaining in the effluent airstream after HEPA filtration. Documentation of the sampling programs from the late 1970s and 1980s indicates that in many cases individual samples collected from ducts or buildings were analyzed for both radioactive contaminants and beryllium. During the 1980s, beryllium analysis was being done on a monthly basis from a ventilation system composite filter sample. However, the plant used a number of different beryllium analytic techniques over time that may have resulted in separate sample collection during some periods of plant operation. The historical radioactive effluent sampling practices relative to sampling system design for particulates, sample apparatus flow rates and velocities, sample line losses, and stack or vent exhaust volume quantification discussed earlier in this report are generally applicable to beryllium sampling, as are the uncertainties in the final emission estimates.

A number of analytic practices were employed historically by Rocky Flats to quantitate beryllium in effluent samples. While the exact periods during which the various practices were used could not be established from plant documentation, a number of published reports and plant procedures describe the beryllium analytic procedures and personnel interviews at the plant that aided in identifying the periods during which the various methods were used. The first reference to beryllium analytic procedures was located in an internal Dow Chemical Company document from January 1964, which provided instrument operation instructions for beryllium quantification using emission spectroscopy (Dow Chemical, 1964). The document described the operation of a spectrograph that utilized photomultiplier tubes that replaced photographic plates as a detector and that was capable of quantitating beryllium in any form in the range of 0.005 to 1000 μg on Whatman 41 filter paper. Plant personnel indicated that emission spectrographs were used during the period from approximately 1958 to 1965.

The next discussion of analytic methods for beryllium related to Rocky Flats was located in a journal article from the scientific literature (Bokowski, 1968). The paper describes the application of direct-reading atomic absorption spectrophotometry (flame) to the analysis of beryllium in air on Whatman 41 filter paper as well as other types of samples. The paper documented good accuracy and precision for the method and an ability to quantitate beryllium in aqueous solution as low as 0.003 micrograms per milliliter. The approximate period of use of this method was 1965 to 1971.

The third significant document addressing beryllium analysis described a study of the use of nonflame (graphite furnace) atomic absorption spectrometry for quantifying submicron amounts of beryllium (Hurlbut and Bokowski, 1974). The discussion of the nonflame method examined the use of both Whatman No. 41 filters and Gelman Type E glass filters and found some analytic interference with the use of the glass filters. The study reported that comparison of results obtained by standard flame atomic absorption analysis and nonflame atomic absorption analysis was good, but the nonflame technique has the advantage that as little as 0.002 micrograms of beryllium per paper filter can be detected, whereas the direct flame technique is limited to about 2 micrograms of beryllium per filter paper. This method has been in use at Rocky Flats from approximately 1971 to the present.

In addition to these documents generated by Rocky Flats employees describing various analytic methods, a fairly lengthy review paper on beryllium prepared by a Rocky Flats employee was also located during records searches. The paper provides a literature review of the history, uses, occurrences, analytic chemistry, and biochemistry of beryllium (Hurlbut, 1974).

While the documents do not specifically describe the programs that were in place for the collection and analysis of routine air samples at Rocky Flats, they do demonstrate that Rocky Flats scientists were actively developing and evaluating accurate and precise methods for quantitating beryllium in environmental samples. This record suggests that some care was taken in the sampling and analysis of airborne plant effluents for beryllium.

3.1.2 Airborne Effluent Data — Beryllium

As described earlier, the industrial hygiene group was responsible for the beryllium sampling program at Rocky Flats and generated documentation of the program. A relatively complete record of the annual beryllium emissions was compiled from detailed sample data logbooks for 1960 through 1970 and annual beryllium releases reported in the Annual Environmental Monitoring Reports for 1971 through 1989. No sampling data was located for the period prior to 1960.

The logbooks from the period of 1960 through 1970 contained daily sample results for both workroom air and building effluents. The building effluent data was entered onto a computerized spreadsheet to calculate the monthly average beryllium concentrations for each stack as well as the annual averages for 1960 through 1970, which are presented in Table 3-1. In the case where less-than values were reported in the logbook, one-half the reported value was used to calculate the averages. The method of replacing less-than values with one-half the limit of detection is supported by the USEPA (1989) and Gilbert (1987). Gilbert states:

3-1 Annual Average Beryllium Concentrations (µg m^{-3})

> The method of replacing less-than values by one-half the limit of detection is unbiased for the mean, but not for the variance, if the analytical measurement technique cannot result in negative measurements, and if all measurements between zero and the Limit of Detection are equally likely to occur (a uniform distribution). Kushner (1976) studied this method when aerometric data below the detection limit are lognormal. For his application (pollution data) he concluded that biases using the mid-point would be overshadowed by measurement error.

In order to evaluate the impact of replacing less-than values with one-half the limit of detection on the release estimates for beryllium, a more detailed analysis was performed on the 1962 and 1968 beryllium monitoring data. Although about 30 percent of the air monitoring data reported in 1962 were below the applicable detection limit (0.0001 µg m^{-3} in most instances), their impact on the release estimate for the year was relatively small. This was demonstrated by calculating annual averages setting less-than values equal to the detection limit and then setting them to zero. The difference between beryllium release estimates for 1962 calculated by these two methods was less than 2 percent. In 1968, less than 1 percent of beryllium air monitoring results were below detection limits, and the difference between release estimates calculated by the two methods described above was less than 1 percent.

As was the case with quantifying radioactive effluents, exhaust flow rates or total exhaust volume must be known to calculate total emissions based on the sampling data. Again, the estimates of these values presented in Table 2-2 had to be used since there is little documentation of this information from the 1960s. An additional problem was encountered in that there was no documentation of ventilation flow rates or volumes for Building 441 from the sources used to compile Table 2-2 since Building 441 was converted from production use to office use in the mid-1960s. In order to estimate beryllium emissions from Building 441, it was necessary to assume that exhaust ventilation rates were equivalent to those of a building of approximately the same size, Building 331. Building 331 is somewhat larger at approximately 23,000 versus approximately 18,000 square feet for Building 441. Both buildings served as research and analytic laboratories in the early 1960s. Given Building 331's larger size, ventilation volumes may have been larger than those of Building 441; however, this would lead to conservative emission estimates (i.e., would result in an overestimate of emissions rather than an underestimate).

The annual beryllium emission estimates for the period from 1960 through 1970 calculated from data compiled from sample data logbooks and using exhaust volume estimates are presented in Table 3-2. As indicated in the table, beryllium data are not consistently available for the identified buildings, and in most cases this is a result of changes in building uses such as:

3-2 Annual Beryllium Releases by Building (grams)

- Building 883 — beryllium operations moved in around 1965, and
- Building 441 — beryllium operations moved out around 1966.

