

APPENDIX D

**AN ANALYSIS OF HISTORICAL SOURCE TERM
ESTIMATES FOR CARBON TETRACHLORIDE AT THE
ROCKY FLATS PLANT**

**AN ANALYSIS OF HISTORICAL SOURCE TERM ESTIMATES
FOR CARBON TETRACHLORIDE AT THE ROCKY FLATS
PLANT**

by

P.D. McGavran, K.R. Meyer, P.G. Voillequé, M. Dreicer and J.E. Till

RAC Report No. 8-CDPHE-RFP-1996

CONTENTS

INTRODUCTION	D-5
CARBON TETRACHLORIDE USE AT THE ROCKY FLATS PLANT	D-6
A REVIEW OF PHASE I RELEASE ESTIMATES	D-6
CARBON TETRACHLORIDE EFFLUENT AND ENVIRONMENTAL MONITORING	D-10
EVALUATION OF HISTORICAL PROCESS CHANGES	D-10
DISCHARGE OF CARBON TETRACHLORIDE TO SURFACE WATER.....	D-11
SURFACE WATER MONITORING.....	D-14
EVALUATION OF CERCLA MONITORING DATA	D-15
CARBON TETRACHLORIDE IN WASTE GENERATED AT ROCKY FLATS.....	D-16
CARBON TETRACHLORIDE IN WASTE SHIPPED TO IDAHO.....	D-18
UNCERTAINTY	D-20
Phase I Estimates of Uncertainty	D-20
PHASE II ESTIMATES OF UNCERTAINTY	D-20
Carbon Tetrachloride Inventory Amounts and Usage Information	D-20
Carbon Tetrachloride in Air	D-20
Carbon Tetrachloride in Surface Water.....	D-21
Carbon Tetrachloride in Groundwater.....	D-21
Carbon Tetrachloride in Waste.....	D-22
CONCLUSIONS.....	D-23
REFERENCES	D-25

INTRODUCTION

Large quantities of carbon tetrachloride were used at Rocky Flats to clean and degrease product components and equipment. Although several short term studies of carbon tetrachloride in airborne effluents were conducted ([Johnson et al. 1974a](#); [Hamilton and Moser 1990](#)), carbon tetrachloride was not routinely monitored in air or water effluents.

In our review of the Phase I Source Term and Uncertainty Estimates ([Grogan et al. 1994](#)), RAC outlined limitations of the Phase I estimates. Phase I estimates of carbon tetrachloride release were based on the assumption that all of the carbon tetrachloride used evaporated into the atmosphere and was an airborne emission. Usage was estimated from inventory amounts. Releases from liquid and solid waste were not addressed explicitly in Phase I because all of the carbon tetrachloride on hand was assumed to have evaporated as it was used, before it became waste. This approach seems justified, especially for determining a maximum emission rate. However, the assumption of complete volatilization is conservative and leads to a worst case estimate rather than a realistic best estimate of solvent releases to the atmosphere.

An attempt is made here to review the carbon tetrachloride emission estimates, determine the environmental and disposal fate of carbon tetrachloride more precisely, define the amount of carbon tetrachloride that may not have volatilized, and address the uncertainty that may be associated with the carbon tetrachloride release estimates. It was hoped that estimates of the quantity of carbon tetrachloride that was disposed of or discharged in other ways might provide a lower bound to an airborne emissions estimate, as well as allow additional exposure pathways to be further investigated and characterized.

The most relevant questions are:

- Can the assumption that total evaporation of all of the carbon tetrachloride used at the RFP be used as a reasonable basis for estimating releases?
- Is it possible to improve the emission estimates for carbon tetrachloride by reevaluating the operations history of the plant?
- How much carbon tetrachloride could have been released to the surface or ground water and could drinking water have been a significant exposure pathway?
- How much carbon tetrachloride was stored in drums at the 903 Pad and subsequently shipped off-site for disposal?
- What are the largest sources of uncertainty in the release estimates?
- Is the information available sufficient to allow some quantitative estimate of uncertainty to be determined?

These questions are addressed in the following sections, along with: a [discussion](#) of how carbon tetrachloride was used at the plant, a [review](#) of the Phase I release estimates, a [review](#) of environmental and effluent monitoring data for carbon tetrachloride, an [evaluation](#) of process changes that may have influenced carbon tetrachloride use and discharge through the years, an [assessment](#) of carbon tetrachloride release to surface water, ground water and carbon tetrachloride in waste that was shipped to Idaho, and a [description](#) of uncertainty associated with these estimates.

CARBON TETRACHLORIDE USE AT THE ROCKY FLATS PLANT

Carbon tetrachloride was used in Buildings 776/777, 707, 774, 460 and 881 to clean glove-box walls, furnaces, product components, scraps and chips, machinery and instruments ([ChemRisk](#) 1992). Building 707, which housed the foundry, casting operations and products assembly and Building 777/776, where assembly and machining were conducted, were the major users of carbon tetrachloride. ChemRisk estimated that about 80% of the total emission estimate came from Building 707 and about 20% from Building 776/777 ([ChemRisk](#) 1994).

Beginning in 1958, machining of plutonium was done using Shell Vitrea cutting oil. Carbon tetrachloride was used during and after machining to wash the oil from parts and equipment. Machining of uranium was also done using a 15:1 oil:carbon tetrachloride mixture ([ChemRisk](#) 1992). Fabrications used carbon tetrachloride to remove coolant oil from parts and work areas during and after machining and in ultrasonic cleaners prior to inspection. Metallurgical Operations used carbon tetrachloride in dip tanks to degrease lathe turnings prior to briquetting ([Musgrave](#) 1975). In fact, the briquetting and chip degreasing emissions had the highest carbon tetrachloride concentrations, up to approximately 13% by volume ([ChemRisk](#) 1992). In Building 707, parts were placed into metal baskets and dipped into a series of five carbon tetrachloride open surface baths, each in a steel tank containing about 4 gallons of carbon tetrachloride. The briquetting operation in Building 776/777 used four carbon tetrachloride baths of similar construction. Carbon tetrachloride was also used in extraction operations on a laboratory scale ([ChemRisk](#) 1992). No emission controls for carbon tetrachloride were present in any of the buildings. Emissions were more directly related to the quantity used and the fraction that evaporated and significant fluctuations due to failure or variability in the effectiveness of control devices was not a factor ([ChemRisk](#) 1992).

The quantity of carbon tetrachloride used was not directly correlated to production. Although carbon tetrachloride was used during the production process, it was also used extensively during periods of downtime to clean equipment and glove-boxes. Solvent baths and ultrasonic cleaners were more likely to have been changed out when the production lines were idle.

A REVIEW OF PHASE I RELEASE ESTIMATES

Release estimates for Phase I were based on original inventories from 1974 and 1988/89 and usage data from 1977. Summary reports and various estimates of emissions based on different kinds of use data were also considered in determining the range of estimates.

The 1974 Inventory reported 12,500 kg of carbon tetrachloride. The 1988/89 Inventory reported 7,060 kg, indicating nearly twice as much carbon tetrachloride was kept on hand in 1974 as in 1988. The 1977 annual usage rate reported in the 1980 Final Environmental Impact Statement was 31,697 kg per year, 2.5 times greater than the 1974 inventory amount and 4.5 times greater than the 1988 inventory amount. ChemRisk made the general assumption that reported inventory quantities represented about 10% of annual usage, which for carbon tetrachloride was a conservative assumption, likely to lead to overestimates of usage. The results of the Phase I Stage 2 Screening yielded a ratio of the actual quantity (12,592 liters or approximately 12,592 kg) to the allowable quantity (0.56 kg) of 2.23×10^4 . Chemicals with ratios greater than one were assumed to be present in sufficient quantities to potentially pose an off-site health hazard and were considered chemicals of concern ([ChemRisk](#) 1991).

Estimates of plausible ranges of historical emissions for chlorinated solvents materials were developed by ChemRisk using various types of inventory and usage documentation, such as Air Pollution Emissions Notifications (APENs), special effluent monitoring studies conducted by the plant, estimates of quantities of materials used, kept on hand or recorded on inventories, and information obtained from personnel interviews. Routine effluent monitoring for carbon tetrachloride was not performed by the plant. Insufficient historical information was found on material purchases, uses, disposal and recycling to apply mass balance calculations ([ChemRisk 1994](#)). It appears that all of the estimates were considered in developing the range of emissions for Phase I and the reasons for ignoring or accepting various estimates are not discussed. Linear trends were assumed for time periods when no information was available. In many cases the emission estimates for volatile organic solvents were based on very little information, but ChemRisk believed that the range of emissions estimated bound the actual plausible emissions from the plant ([ChemRisk 1994](#)).

The period of operation, 1953-1989 was broken down into three time periods related to the estimates of emissions.

- 1953 - 1957: Large scale plutonium production began in 1957. Before 1957, plutonium was worked dry, with no cutting oils. Carbon tetrachloride was used as a coolant from a squeeze bottle or in an oil mixture for both plutonium and uranium machining. Carbon tetrachloride was also used to clean typewriters and other equipment. The Phase I estimate for emissions during this period was 4-20 tons per year which is about one-tenth of the release estimate for the next time period of 1958-1970 ([ChemRisk 1994](#)).
- 1958-1970: This was the time period of maximum use. Most carbon tetrachloride was used in routine maintenance activities and cleaning. The release estimate for this period is 40–200 tons per year. The upper bound of 200 tons is 30% greater than the release rate of 153 tons per year that corresponds to the maximum level of carbon tetrachloride measured in 1974 and reported by [Hobbs \(1982\)](#), but the 153 tons per year represents peak measurements, not average measurements for that study ([Hobbs 1982](#)).
- 1971-1989: Attempts were made in the early 1970s to gradually eliminate carbon tetrachloride from some operations, due in part to the fact that effluent measurements from building stacks were occasionally high enough to exceed permissible exposure levels at ground level ([Musgrave 1975](#)). In 1974, Dow Chemical personnel recommended that trichloroethane replace carbon tetrachloride in the ultrasonic cleaners in Building 707. Carbon tetrachloride use was very slowly decreased at the plant but at the time of shutdown in 1989, carbon tetrachloride was still used in the plutonium facilities ([ChemRisk 1994](#)). [ChemRisk \(1994\)](#) 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.