It is believed that the plant initiated a broader sampling program for beryllium in 1970 that led to the inclusion of Buildings 886 and 774. The broader sampling program was likely a result of greater environmental awareness. Beryllium was not machined in either building, but may have been present in wastes in Building 774 or parts in Building 886. No data for beryllium emissions were located for the period prior to 1960. While it is likely that beryllium was present on-site during initial years of operation, it was not used in the manufacturing process until 1958, and this use was only in Buildings 441 and 444. In the absence of any data, it is believed reasonable to assume that emissions from these buildings during 1958 and 1959 were approximately the same as those reported in 1960.

Beryllium releases for the period from 1971 through 1989 have been documented in the Annual Environmental Monitoring Reports issued by the plant. In many cases, the Annual Environmental Monitoring Reports reported beryllium release totals as less-than values. The 1975 annual report stated that samples with concentrations below the minimum detectable concentrations (MDC) were considered to be at the MDC for averaging purposes. Averages calculated with below-MDC results were identified with a less-than sign (<). In addition, the annual emission total for 1983 was reported as a negative number. The explanation in the text of the document was that this indicated that the air sampled for the year could not be distinguished from the background level associated with the analysis. A summary of the annual beryllium release totals for this period is presented in Table 3-3.

A beryllium release total for 1984 was independently calculated by ChemRisk as part of this study. In order to perform the calculations, a data base of the analytical results of beryllium emissions was created. The calculated airborne beryllium release total for 1984 is 0.31 grams. Release totals for individual stacks for 1984 are contained in Table 3-4. The value of 0.31 grams is in good agreement with the value of 0.3 grams reported in the Rocky Flats plant 1984 Annual Environmental Report and presented in Table 3-3.

Concern has been identified for potential beryllium release during fires. Three reports of fires in beryllium areas at Rocky Flats were located. Two of the fires, one on June 25, 1962 and one on February 14, 1964 were confined to workrooms in Building 444. Any beryllium released as a result of the fires would have passed through the plenums and been monitored by the stack sampling equipment (Reyland and Rogers, 1964; Boatman, 1962). The third fire reported in Rocky Flats literature occurred on February 23, 1978 in the plenum building serving Building 444. Based on witness accounts the report indicates that the HEPA filters continued to function until water was applied. However, the fire did burn through the plenum prefilters. The stack

3-3 Reported Annual Beryllium Releases

3-4 1984 Beryllium Emissions Data

Table 3-4 Continued

air monitoring equipment operated throughout the incident and the report quantifies the beryllium released to ambient air at 14.5 grams (Hess, 1978). The water used to fight the fire was impounded in areas south and east of Building 444.

The beryllium concentrations in this water were 4.3 mg L^{-1} and 1.6 mg L^{-1}, respectively. Because the stack monitoring equipment was operating during these fires, the beryllium routine release totals for 1962, 1964 and 1978 include any releases associated with these fires.

The beryllium release summaries suggest extremely low environmental emissions of beryllium averaging in the tens of grams or less annually. A 1980 plant internal letter indicated that, based on an evaluation by the plant's General Service Laboratory, use of the minimum detectable amount (MDA) value for beryllium at each effluent measurement location would result in a calculated minimum beryllium discharge per month of 0.4 gram (Hornbacher, 1980). This would lead to a reported yearly minimum discharge of about 4 to 5 grams even if none of the samples had a positive analysis result. The information that was reviewed suggests that the beryllium data handling practices may have led to the reporting of annual emissions that were higher than the actual releases. However, given the low magnitude of the reported emissions, the uncertainty introduced by this practice has not been characterized.

The sources of uncertainty related to the collection of samples and the quantification of exhaust volumes discussed for plutonium and uranium measurements also apply to beryllium measurements. Therefore, the range of beryllium emissions was characterized using the same approach described for quantifying uncertainties associated with plutonium and uranium release estimates. This approach included uncertainties in exhaust flow rate estimates, in sampling flow rate estimates, and in analytical results. As described in Appendix G, Monte Carlo simulation was used to combine the different sources of uncertainty and calculate the overall uncertainty factor of airborne beryllium emissions.

3.2 Organic Solvents — Airborne Emissions

The organic solvents that have been identified as being of potential concern at the Rocky Flats Plant have been used in a variety of applications. The nature of recent-day use (late 1980s) of these materials has been exhaustively evaluated in reports prepared by EG&G Rocky Flats titled Air Pollution Emission Notices (APEN). APEN project work involved more than thirty full-time project personnel and ten part-time personnel devoted to the project for over a year and a half preparing reports for essentially every Rocky Flats building. Each APEN report documents the configurations of the modern-day air handling systems, the processes conducted in each building, vents and/or stacks associated with emissions, and assumptions and factors used by EG&G and its subcontractors to calculate process emissions. The APEN reports describe modern-day plant processes and activities.

While these reports provide an excellent resource for establishing current-day releases of the organic solvents of interest, they are generally not a useful source of historical information.

The extent and quality of historical documentation of the use and release of the organic solvents are meager at best in comparison to the documentation provided by the APEN reports. In many cases, the actual nature of the historical use of the material is poorly documented, and in all cases there is insufficient historical information on material purchases, uses, disposal, and recycling to apply any of the estimating techniques such as mass balance calculations or use of emission factors that were employed to prepare the APENs. The historical information that is available consists of some limited historical inventory information, limited documentation of specific usage, reports of special effluent sampling or quantification efforts, and information obtained as a result of personnel interviews. Due to the limited availability of historical data, plausible ranges of historical emissions were estimated for screening purposes only, to establish a basis for determining level of concern.

Unlike radionuclides and beryllium, there were no efforts at Rocky Flats to control organic solvent emissions by use of exhaust system recovery devices, scrubbers, or traps. Because of this fact, significant fluctuations due to failure of control devices did not occur. Emissions were more directly related to the quantities of each solvent that were historically used and the fractions of the quantities that were used that became airborne.

The following sections review the information that was identified as being useful for the development of emission estimates for each of the organic solvents of concern. In cases where more historical data were available, an estimate of the probable range of the historical annual airborne release is provided. The estimated range of release has been established following the review of all the identified data. The data often only provide a rough guide to the actual possible emissions, but the estimated range of emissions derived from the data is believed to encompass the actual emission rates. In cases where no data or information is available for a given period of time, it has been assumed that emissions were the same as those estimated during the nearest point in time for which some type of information is available. Where data and information indicate trends in release rates over time, a simplifying assumption of linear change over time is made in the absence of information to the contrary.

Detailed documentation of all available sources of information on emission estimates for the organic solvents of concern can be found in Appendix E.