The ChemRisk release estimates, which were given in ranges for three different time periods, were based on seven inventory, use survey or usage estimates, two solvent use studies, and four analyses of two short-term monitoring programs. These data sources are further described in [Table 1](#), the contents of which are taken from the narrative and tables in Appendix E of the Phase I, Task 5 Report ([ChemRisk 1994](#)).

Table 1. Carbon Tetrachloride Emission Estimates^c

Resource	Estimate Basis	Estimate Year	Emission Estimate tons/year		
			Building 707	Building 776/777	Total
Air Pollution Emissions Notice (APEN) (EG&G Rocky Flats 1990)	Use	1989	32	8	40 (includes Buildings 460 and 881)
DOE 1980	Use	1977			36
DOE 1980	Monitoring	1975			66
Fruehauf and Richter 1974	Use (monthly estimate from warehouse dispensing records)	1973	80		81
Hamilton and Moser 1990	Monitoring (small volumes, several sampling methods)	1989	53	33	89
USDOE 1989	Use (environmental team audit, 11 month usage rate)	1988			93
APEN (EG&G Rocky Flats 1990)	Use (air stack release tabulation)	1988			65
APEN (EG&G Rocky Flats 1990)	Use (air stack release tabulation)	1989			24
Hobbs 1982	Monitoring (data from Johnson et al. 1974)	1974-1975	46 (average)		56 (average)
Hobbs 1982	Monitoring (data from Johnson et al. 1974)	1974-1975	120 (maximum)		153 (maximum)
Hobbs 1982	Material Balance	1974-1975	20	15	34
Hobbs 1982	Material Balance	1974-1975			106 ^a
Ferrera 1988	Use (usage rate for 5 months in 1988)	1988-1989	50 (average)		48
Ferrera 1988	Use	1988	80 (maximum)		
Ferrera 1988	Use	1987-1988	93		
Dow Chemical (Johnson et al. 1974a) ^b	Monitoring (46 days in 1973)	1973		10 (average)	
Dow Chemical (Johnson et al. 1974a) ^b	Monitoring (46 days in 1973)	1973		34 (maximum)	
Rockwell 1988	Use (8 week solvent use study)	1988	66		
Rockwell 1989	Use (solvent use study)	1988-1989	48 (average)		
Rockwell 1989	Use	1988-1989	76 (maximum)		

^a ChemRisk stated that an explanation for the difference in the two estimates derived from mass balance provided in this report (Hobbs 1982) was not located.

^b In the Phase I, Task 2, 3&4 and 5 Reports, Dow Chemical (1974) is used to refer to both the 1974 Inventory, (best referenced as Barrick 1974) and the 1974 Hydrocarbon Emissions Booster No. One Report, (best referenced as Johnson et al. 1974a or referenced in either of two memos, Johnson 1971 and Johnson 1973).

^c In most cases, the 'use' estimates are based on inventory records and what was known about cleaning and machining practices

Most of the estimates were based on use and inventory data. These were compared to estimates which used monitoring data or material balance data, such as [Hobbs](#) (1982), which based emission estimates on the highest concentrations measured. The release estimates in [Hobbs](#) (1982) were made using material balance information, 1974-1975 monitoring data ([Johnson](#) 1973; [Johnson et al.](#) 1974b), and also included estimates of uncertainty: for carbon tetrachloride concentration fluctuations ($\pm 10\%$) and for questionable air flow measurements during monitoring ($\pm 12\%$). In general, the emissions estimates based on monitoring are not less than those based on use and inventory information. The estimates for Building 776/777 based on material balance ([Hobbs](#) 1982) were lower than other estimates based on use and monitoring.

In compiling the estimates, data from various reports in different units such as pounds per hour or kg per day were converted into tons per year. The assumptions that ChemRisk made about the workweek, workshifts, hours of operation per year, holidays, weekends, inventory periods, etc. and the duration of average emissions versus maximum emissions are important. In general, the same assumptions used in calculating the APEN report emissions were used whenever possible. Therefore the assumptions were consistent but perhaps not necessarily correct.

APEN reports for Buildings 707, 776/777, 460, 881 and 774 were considered. ChemRisk checked the calculations in the reports and found no significant flaws. The emission estimate for each APEN report was usually derived from a user estimate obtained from inventory information and an derived evaporation rate. For carbon tetrachloride, emission estimates in the APENs were calculated using standard emission factors for solvent degreasing operations published by the [USEPA](#) in AP-42 (1985). A reduction factor of 28%, based on good operating procedures and considered by ChemRisk to be conservative, was applied. The APEN estimates assumed complete volatilization of all carbon tetrachloride used in the buildings. Waste collection was not included since all of the carbon tetrachloride was assumed to have evaporated during use in the production operations. Each APEN accounted for all of the building vents in detail to demonstrate inclusion of all emissions, but none of the APENs estimates were based on monitoring data.

Support for the Phase I assumption of 100% evaporation comes simply from the physical characteristic of the rapid volatility of carbon tetrachloride. Although there is literature on the volatilization rates of carbon tetrachloride in soil and surface water, there is little information on volatilization from industrial processes. In a 1978 report by the Panel on Low Molecular Weight Halogenated Hydrocarbons it was estimated that dispersive losses accounted for as much as 90% of all losses to the environment. For carbon tetrachloride specifically, direct losses from production, transport and storage were estimated to represent about 7% of the total environmental release in the United States. The Panel surmised that most losses were fugitive transient losses such as those from leaky seals and valves or as a result of equipment malfunctions. They estimated that 22% of the atmospheric discharge was from dispersive losses in the use of the product (such as degreasing and dipping in baths as was done at the Rocky Flats Plant). The major dispersive use of carbon tetrachloride was thought to be from its use as a component of liquid grain fumigants in marine transportation. Losses occurred when carbon tetrachloride is pumped into the hold of ships, during transit and when the grain is unloaded. Other dispersive uses were thought to be minor contributors to environmental release ([NAS](#) 1978).

CARBON TETRACHLORIDE EFFLUENT AND ENVIRONMENTAL MONITORING

[ChemRisk](#) (1992) did attempt to use available monitoring data to estimate a release value. In the mid-1970s, the plant identified various processes at 14 locations in the RF facilities that used organic solvents in sufficient quantities to justify a stack surveillance program. Plant reports recognized that although the liquids were controlled and disposed of in an acceptable manner, the vapors were generally not controlled and were exhausted to the atmosphere through building exhaust systems. Building 776-777 was targeted for monitoring because of the large amounts used. Several special monitoring studies for carbon tetrachloride and other chlorinated solvents were located by ChemRisk ([Johnson et al.](#) 1974b; [Hamilton and Moser](#) 1990). The data collected in 1974 have been used in other reports which were also considered by ChemRisk ([Hobbs](#) 1982). The reliability of the monitoring data has been questioned. The flow measurements taken as a part of the 1974-1975 monitoring study were subject to error because of inaccuracies in measuring the air flow. The measurements were thought to be “moderately suspect” by the study’s authors ([Johnson et al.](#) 1974b).

Other than recently conducted monitoring associated with remedial investigations and feasibility studies done under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and a study of fish discussed on [page 14](#) of this memorandum, no documentation of monitoring data not used in Phase I has been located.

EVALUATION OF HISTORICAL PROCESS CHANGES

As noted in the Phase I Task 2 Report, the rate of use of cleaning and degreasing agents are likely to be correlated to changes in the facility size and production rate. *RAC* suggested that it might be possible to improve the emission estimates for a few of the chemicals of concern by reevaluating the operations history of the plant ([Grogan et al.](#) 1994).

Unfortunately, the amount of carbon tetrachloride used at the plant was not directly correlated to production. Although carbon tetrachloride was used during the production process (and it seems reasonable to think that the more parts that were produced - the more solvent would have been used to clean them), carbon tetrachloride was also used extensively during periods of low or no production to clean equipment and glove-boxes. Solvent baths and ultrasonic cleaners were often cleaned out when the production lines were idle.

Process information for materials like carbon tetrachloride, compiled in Phase I was primarily based on use information from the late 1980s, described and evaluated in unclassified reports prepared by EG&G Rocky Flats called Air Pollution Emission Notices (APENs). APEN reports were prepared for each building to characterize airborne emissions and waste streams. In preparing the APENs, EG&G noted that historical documentation of use and release of organic solvents was lacking. In addition, there was no chemical tracking system to document chemical use and transport, and there was insufficient historical information to apply material balance techniques to estimate releases. ChemRisk acknowledged that these reports provided a level of detail generally adequate to support a preliminary understanding of uses of key materials. ChemRisk recognized that the difficult part of the task was to go backwards in time and describe how processes and facilities had changed over the years as material substitutions were made and

better technology became available. When historical data were not available, linear change in usage of chemicals over time was assumed ([ChemRisk](#) 1992).

Several process changes of potential importance to volatile organic chemical emissions were recognized and noted in Phase I ([ChemRisk](#) 1991). In the late 1950s, machining methods employing lubricants were introduced to what had previously been a dry process, greatly increasing the use of carbon tetrachloride as a degreaser and cleaner. In the 1950s, the physical form of plutonium used by the plant changed, but how this change relates to carbon tetrachloride use is unclear. In the 1970s a general trend to reduce the use of carcinogenic compounds and substitute toxic degreasers occurred with time. In the mid-1970s, the plant attempted to find cleaning and degreasing solvents more chemically compatible with plutonium and glovebox materials. Losses to the environment and workplace through evaporation did not appear to be a consideration in evaluating materials, because the lower the rate of evaporation the more difficult the removal of the solvent from the part after cleaning. Perchloroethylene was substituted for carbon tetrachloride in 1966, but with undesirable results. Its use was discontinued for efficiency and safety reasons ([Hobbs](#) 1970). In 1974, it was recommended that 1,1,1-trichloroethane replace carbon tetrachloride for ultrasonic cleaning in Building 707 ([Musgrave](#) 1975).

As a result of their investigations into historical operations, ChemRisk indicated that the overall manufacturing facilities and production processes have remained largely the same over the years. ChemRisk's document review did not identify any documentation of significant process changes that may have created significant changes in chemical usage at the plant. Interviewees suggested that processes changed, but not dramatically ([ChemRisk](#) 1991). The most significant processes changes were adequately considered by the breakdown of time periods used for the Phase I estimates of carbon tetrachloride release. Additional attempts to refine the release estimates would not reduce the uncertainty of these estimates unless additional information was used.