3.2.1 Carbon Tetrachloride

As described in the Tasks 3 and 4 report, carbon tetrachloride was used at Rocky Flats to clean glove-box walls, furnaces, product components, metal chips, machinery, and instruments. Estimated historical emission rates of carbon tetrachloride have been based on airborne concentration measurements, estimates of quantities of the material used or kept on hand, and statements made by retired and active workers during interviews. The time period of interest from 1953 to 1989 can be broken into three distinct time spans relative to estimates of annual emission quantities based on the available information and factors discussed below.

1953 to 1957

Investigations have indicated that carbon tetrachloride was used extensively in plutonium operations, but not in uranium, beryllium, or stainless steel operations. Large-scale plutonium production did not begin until approximately 1957, when a change in weapon design concept called for increased use of plutonium in fissionable weapon components. In these early years, plutonium was machined in a "dry" state, that is without use of cutting oils. Carbon tetrachloride was used as a coolant, sometimes being applied with a squeeze bottle (ChemRisk, 1991-1992, Interview No. 78). Uranium machining during these years was typically performed with a 15:1 oil and tetrachloroethylene mixture (Navratil and Miner, 1984).

Plant personnel were cognizant of the hazards of carbon tetrachloride use as early as 1953, but documented efforts at solvent substitution in these early years were limited to non-production operations, such as cleaning of typewriters and desks (Hicks and Langell, 1952). Tetrachloroethylene and trichloroethylene were recommended in these applications.

It is estimated that carbon tetrachloride emissions prior to 1958 were approximately one-tenth of emissions from 1958 to 1970, or ranged between 4 to 20 tons per year. Given the documented, albeit relatively minor, uses of the solvent during this period, it is unlikely that annual uses or emissions were below about 600 gallons or 4 tons or that emissions exceeded 10 percent of those experienced after the significant increase in plutonium machining that occurred around 1957.

1958 to 1970

The period from 1958 to 1970 was the period of maximum use of carbon tetrachloride at Rocky Flats. Because many major uses of carbon tetrachloride were tied to routine maintenance activities, for example glove-box cleaning during regularly scheduled inventories, emissions of the solvent are thought to have been relatively constant during this period rather than following any ups and downs of production rates. Based on available information, it is believed that the transition to large-scale plutonium production may have taken up to three years, from 1958 to 1961. By 1961, carbon tetrachloride emissions had reached levels similar to those of the early 1970s before solvent substitution began to decrease carbon tetrachloride use. Based on documentation of early 1970s use, measurement, and inventory data described below, estimates of carbon tetrachloride emissions range between 40 and 200 tons per year for 1961 to 1970.

The upper bound of 200 tons per year is approximately 30 percent above the release rate (153 tons per year) that corresponds to peak levels of carbon tetrachloride measured around 1974/1975 by Hobbs (1982). The upper bound is above the estimated 1974 peak emission rate to account for some decrease in carbon tetrachloride use beginning around 1972. The fact that carbon tetrachloride usage was in a downward trend was likely offset somewhat by the fact that the 153 tons per year estimate reflects peak measurements rather than average emissions over long periods of time. The elimination of uses of carbon tetrachloride at Rocky Flats was neither immediate nor comprehensive- significant uses remained in 1970. In fact, at the time of plant shutdown in 1989, procedures still called for use of carbon tetrachloride in plutonium facilities.

Between 1958 and 1968, approximately 3,500 drums containing plutonium-contaminated oil were stored at the Building 903 drum storage area (Seed *et al.*, 1971). These drums included carbon tetrachloride in varying proportions with straight-chain hydrocarbon mineral oil (Shell Vitrea) and other liquids. Assuming that each 55-gallon drum contained 20 percent carbon tetrachloride, the amount stored over the 10-year period is estimated to have been approximately 256 tons. This is equivalent to about 26 tons per year or about 13 percent of the estimated annual emission of that period of time. Since only a fraction of the stored carbon tetrachloride was released into the environment through leakage of storage drums, the assumption of complete volatilization of the carbon tetrachloride used at Rocky Flats that is the basis of various historical emission estimates apparently results in the estimates being conservative in this regard.

1971 to 1989

Starting around 1972, attempts were made to eliminate carbon tetrachloride from some production operations, due in part to measurements of carbon tetrachloride emissions from building stacks that were occasionally high enough to exceed permissible exposure levels at ground level (Musgrave, 1975). Carbon tetrachloride was used during and after plutonium machining to remove coolant oil from parts, in ultrasonic cleaners prior to inspection, and in dip tanks to degrease lathe turnings prior to briquetting (Musgrave, 1975). In 1974, 1,1,1-trichloroethane (TCA) was recommended to replace carbon tetrachloride in ultrasonic cleaning in Building 707 (Musgrave, 1975).

Various studies and projects involving estimation of carbon tetrachloride use at Rocky Flats or measurement of airborne concentrations of the solvent are available for the period from 1971 to 1989. Emission estimates based on these resources are shown as points on Figure 3-1. Results of past studies addressing carbon tetrachloride are summarized in Table 3-5 and are also described in Appendix E.

Hazardous material records indicate that there was a 44 percent decrease (from 22 to 12 tons per year) in carbon tetrachloride inventory from 1974 to 1989 (Barrick, 1974; Setlock, 1990). The Final Environmental Impact Statement for the Rocky Flats Plant site (USDOE, 1980) includes a tabulation of consumption rates of the "major chemicals" for fiscal year 1977. The reported annual usage of carbon tetrachloride is 5,334 gallons (36 tons). The same report included an estimated Rocky Flats plant airborne discharge rate of 4.73 grams per second (66 tons per year) in 1975. An estimate of carbon tetrachloride inventory in production areas for 1973 is 81 tons per year (Kruehauf and Richter, 1974). Release estimate based on material balance estimates for 1974-1975 ranged from 34 to 106 tons per year (Hobbs, 1982). Monitoring during the same period indicated average carbon tetrachloride emissions of 56 tons per year and maximum emission of 153 tons per year (Hobbs, 1982). Based on the available use, monitoring, and inventory data points, it is estimated that carbon tetrachloride emissions ranged between 40 and 200 tons per year in 1970 and decreased linearly to between 20 and 100 tons per year in 1989. These estimates are not inconsistent with other estimates of carbon tetrachloride use from 1988 to 1990, ranging from 40 to 93 tons per year (EG&G, circa 1990; EG&G, 1990-1991; Hamilton and Moser, 1990; USDOE, 1989).