DISCHARGE OF CARBON TETRACHLORIDE TO SURFACE WATER

Discharge of carbon tetrachloride to surface water would not decrease the atmospheric source term because carbon tetrachloride released into surface waters would be expected to eventually evaporate and become an airborne emission. However, contamination of surface water could be an important exposure pathway for people drinking the water or aerating carbon tetrachloride out of the water while showering, bathing, boiling water, watering plants or washing clothes. An analysis of discharge to surface waters would also expand the number of release points evaluated because points along the surface water effluent route (such as holding ponds, creeks and reservoirs) would be considered points of discharge to the atmosphere.

Surface water discharges of greatest concern would be those to Walnut Creek which runs into the Great Western Reservoir which supplies water to the City of Broomfield. Woman Creek and Standley Lake provide water for the City of Westminster but these and other potential surface water sources such as Leyden Lake and Ralston Reservoir are unlikely to have been affected by carbon tetrachloride discharges.

In the Task 2 report, ChemRisk outlines their methodology for Stage 2 screening for drinking water exposure to chemicals. Although the more conservative oral reference dose was used for carbon tetrachloride in the screening, the inhalation pathway appeared to be the only exposure pathway considered. [ChemRisk](#) (1991) assumed that carbon tetrachloride discharged to surface

water evaporated entirely before the water reached human receptors offsite. The ChemRisk Task 5 report states, "Since the early days of RF operations, liquid wastes discharged from the facility were temporarily stored in retention ponds prior to release. As a result, volatile contaminants of concern released with liquid effluents are unlikely to have transported offsite in surface waters to any significant extent." They acknowledged that environmental degradation half-lives range from minutes to days depending on the nature of the effluent and the mixing conditions of the water.

There is no doubt that retention times of several weeks or months in holding ponds would have been very effective for allowing the carbon tetrachloride to evaporate. In 1953 and 1954, liquid effluents from Building 71 were discharged directly to North Walnut Creek. The first holding pond, A-1, was used in 1955. The use of this holding pond, and others built subsequently, dramatically reduced the alpha activity in North Walnut Creek ([Meyer and Till 1999](#)). Although the alpha activity is associated with radionuclides that were more likely affected by sedimentation than volatilization, the retention time in the ponds would have greatly increased the amount of carbon tetrachloride that volatilized and decreased the amount transferred to Walnut Creek.

The ChemRisk comments on volatilization were generic for all of the volatile organic chemicals of concern. In the Task 5 Report, ChemRisk states, "we have provided appropriate references to support the assumption of nearly 100% evaporation of volatiles from surface waters." The references referred to are summaries of transport and environmental fate studies or modeling which indicate that the volatilization of carbon tetrachloride from surface water varies from minutes to months depending on the mixing and flow of the water and other conditions. This environmental fate information was not correlated to any estimated transit times or flux of Rocky Flats liquid effluents from sewers or holding ponds, through creeks to reservoirs. No reports of studies, applicable to this problem, to determine the time it took for liquid effluents to reach domestic water sources have been located.

However, a USGS characterization of the Rocky Flats area hydrology published in 1976 ([Hurr](#)) suggests that flow rates of surface water are extremely variable. Flow can be very rapid under intense thunderstorm conditions. During periods of little or no rain, the creeks may be dry. The USGS attempted to characterize the volume and rate of the movement of water in order to evaluate the effects of possible contaminant releases from the RFP on downstream areas. Gauging stations were placed on creeks, including North and South Walnut Creeks. Channel reservoirs and numerous ditches complicated the characterization. Quantitative rainfall-runoff relationships could not be developed for Walnut Creek because of numerous water management changes made at the RFP during the course of the USGS investigation. However a travel time coefficient was estimated for Woman Creek and the report states, "because of similar physical characteristics of the basins, Walnut Creek probably has runoff characteristics similar to Woman Creek." The greatest flow and minimum transit time was estimated to occur during periods of intense thunderstorms. The flow varied greatly with storm location. Under open channel flow conditions following intense thunderstorms, a contaminant might move at a rate of approximately 420 feet per minute. Under pool and riffle conditions a contaminant might move through the surface water system at a rate of 60 feet per minute ([Hurr 1976](#)). A travel time coefficient of 0.0024 minutes per foot was derived ([Hurr 1976](#)) which can be multiplied by the distance between two points to determine the travel time of water between the two points.

Using these worst case conditions and acknowledging that high flows are not the common conditions around the site, a transit time can be calculated. The distance from RFP effluent

discharge points to Great Western Reservoir is about 1.5 miles. If we conservatively assume the surface water flows in a straight line (it is undoubtedly more convoluted and covers a greater distance), then under downpour conditions, surface water could reach the reservoir in 19 minutes (7920 feet \times 0.0024 minutes/foot). Under pool and riffle conditions the transit time estimate is 132 minutes. These estimates seem to represent the lowest, most rapid transit time which could be used in a conservative estimation of the time it took effluent to reach domestic water supplies. During periods when the creeks were dry, the flow in the creeks may have been close to zero, depending on the effluent discharge rate, and how full the holding ponds were.

Carbon tetrachloride volatilization from surface water increases with increased turbulence and aeration of the water. Conditions of high flow and rapid transport are also conditions of more rapid volatility. Additional potential sources of information on transit times of liquid effluent are reports of an accidental tritium release from the RFP summarized in recent RAC ([Meyer and Till 1999](#)) and [ChemRisk](#) (1994) reports. On March 19, 1973, Rocky Flats received scrap plutonium metal contaminated with tritium from the Lawrence Livermore Laboratory. Processing of the tritium-contaminated plutonium metal occurred from April 9 - 25, 1973 in Room 154 of Building 779A. Much of the tritium was released through the stacks in airborne effluents. The remaining tritium followed the normal liquid waste processing flow. The treated liquid wastes were discharged to the sanitary sewer or to the evaporation ponds over time. It was estimated that about 50 to 100 curies accumulated in Great Western Reservoir ([Ofte et al. 1974](#)). The first significant 'above background' tritium concentrations after this incident were detected in Walnut Creek at Indiana Street and in the Great Western Reservoir on April 24, 1973. Tritium levels rose to a maximum of 3,000,000 pCi/L on May 23, 1973. The tritium concentration in the reservoir slowly decreased during the next several months ([Meyer and Till 1999](#)). Unfortunately monitoring for tritium was not done on a regular schedule or with great enough frequency to know when tritium may have first reached Walnut Creek and the Great Western Reservoir.

From the sequence of events that occurred after the release and from the available monitoring data, it appears that an increase in the tritium concentration in Walnut Creek was first detected roughly two weeks (April 24) after processing of the material first began (April 9). Higher than 'normal' levels of tritium were also measured in the Great Western Reservoir on April 24. Approximate transit times based on these limited data are on the order of days or weeks rather than months. Unfortunately the tritium monitoring data do not allow more refined estimates of transit time to be derived. Another important consideration is the contribution of site effluent and runoff to Great Western Reservoir. It is estimated that the water in the Walnut Creek drainage contributes 2% to 4% of the volume of the Reservoir ([Zillich 1974](#)).

Although data on the volume of liquid effluent released from the Rocky Flats Plant have been compiled on a monthly basis from September 1955 to September 1960 and from March 1969 to November 1970 ([Meyer and Till 1999](#)), no data on the concentration of carbon tetrachloride in effluent are available. The rate of effluent discharge was not reported so the volumes can not be associated with flow rates or used to determine transit times.

Interview reports suggest that waste containing carbon tetrachloride was discharged to the solar evaporation ponds, and/or subject to effluent treatment which would have resulted in volatilization of much of the carbon tetrachloride. It is difficult to estimate how much was discharged in the effluent that flowed into Walnut Creek. Although most of the carbon tetrachloride released from the site was released to the air, discharges of carbon tetrachloride to surface water may warrant further study.

SURFACE WATER MONITORING

Waterborne effluents were not monitored for any of the nonradioactive chemicals of concern ([ChemRisk](#) 1994). Surface water measurements of carbon tetrachloride that could be used to quantify releases of nonradioactive materials to surface waters have not been found.

Although sampling of surface waters for carbon tetrachloride was not conducted, [Zillich](#) (1974) published a study of fish, macroinvertebrates and water quality in surface water around the plant. Although the document states that no RFP materials are known to biomagnify in the food chain, the authors also discuss bioconcentration of 'hydrocarbon solvents' and seem to incorrectly assume that carbon tetrachloride and the other chlorinated hydrocarbons measured are insoluble in water and bioconcentrate in fish. (The log of the bioconcentration factor for carbon tetrachloride is 1.24 for trout and 1.48 for bluegill. A bioconcentration factor for bullheads has not been reported ([Howard](#) 1990). They compare their results to FDA standards for PCBs in fish, standards which would not be applicable to carbon tetrachloride. The researchers tested several carp and a sunfish from Great Western Reservoir and detected no carbon tetrachloride in their tissues. Three white suckers taken from Walnut Creek were tested and carbon tetrachloride levels of less than 0.2 ppm were reported. Bullheads exposed for two weeks to water from South Walnut Creek and to water from further downstream where Indiana Avenue crosses Walnut Creek, had carbon tetrachloride levels of 0.35 and 0.38 ppm, respectively. Unexposed fish had levels of 0.03 ppm ([Zillich](#) 1974). This is consistent with other reports of background levels, which range from 0.003 to 0.2 ppm but generally average about 0.02 ppm ([Howard](#) 1990). [Zillich](#) (1974) concluded that carbon tetrachloride concentrations in fish were insignificant. However, the levels of carbon tetrachloride in bullheads put into Walnut Creek water were about 10 fold greater than the levels in unexposed fish. In light of the fact that carbon tetrachloride has a low bioconcentration potential, these levels indicate that the fish were exposed to water with carbon tetrachloride concentrations as high as ten fold greater than the concentrations in the waters in which the unexposed fish were placed.