3.2.2 Chloroform

As described in the Tasks 3 and 4 report, historical uses of chloroform at Rocky Flats are not well documented. Activities that have involved use of chloroform include laboratory analyses of gallium content of plutonium samples, as a "glue" used by carpenters to join Plexiglas, and for dissolving of plastics and photoresists. The estimated historical emission rates of chloroform have been based on reports of quantities of the material used or kept on hand, limited warehouse purchasing records, and statements made by retired and active workers during interviews. The period from 1952 to 1989 has been divided into two time spans based on the available information and factors discussed below.

3-1 Carbon Tetrachloride Emission Estimates

3-5 Carbon Tetrachloride Emission and Inventory Estimates

1953 to 1974

A 1974 Harmful and Potentially Harmful Materials Inventory (Barrick, 1974) indicated a chloroform inventory of 5,513 liters, or 8.9 tons. It is estimated that chloroform supplies were replenished at a rate such that approximately two-times the indicated inventory quantity (or about 18 tons per year) were used and released each year. Based upon the reported nature and extent of chloroform uses, it was unlikely that the replenishment rate for the solvent was significantly greater than this or that annual emissions were less than approximately one-quarter of the quantity kept on hand. Chloroform emissions of between 2 and 20 tons per year from 1953 to 1974 are estimated for screening purposes.

1975 to 1989

A number of data points relating to chloroform inventories, purchases, and usage rates at Rocky Flats after 1972 are shown in Figure 3-2 and summarized in Table 3-6. Additional details regarding emissions are presented in Appendix E. The Final Environmental Impact Statement for the Rocky Flats Plant Site (USDOE, 1980) includes a tabulation of consumption rates of the "major chemicals" for fiscal year 1977. No mention of chloroform use is included. Purchasing records from the Rocky Flats warehouse (EG&G, 1974-1988) indicate that chloroform orders totaled 360 gallons (2.2 tons) in 1985 and 300 gallons (1.8 tons) in 1986.

APEN calculations indicate a site-total chloroform emission rate of 0.84 ton per year based on 1986 usage data (EG&G, 1990-1991). A chemical inventory database containing estimates of quantities of hazardous materials kept on hand in 1988-1989 indicated that approximately 0.55 ton of chloroform was at the Rocky Flats facility (Setlock, 1990). It is estimated that chloroform emissions decreased linearly from a range of 2 to 20 tons per year in 1974 to a range of 0.5 and 5 tons per year in 1989. The 1989 value that defines the lower bound of plausible chloroform emissions for this period (.5 ton per year) is approximately 25 percent below the APEN chloroform emission estimate and slightly below the 1988/1989 inventory quantity for chloroform. In the later years of Rocky Flats operations, uses of chloroform were relatively minor. As a result, there was an increasing likelihood that minor operations contributing significant proportions to the site emission total went unidentified. While the APEN assumption of complete volatilization likely tended to cause emissions to be overstated, it is also possible that unidentified minor chloroform emission sources existed and that inventories reported in 1988/1989 underwent some replenishment during each year.

Review of available information indicates that it is unlikely that emissions of chloroform in the late-1980s exceeded the 1988/1989 inventory quantity by a factor of ten. As a result, the 1989 chloroform emission rate that defines the upper bound of plausible chloroform emissions was estimated to be 5 tons per year.

3-2 Chloroform Emission Estimates

3-6 Chloroform Emission and Inventory Estimates

3.2.3 Methylene Chloride

As described in the Tasks 3 and 4 report, historical uses of methylene chloride at Rocky Flats are not well documented. Methylene chloride has been present in paints and paint strippers used at the plant, it is an ingredient in the Cee Bee® solution used in aqueous component cleaning in Building 460, and has been used in several laboratories and process areas for sample preparation and analysis. Historical emission rates of methylene chloride have been established based on estimates of quantities of the material used or kept on hand, limited warehouse purchasing records, and statements made during interviews of retired and active workers. The time period from 1952 to 1989 has been divided into two time spans based on the available information and factors discussed below.

1953 to 1974

A 1974 Harmful and Potentially Harmful Materials Inventory (Barrick, 1974) indicated a methylene chloride inventory of 1,502 liters, or 2.2 tons. A range of between 3 and 15 tons per year is estimated for screening purposes for the period from 1953 to 1974. Based upon the 1974 inventory quantity of 2.2 tons, purchasing record indications of replenishment during the year, and the indication in worker interviews that methylene chloride usage was significant before 1974, it is unlikely that emissions from 1953 to 1974 were less than 3 tons per year. The plausible upper bound of annual methylene chloride emissions is consistent with an ordering frequency of between five and seven times per year observed in warehouse purchasing records (EG&G, 1974-1988) and the 1974 inventory of 2.2 tons.

1975 to 1989

A number of data points relating to methylene chloride inventories, purchases, and usage rates at Rocky Flats after 1974 are shown in Figure 3-3 and summarized in Table 3-7. Additional details regarding emissions are presented in Appendix E. The Final Environmental Impact Statement for the Rocky Flats Plant Site (USDOE, 1980) includes a tabulation of consumption rates of the "major chemicals" for fiscal year 1977. No mention of methylene chloride use is included. Purchasing records from the Rocky Flats warehouse (EG&G, 1974-1988) indicate that methylene chloride orders totaled about 825 gallons (4.6 tons) in 1980 and about 600 gallons (3.4 tons) in 1984.

APEN calculations indicate a site-total methylene chloride emission rate of 3.3 tons per year (EG&G, 1990-1991). A chemical inventory database containing estimates of quantities of hazardous materials kept on hand in 1988-1989 indicated that approximately 0.31 ton of methylene chloride was at the Rocky Flats facility (Setlock, 1990). Another report of Rocky

3-3 Methylene Chloride Emission Estimates

3-7 Methylene Chloride Emission and Inventory Estimates

Flats methylene chloride usage in 1989 listed a total of 616 pounds (0.3 ton) of methylene chloride (Grocki, 1989a).

It is assumed that methylene chloride emissions decreased linearly, ranging from between 3 to 15 tons per year in 1974 to between 0.5 and 5 tons per year in 1989. Based upon the 1989 inventory of 0.31 tons of methylene chloride, documented replenishment rates during the 1980s, and the APEN emission estimate of 3.3 tons per year, it is unlikely that annual emissions of methylene chloride were less than 0.5 ton per year.

The 1989 point (5 tons per year) that defines the upper bound of methylene chloride emissions is based upon the APEN emission estimate of 3.3 tons per year and the possibility that; due to the continued widespread U.S. use of methylene chloride in paint strippers, pesticides, and certain aerosol products (ATSDR, 1991); unidentified minor methylene chloride emission sources existed. It is unlikely that actual emissions significantly exceeded the APEN estimate, however, due to the conservative assumption in the APEN assessment that all methylene chloride that was used was lost to the atmosphere.