Acknowledging that the [Zillich](#) study (1974) was done over a short time period with very few fish, these data can be used to estimate concentrations of carbon tetrachloride which may have been in the water in Walnut Creek at the time of the study. If we assume that an equilibrium was established between the fish and water in the creek then the bioconcentration factor is equal to the ratio of the concentration in fish to the concentration in the water. If the carbon tetrachloride concentration in the fish was 0.38 mg L⁻¹, and we apply the bioconcentration factors for trout and bluegill of 17 and 30, respectively, then the creek water concentration could be equal to 12 and 22 µg L⁻¹. If Walnut Creek provides from 2% to 4% of the total inflow into Great Western Reservoir, then the Reservoir concentration might range from 0.20 µg L⁻¹ to 0.8 µg L⁻¹. The drinking water standard (MCL) set by the US EPA is 5.0 µg L⁻¹. The ambient water quality criteria value for protection of human health from the water and from ingestion of fish and other organisms in the water is 4.0 µg L⁻¹.

The City of Broomfield, Radiometric Monitoring Reports, 1988-1991 monitoring reports indicate that levels of carbon tetrachloride were below the practical detection limit. The City of Westminster monitored for several volatile organic chemicals in 1989-1991, but did not monitor for carbon tetrachloride specifically.

EVALUATION OF CERCLA MONITORING DATA

The current site monitoring and remediation activities being carried out by the RCRA and CERCLA Programs were reviewed for data on spills, leaks and contamination of soil and groundwater. Several remedial investigation reports have been completed that demonstrate that chlorinated solvents were detected in soil or groundwater at the RFP. Carbon tetrachloride has been found around the 903 Pad and in several of the industrial areas but contamination of soil or groundwater near the East Trenches, and Solar Ponds has not been confirmed ([ChemRisk 1991](#)).

Current sampling programs for Operable Unit 3 (offsite areas) have not detected carbon tetrachloride in Mower Reservoir sediments or water ([EG&G 1994](#)). It appears that carbon tetrachloride-contaminated groundwater has not moved offsite and groundwater is not an exposure pathway for carbon tetrachloride. However, carbon tetrachloride in the groundwater on site could, theoretically, be subtracted from the amount assumed to have been released into the atmosphere.

The approximate volume of groundwater in a defined area contaminated with carbon tetrachloride was estimated using Operable Unit 2 saturated thickness maps published in 1993 for the second quarter of 1992. Carbon tetrachloride concentrations in the same area were compiled using carbon tetrachloride isoconcentration maps for the alluvial/colluvial groundwater flow system for the same time period, (a period when water flows are high and wells are less likely to be dry). In addition to the isopleths, specific well data for carbon tetrachloride were evaluated. The defined area included the 903 Pad, the Mound Site, Trenches T-2, T-3, T-4, T-120, T-11, and Oil Burn Pit No. 2.

The area multiplied by the saturated thickness gave an estimate of 7.6×10^7 cubic feet of water, or 2.15×10^9 liters. A reasonable, average porosity value for the Operable Unit 2 area would suggest a reduction to 30% of the saturated thickness value to 2.3×10^7 cubic feet or 6.45×10^6 liters of water. Because of the assumption that the entire area had a uniform thickness of water according to the isopleths, the estimate of the total volume of water is likely to be an upper bound estimate.

The isopleths do not necessarily match specific well data and carbon tetrachloride levels from wells quite close to one another. In the industrial areas and near the 903 Pad the carbon tetrachloride levels in groundwater may vary up to two orders of magnitude. Much of the soil in this area has low hydraulic conductivity, and contaminant plumes are expected to be moving very slowly. To facilitate a consistent and reproducible approach, the concentration isopleths, which tend to be an average of most of the well concentration data were used. The carbon tetrachloride concentrations in the area range from the limit of detection to 54,000 micrograms (10^{-6} g) per liter ($\mu\text{g L}^{-1}$). The percentage of area corresponding to each isopleth line was: 21% of the total area at the limit of detection, 31% $\geq 500 \mu\text{g L}^{-1}$, 18% $\geq 50 \mu\text{g L}^{-1}$, and 29% $\geq 5 \mu\text{g/l}$. Normalizing each value by the area it covered, the average level over the entire area is approximately $167 \mu\text{g L}^{-1}$. This concentration of $167 \mu\text{g L}^{-1}$ multiplied by the estimated volume of water of $6.54 \times 10^6 \text{ L}$ equals $1.07 \times 10^9 \mu\text{g}$, or 1.07 kg, of carbon tetrachloride in the defined area. This represents a lower bound estimate. An upper bound estimate for carbon tetrachloride might be derived from the higher 1992 well data which is very variable. The mean values for the 16 wells in the area sampled in 1992 ranged from 1 to 25,500 $\mu\text{g L}^{-1}$. The average of the mean concentrations was

2,406 $\mu\text{g L}^{-1}$. If the entire area had levels of 2,406 $\mu\text{g L}^{-1}$, the total carbon tetrachloride mass estimate is 15 kg. If the entire area had levels of 25,500 $\mu\text{g L}^{-1}$, about 100 kg might have contaminated the groundwater.

Data collected in 1995, and not yet published, from wells very close to the plant not previously sampled and from new sample points adjacent to disposal areas, show very high carbon tetrachloride concentrations, believed to be from leaking tanks or concentrated waste buried in the trenches. In some cases, for example at Trench T-2, pure solvent was detected. Due to the extreme variation in sample results and heterogeneity of the waste in the trenches, calculation of the total amount of carbon tetrachloride in the buried waste was not possible (Pottorff 1995; Siders 1995).