3.2.4 Tetrachloroethylene

As described in the report of Tasks 3 and 4, tetrachloroethylene (PCE) was widely used for uranium and plutonium part cleaning and degreasing in Buildings 881, 444, 883, 771, and 776 (ChemRisk, 1991-1992, Interview Nos. 39,48,53,78) for a large portion of Rocky Flats history. The estimated range of historical emissions of PCE is based on estimates of quantities of material used or kept on hand and statements made by retired and active workers during interviews. The period of interest from 1953 to 1989 can be broken into the following time spans based on the available information summarized below.

1953 to 1961

Uranium machining during the early years of Rocky Flats operation was typically performed with a 15:1 Shell Vitrea 923-8D oil and tetrachloroethylene mixture (Navratil and Miner, 1984). Because PCE has a relatively low volatility, it was not widely used on plutonium. PCE was substituted for carbon tetrachloride for about four months in 1966, but residue built up on inspection devices and on the plutonium, and its use was abandoned (Musgrave and Hornbacher, 1973). According to a former Building 881 worker, about 25 drums (assumed to contain 55 gallons each) per month of PCE were used in enriched uranium operations, with about 10 percent recovered (ChemRisk, 1991-1992, Interview No. 39). PCE was distilled from oil in Building 881 (Navratil and Miner, 1984).

Based upon the reported quantity of PCE used in Building 881 and the reported but unquantified used of the solvent in four other Rocky Flats buildings, an upper bound of plausible PCE emission was set at 300 tons per year. It is unlikely that site-total emissions exceeded three times the Building 881 estimate because PCE was used mainly in fabrication of uranium weapon components, and the assumption of complete evaporation of the PCE that was used is quite conservative given the relatively low volatility of the solvent.

Even with the relatively low volatility of PCE, the reported quantity of the solvent used in Building 881 alone during the period (100 tons per year) indicates that it is unlikely that annual emissions were less than 50 tons per year. A lower bound of plausible PCE emission was set at 50 tons per year for the period from 1953 through 1961.

1962 to 1966

Around 1962, enriched uranium operations (the oralloy line) were lost to the Oak Ridge Y-12 Plant as the Department of Defense moved to eliminate functional redundancy among the nation's weapon production facilities. Over the period from 1962 to 1966, use of PCE decreased due to phase-out of enriched uranium recovery and machining activities. PCE emissions are estimated to have decreased to about one-third of their peak values over the four-year period between when oralloy operations were phased out of Building 881 and when they were replaced by J-line stainless steel operations in 1966. PCE emissions are estimated to have decreased linearly, ranging from between 50 and 300 tons per year in 1961 to between 20 and 100 tons per year in 1966.

1967 to 1977

A few data points relating to PCE inventories and usage rates at Rocky Flats after 1972 are shown in Figure 3-4 and in Table 3-8. Additional details regarding emissions are presented in Appendix E. Beginning around 1973, solvent substitution efforts saw PCE being replaced by TCA for plutonium component degreasing. A 1974 Harmful and Potentially Harmful Materials Inventory (Barrick, 1974) indicated a PCE inventory of only 8 tons. The Final Environmental Impact Statement for the Rocky Flats Plant site (USDOE, 1980) includes a tabulation of consumption rates of the "major chemicals" for fiscal year 1977. No mention of PCE use is included. Based on these few data points, it is assumed for screening purposes that PCE emissions decreased linearly from a range of 20 to 100 tons per year in 1966 to between 0.000010 and 1.0 ton per year in 1977.

3-4 Tetrachloroethylene Emission Estimates

3-8 Tetrachloroethylene Emission and Inventory Estimates

1978 to 1989

APEN calculations indicate a site-total PCE emission rate of 0.00007 ton per year for 1986-1987 (EG&G, 1990-1991). A chemical inventory database containing estimates of inventories of hazardous materials kept on hand in 1988-1989 indicated that approximately 0.003 ton of PCE was at the Rocky Flats facility (Setlock, 1990). Another report of Rocky Flats PCE usage in 1989 listed a total of .0882 pound (.00004 ton) of PCE (Grocki, 1989a). Based on this information, PCE emissions are estimated for screening purposes to have ranged from between 0.000010 and 1.0 ton per year during 1978 to 1989.

3.2.5 1,1,1-Trichloroethane

As described in the Tasks 3 and 4 report, 1,1,1-trichloroethane (TCA) was used in cleaning and degreasing of metal parts for a large portion of Rocky Flats history. It is probable that use of the solvent began with the increased use of oils and solvents around 1957, when increased demand for plutonium components brought about the end of "dry" machining of plutonium. Various sources of information concerning TCA usage at Rocky Flats and emissions from 1974 to 1989 are summarized in Table 3-9 and depicted in Figure 3-5. Additional details regarding emissions are presented in Appendix E. The time period of interest from 1953 to 1989 can be broken into the following time spans.

1953 to 1957

There are no indications of TCA use prior to 1957. For screening purposes it is assumed that airborne emissions ranged between 0 and 5 tons per year from 1953 to 1957.

1958 to 1973

Although the earliest documented use of TCA was in 1963, it is probable that use of the solvent began with the increased use of oils and solvents around 1957. Available information suggests that TCA was used to clean parts in plutonium production areas of Buildings 771 and 776 from approximately 1958 to 1973. TCA was initially avoided in plutonium machining applications due to explosion hazard; in at least one instance, an explosion occurred when TCA was inadvertently substituted for TCE in a plutonium machining operation (Hobbs, 1970).

The airborne emissions for this period are assumed to be relatively consistent with the 1974 inventory quantity of 34 tons (Barrick, 1974). It is estimated that 1958 to 1963 was a period of transition to increased use of TCA, and that TCA emissions for the period from 1963 to 1973 ranged from 20 to 60 tons per year.

3-9 1,1,1-Trichloroethane Emission and Inventory Estimates

3-5 1,1,1-Trichloroethane Emission Estimates

1974 to 1984

TCA began replacing trichloroethylene (TCE) for vapor degreasing of parts in plutonium areas beginning around 1973. By the end of 1974, TCE remained in use in only one plutonium operation, and was used only in research and analytical activities by February 1975. The Final Environmental Impact Statement (USDOE, 1980) reported annual usage of TCA in 1977 of 4,675 gallons (26 tons).

As a result of the substitution of TCA for TCE, emissions of TCA are estimated to have reached a range of between 40 and 120 tons per year during the late 1970s based on a limited number of warehouse purchasing records from the early 1980s, suggesting purchases of 70 to 80 tons per year (EG&G, 1974-1988).

1985 to 1989

As mentioned above, purchasing records from the Rocky Flats warehouse (EG&G, 1974-1988) indicate that TCA orders totaled between 70 and 80 tons per year in the early 1980s. In the middle to late 1980s, another round of solvent substitution efforts began that included use of isopropyl alcohol and De-Solv-it® in place of TCA in a number of non-plutonium cleaning operations. In 1988, cleaning practices in Building 447 involved submerging parts in a TCA tank to remove oils, grease, or wax, followed by submersion in Oakite® detergent solution and then an aqueous rinse tank. At that time, use of De-Solv-it® instead of TCA was recommended in order to eliminate use of chlorinated solvents (Weis, 1988a). Water and detergent solutions could not be used on plutonium, however, because water rapidly corrodes plutonium (Musgrave and Hornbacher, 1973). Orders of TCA dropped to 33 tons in 1987, and the 1988-1989 inventory of 2.6 tons (Setlock, 1990) represents a 92% decrease from the 1974 value. Based on these factors and the identified data points from studies addressing TCA uses and emissions from 1987 to 1989, it is estimated that TCA emissions decreased linearly from between 40 and 120 tons per year in 1984 to between 10 and 60 tons per year in 1989. These estimates are not inconsistent with other estimates of TCA use in 1988 and 1989 ranging from 17 to 46 tons per year (EG&G, circa 1990; EG&G, 1990-1991; Ferrera, 1988; Church, 1989; Hamilton and Moser, 1990; USDOE, 1989; Weis, 1988b).

3.2.6 Trichloroethylene

As described in the Tasks 3 and 4 report, trichloroethylene (TCE) was used in large quantities at Rocky Flats to clean and degrease beryllium, plutonium, and uranium parts. Historical emissions of TCE have been estimated based on quantities of the solvent used or kept on hand, warehouse purchasing records, some limited effluent monitoring data, and statements from active and retired workers. The time period of interest from 1953 to 1989 can be broken into the following time spans based on the available information and factors discussed below.

1953 to 1962

According to a former Building 881 worker, about 25 drums (assumed to contain 55 gallons each) per month of TCE were used in enriched uranium operations, with about 10 percent recovered. TCE was used in the Soxhlet extraction process for enriched uranium recovery (ChemRisk, 1991-1992, Interview No. 39) and was widely used in vapor degreasers for part cleaning. TCE was distilled from oil in Building 881 (Navratil and Miner, 1984). Based on this reported level of use of the solvent, the estimated TCE emissions for this period range between 50 and 200 tons per year.

1963 to 1973

During 1962, enriched uranium operations (the oralloy line) were moved to the Oak Ridge Y-12 Plant as the Department of Defense moved to eliminate functional redundancy among the nation's weapon production facilities. Over the period from 1962 to 1963, use of TCE decreased due to the phase-out of enriched uranium recovery and machining activities. The decrease in TCE usage due to loss of oralloy operations was somewhat offset by efforts to substitute TCE for acetone, isopropyl alcohol, and other solvents for cleaning plutonium, beryllium, and uranium parts. An internal Rocky Flats Plant memo indicates that 10,000 gallons (or about 62 tons) of TCE were used plant-wide during 1973 (Musgrave and Hornbacher, 1973). A report on the annual usage of TCE indicated site-total consumption of 60 tons of TCE during 1973 (Dow Chemical, 1972-1974). Based on these reported levels of use of the solvent, and the reported reduction in use during 1962 and 1963, TCE emissions for 1973 are estimated to have ranged between 30 and 90 tons per year.

1974 to 1975

Various data points relating to TCE inventories, purchases, and usage rates at Rocky Flats after 1972 are shown in Figure 3-6 and summarized in Table 3-10. Additional details concerning emissions are presented in Appendix C. In late 1973, the Rocky Flats Area Office of the Atomic Energy Commission (USAEC) made commitments to the Environmental Protection Agency (USEPA) regarding elimination of TCE use in certain Rocky Flats buildings that were estimated to be exceeding TCE emission limits (Thompson, 1973). By the end of 1974, TCE remained in use in only one plutonium operation and was used only in research and analytical activities by February 1975 (Bean, 1975). A 1974 Harmful and Potentially Harmful Materials Inventory (Barrick, 1974) indicated a TCE inventory of 25 tons, while purchasing records from the Rocky Flats warehouse (EG&G, 1974-1988) indicate that TCE orders totaled only 15 drums

3-6 Trichloroethylene Emission Estimates

3-10 Trichloroethylene Emission and Inventory Estimates (about 5 tons) in 1974. It is estimated that TCE emissions decreased linearly from between 30 to 90 tons per year in 1973 to between 5 and 25 tons per year in 1975.

<u>1976 to 1989</u>

TCE was used only for research and analytical activities by February 1975 (Bean, 1975). An Air Pollution Emission Notice for Building 460 erroneously reported the release of TCE in the amount of 0.15 ton per year for 1986-1989, when in fact TCA had actually been used (Costain, 1992). APEN emission estimates for Building 374, the only other APEN reporting TCE release, were extremely minor at 1.5 x 10^{-3} ton per year (EG&G, 1991d). The Rocky Flats Plant Final Environmental Impact Statement (USDOE, 1980) indicated that 330 gallons (2 tons) per year of TCE were consumed at the plant in 1977. A chemical inventory database containing estimates of inventories of hazardous materials kept on hand in 1988-1989 indicated that approximately 0.15 ton of TCE was at the Rocky Flats facility (Setlock, 1990), while purchasing records from the Rocky Flats warehouse (EG&G, 1974-1988) indicate that TCE orders totaled 2 or 3 drums every two years from 1979 to 1983. Another report of Rocky Flats TCE usage in 1989 listed a total of 13 milliliters of TCE present, all of which was located in laboratory areas (Grocki, 1989b). Based on this documentation, it is estimated for screening purposes that TCE emissions decreased linearly from between 5 and 25 tons per year in 1975 to between 0.0010 and 1.0 ton per year in 1989.

3.2.7 Emission Estimates of Organic Solvents

Unlike airborne releases of radioactive materials and beryllium, there is little or no routine effluent sampling data for organic solvents. In this section, the ranges of plausible emissions of organic solvents are presented based on historical information on material purchases, uses, disposal, and recycling. Upper and lower bounds of emissions for carbon tetrachloride, chloroform, methylene chloride, tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene from 1953 through 1989 are listed in Table 3-11 through 3-16. The emission bounds have been established with the intent of ensuring that the ranges encompass the actual value for any one year.

3-11 Upper and Lower Bound of Carbon Tetrachloride Emission (1953-1989)

3-12 Upper and Lower Bounds of Chloroform Emission (1953-1989)

3-13 Upper and Lower Bounds of Methylene Chloride Emission (1953-1989)

3-14 Upper and Lower Bounds of Tetrachloroethylene Emission (1953-1989)

3-15 Upper and Lower Bounds of 1,1,1-Trichloroethane Emission (1953-1989)

3-16 Upper and Lower Bounds of Trichloroethylene Emission (1953-1989)

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4.0 UNCERTAINTY IN AIRBORNE EMISSION ESTIMATES

Uncertainties in emission estimates can arise from a number of sources, and many of these sources have been described and discussed in the preceding sections and are further elaborated on here. Two general approaches to quantifying the uncertainty in emission estimates have been adopted in this report. The first approach, which is employed when emission estimates are developed primarily from effluent monitoring data, involves the examination and quantification of the potential error introduced as a result of the various elements of the sampling and analytic programs.

The second approach to quantifying uncertainty is used when there is little or no routine effluent sampling data and estimates must be developed based on a variety of documents and information obtained from personnel interviews. In this case, the range of potential emissions for specified periods of the plant's operating history are bounded for a particular material of concern. Upper and lower bounds of estimated solvent emissions were presented in Section 3. The bounds have been established with the intent of ensuring that the range encompasses the actual value for any one year.

The purpose of this section is to quantify on the uncertainties in the emission estimates of radioactive and nonradioactive materials that were based on effluent monitoring data.

4.1 Random and Systematic Errors

Errors associated with a measurement can be either random or systematic. When a measuring instrument is used repeatedly to measure some attribute, the readings or results will typically be distributed around a given value. The fluctuation of readings around a given value is dependent on the sample matrix, the instrument, and the experimental condition. This type of measurement error, also called random error, can be reduced but can never be completely eliminated. Random error may be reduced either by improving the precision of the instrument or by tightening the control of the sampling conditions, or both.

The influence of random errors in estimating some value can also be reduced by taking many measurements and averaging them. When many measurements are taken, readings above the true value are likely to be balanced by readings below the true value. As a result, averaging many measurements will reduce the uncertainty in a value due to random error. It has been shown that the random error of an average is inversely proportional to $\sqrt{n}$, where n is the number of measurements.

On the other hand, systematic error may occur as a result of inaccurate or poorly designed sampling or analytic instruments. In this case, an instrument may give readings consistently higher or lower than the true value. Unlike random error, systematic error cannot be reduced by taking many measurements and calculating the average. However, systematic error in a sampling or analytical method can be detected and quantified by either measuring a standard, or comparing results with another method of known accuracy. Once the systematic error of an instrument or method is quantified, its effect on subsequent measurement results can be compensated for by using a correction factor. It is the purpose of this section to identify and quantify potential sources of systematic errors in developing release estimates of the contaminants of concern.

4.2 Uncertainty in Effluent Monitoring Program Results

As has been described, the sampling of contaminants in airborne effluents at the plant relies on the performance of the following basic calculation:

$$C = \frac{A}{V}$$

Where:

C = Concentration of a contaminant in effluent (quantity per cubic meter of air)

A = Quantity of contaminant in a sample (e.g., disintegrations per minute or micrograms)

V = Volume of sample (cubic meters of air)

Annual emissions from the facility (E) are then calculated by multiplying the concentration of a contaminant in an effluent (C) times the total amount of air released annually from the particular emission point and adding the resulting values up for the entire facility. The total amount of air released is based on the flow rate (Q) and the length of operation (T) of the exhaust system:

$$\mathbf{E = C \times Q \times T}$$

In order to perform these calculations, the plant performed the following activities, each having attendant uncertainties:

1) A fraction of the effluent stream was extracted,

2) Contaminants were collected from the extracted sample on filter paper,

3) Contamination was measured on a sample filter, and

4) The total volume of effluent air associated with the sampled stream was estimated or measured.

One of the objectives of the investigation and review of the sampling and analytic systems used by the plant and described in this report was to identify practices that would have led to systematic errors in the effluent data that were produced. The areas that were examined for systematic error included potential bias arising from the following plant activities:

1) Extraction of a fraction of the effluent stream.
   - Non-isokinetic sampling.
   - Nonrepresentative sampling.
2) Contaminant collection from the extracted sample on filter paper.
   - Sample line loss.
   - Sampling apparatus filter efficiency.
3) Contamination measurement on a sample filter
   - Self-absorption.
   - Insufficient sensitivity of methods.

As described in Section 2.2, most of these has been discussed in some detail and ruled out as significant sources of systematic error in the airborne contaminant monitoring system, in many cases, because of correction factors used by the plant to compensate for these errors.

Two areas that were identified as the largest potential sources of error or uncertainty for particulate sampling and that are also important in tritium sampling involve the first and last steps of the process. As part of the first step involving the extraction of a fraction of the effluent stream, the determination of the size of the fraction (V, or volume of sample) that is extracted is dependent on knowledge of the flow rate of the sampling device. However, documentation suggests that in mid-1974 the target sampling flow rate (2 ft^3 min^{-1} or 56.6 L min^{-1}) was routinely used as opposed to the actual measured rate (Rockwell, 1976b) for particulate sampling and 50 cubic centimeters per minute for tritium sampling. To the extent that flow rates were regularly readjusted to the target rate, fluctuations around the target resulted in random errors that were unimportant given the thousands of measurements made. However, the limited review of some actual particulate sampling flow rates during the period after 1974 suggests that actual flow rates may frequently have varied significantly from the target rate, more frequently low than high, which would lead to the underestimation of emissions. Based on the result of a special study, a frequency distribution of the measured sampling flow rates divided by 56.6 L min^{-1} is presented in Figure 2-2. This figure represents a distribution of values that can be used to compensate for the bias in sampling flow rate. For the purpose of this analysis, the correction factor of sampling flow rate was assumed to be normally distributed with a calculated mean of 0.92 and a standard deviation of 0.11.

As described in Section 2.2.1.2, sampling flow rates have historically been set at approximately 50 cm^3 min^{-1} for tritium samplers. However, the actual average sampling flow rate is likely to be larger than this value. It is because water was used as the trapping medium for tritium; as sampled air was bubbled through the medium, a portion of water was lost to evaporation. This resulted in a drop in resistance to air flow and an increase of sampling flow rate. Since data to characterize the variability of the actual sample flow rates were not located, it is assumed that the correction factor of tritium sampling has a triangular distribution with a best estimate of 1.2 and an upper and lower bounds of 1.5 and 0.9, respectively.

The second identified source of potential significant error is in the last step of the process, the quantification of the effluent flow rate (Q) needed to establish the total volume of air released from the plant. As discussed in Section 2.2.1.5, there was little documentation of the methods used to establish the flow rates or the actual air volumes used to calculate emissions from the plant during the 1950s, 1960s, and early 1970s. The data review suggested that the basis for the flow rates used by the plant may have ranged from engineering design flow rates to rates based on a variety of different sampling or testing programs. In the mid-1970s, the plant began to employ flow totalizers to quantify flow rates in the exhaust systems, which should have reduced the importance of the flow rate factor as a source of uncertainty; however, indications from a recent study are that this may not be the case. It is estimated that the actual average annual exhaust flow volumes may have ranged from one-half to two times the standard volumes that were used in most calculations. Therefore, the uncertainty in emissions estimated due to the lack of documentation of exhaust flow volumes was represented by treating emission estimates as triangular distributions with lower and upper bounds at 0.5 and 2 times the reported value, with the most probable value equal to the reported value.

Beginning in 1974, the plant also began reporting the average relative error associated with the techniques used to quantify the various contaminants present in effluents. The plant annual environmental reports indicate that these error terms include all random and systematic errors in the standards, analytical chemistry, and measurement process for elements collected on effluent filters. Investigators were unable to clearly establish whether the plant corrected the reported release estimates for these errors; however, it is believed that they did not. In order to compensate for the analytical bias, correction factors based on the relative errors will be applied to the release estimates reported between 1974 and 1989 (Table 4-1).

Information about the accuracy of the long-lived gross alpha data measured before 1974 is not available. As there was a continuous improvement of radiation detection technology in the 1960s and 1970s, it is reasonable to assume that the relative error introduced by the counting procedure had also decreased over time. For the purpose of this evaluation, it was assumed that the uncertainty associated with gross alpha counting before 1974 is about twice as large as that of Pu-239/240 measured between 1974 and 1989. Using this approach, the relative error associated with gross alpha analysis performed between 1953 and 1973 was represented by a normal distribution with a mean of 1.1 and a standard deviation of 0.3.

In the case of tritium sampling, a study (described in Section 2.2.1.1.) was also identified that indicates that poor efficiency with the standard sampling device. Poor tritium collection efficiencies are believed to result in the underestimation of tritium emissions. The uncertainty associated with tritium sampling efficiency was represented by treating emission estimates as triangular distributions with lower and upper bounds at 1.3 to 4.8 times the reported values and a most probable value of 3.0.

4.3 Uncertainty Associated with Estimating Specific Isotopic Releases Based on Nonspecific Monitoring Data

Before 1973, only long-lived gross alpha activities in effluent flows were routinely measured and reported. As described in Section 2.4, release estimates of specific isotopes for this time period were carried out in two steps. First, long-lived gross alpha activity sampled in effluents from buildings in which plutonium was handled was assumed to consist solely of those alpha-emitting nuclides associated with weapons grade plutonium, and activity in effluents from buildings in which uranium was handled was assumed to consist solely of those radionuclides associated with enriched or depleted uranium, depending on the type of uranium handled. Second, based on known ratios of and Am-241 to Pu-239/240 and Pu-241 to Pu-239/240, release estimates of Pu-239/240, Am-241 and Pu-241 were calculated from the gross alpha data. Potential sources of uncertainty associated with this approach are evaluated and estimated in Appendix F.

4-1 Correction Factors to Compensate for the Analytical Errors in the Monitoring Results Reported from 1974 through 1989

Even after 1973, airborne releases of beta-emitting Pu-241 were not routinely measured by the plant. Therefore, source terms of Pu-241 from 1974 to 1989 were calculated from release estimates of Pu-239/240 and special study results which quantified the ratio of Pu-241 to Pu-239/240 in effluent releases. Uncertainty associated with this calculation is also estimated in Appendix F.

4.4 Overall Uncertainty Associated with Release Estimates of Contaminants

In summary, review of the sampling and analytic systems used to monitor plant effluent identified a number of potential sources of random and systematic errors. The potential sources of random error are numerous; however, the contribution of these sources of error to the overall uncertainty in the annual emission estimates is small given the large number of samples that were collected to establish the annual estimate. Potential sources of systematic error due to lack of information about the identity of the analyte and estimation of sampling flow rates and exhaust flow rates are identified. Uncertainty factors were developed to represent these potential sources of uncertainty. As described in Appendix G, overall uncertainty factors for the release estimates of the contaminants of concern were calculated using a statistical technique called Monte Carlo simulation. A brief description of Monte Carlo simulation and its application in this evaluation is provided in Appendix H.

The annual emission estimates were then multiplied by the appropriate overall uncertainty factors to generate a probability distribution for the annual emissions. It is believed that the use of these emission probability distributions will bound the actual emissions in a year. If dose assessment results suggest the need, the range of uncertainty in these emissions could probably be reduced following further evaluation of plant practices. The historical emission estimates and their uncertainties that will be used to estimate off-site doses resulting from plant operations are summarized in Table 4-2 through 4-4 and Figures 4-1 through 4-6 for plutonium, uranium, americium-241, and tritium. The lower and upper bounds identified in the tables and figures represent the boundaries of the 95 percent confidence interval centered on the geometric mean.

The emission estimates for tritium prior to 1974 are not based on measurements. The estimated range of annual tritium emissions for this period was treated as a uniform distribution with the identified lower and upper bounds of 1 and 800 for the period of 1953 through 1967 and 140 and 390 for the period of 1968 through 1973.

Table 4-5 and Figure 4-7 provide the release estimates and the uncertainties for beryllium. They are based on the release estimates reported in Section 3.1 and the two overall uncertainty factors of beryllium developed as described in Appendix G. The lower and upper bounds identified in the table and figures represent the boundaries of the 95 percent confidence interval centered on the geometric mean.

4-2 Airborne Emission Estimates and Uncertainties - Plutonium

4-3 Airborne Emission Estimates and Uncertainties - Uranium

4-4 Airborne Emission Estimates and Uncertainties - Americium-241 and Tritium

4-1 Airborne Release Estimates and Uncertainties - Plutonium Alpha

4-2 Airborne Release Estimates and Uncertainties - Plutonium-241

4-3 Airborne Release Estimates and Uncertainties - Enriched Uranium

4-4 Airborne Release Estimates and Uncertainties - Depleted Uranium

4-5 Airborne Release Estimates and Uncertainties - Americium-241

4-6 Airborne Release Estimates and Uncertainties - Tritium

4-5 Airborne Emission Estimates and Uncertainties - Beryllium

4-7 Airborne Release Estimates and Uncertainties - Beryllium