Calculations of this type, to estimate the total mass of specific contaminants, are being done as a part of ongoing remedial investigations. Estimates of the volume of water in a different plume which covers most of the OU2 area was approximately 10^6 cubic feet (Roberts 1995). Perhaps when additional concentration data are collected and further characterization of the groundwater is done, a better estimate of the volumes of water and mass of contaminants can be compiled and used to better estimate losses of carbon tetrachloride to groundwater.

CARBON TETRACHLORIDE IN WASTE GENERATED AT ROCKY FLATS

Thousands of 55-gallon drums of contaminated waste were generated at the RFP each year. Although the amounts of plutonium, uranium, americium and beryllium were often measured or estimated and noted, other chemical contaminants, like carbon tetrachloride were not inventoried (Plock 1972).

Organic liquid waste, composed of carbon tetrachloride and oil was not shipped offsite for disposal because assuring secure packaging was cost prohibitive. The burial ground could not accept the waste for fear of leakage and leaching (Ryan et al. 1965). Much of the cutting and degreasing liquid waste was stored awaiting technology for plutonium recovery.

From 1951 to 1972 portions of the 'hillside area' near Building 881 were used as oil sludge pits, chemical burial sites, liquid disposal areas and solvent drum storage sites. Soil and groundwater in some of the areas have become contaminated with carbon tetrachloride. Much of the oil sludge is from storage tank cleanup and may not have been contaminated with carbon tetrachloride. Another potential source of carbon tetrachloride contamination to soil and groundwater is the Solvent Burning Ground, SWMU 171. This area, north of Building 331, was used to train fire personnel. The amounts and types of wastes taken to the solvent burning ground are not well documented.

Building 776 housed a centralized oil collection and separation point and the waste oil was sent to Building 771 or 774 where it was stored or processed. In Building 707, all waste carbon tetrachloride was pumped to the C-Pit, a basement area under Module C, with two storage tanks and 16 pencil tanks for storing carbon tetrachloride. The waste carbon tetrachloride was eventually pumped to Building 774. All potential emissions from the C-pit area were considered accounted for in the Phase I estimates by assuming all of the carbon tetrachloride used evaporated from each source.

In Building 771 the spent oil and carbon tetrachloride were put into drums for storage until a satisfactory method of treating the contaminated material could be found. The drums were first buried, then in later years, stored at what is now known as the 903 Pad.

Eighty nine drums of oils with carbon tetrachloride from Building 776 and 46 drums of oils with carbon tetrachloride from Building 771 were buried at the Mound Area. Complete retrieval and offsite disposal of these barrels was achieved in May 1970, under the observation of CDH ([ChemRisk](#) 1994). No plutonium was detected in soil samples which suggests that the drums did not leak. In 1970, a Task force on Potential Offsite Contamination reported that the burial mound contained at that time (1969) 1400 drums of contaminated solid wastes, and about 80 drums of contaminated coolant oil in liquid form from Buildings 776 and 771. They did not know if the drums were leaking. No sampling had been done ([Love](#) 1970).

There are conflicting reports on the number of barrels placed in and removed from the 903 area over the years. Approximately 5,240 drums of oil containing radioactivity were stored at the 903 drum storage area between 1958 and 1968 ([ChemRisk](#) 1994). About 3,500 drums containing plutonium-contaminated oil were stored at the 903 storage area ([Seed et al.](#) 1971). [Seed et al.](#) (1971) estimated that 5,240 30 and 55-gallon drums containing up to 262,000 gallons of waste organic liquids were stored at the 903 Pad. [Barrick](#) (1981) states that, "Liquids were mainly machining lubricants and chlorinated solvents originating in plutonium (3,570 drums), uranium and miscellaneous (1,670 drums) operations." There is no leakage information on the uranium and miscellaneous drums ([Barrick](#) 1981) but [Seed et al.](#) (1971) estimated that 5000 gallons of oil containing 42 to 170 grams of plutonium leaked into the soil. The amount of carbon tetrachloride in the drums and the number of drums containing carbon tetrachloride was not recorded. Phase I results reiterated the findings of [Seed et al.](#) (1971), which led to estimates that 5000 gallons of 903 Pad oil containing 86 g of plutonium leaked. It is thought that about 420 drums leaked and 50 leaked until totally empty ([ChemRisk](#) 1994).

In response to a comment on Task 5, Number 70, which asked how the carbon tetrachloride known to be stored at the 903 Pad was accounted for, ChemRisk added a paragraph to section 3.2.1 of Task 5 report which acknowledges that carbon tetrachloride was stored in the drums at the 903 Pad and estimated how leaking carbon tetrachloride could be added to the atmospheric source term. Using the estimate of 3,500 drums reported to contain plutonium-contaminated oil which was approximately 20% carbon tetrachloride, ChemRisk says in the Task 5 report, "if all the carbon tetrachloride estimated to have been contained in the drums (about 260 tons) volatilized, emissions could have approached approximately 13% of the upper-bound annual release estimate for the period".

However, carbon tetrachloride stored at the 903 Pad could be considered in a different way, that is, the assumption could be made that only a small fraction of the carbon tetrachloride leaked from the drums. Nearly all of the material processed and stored did not volatilize but was shipped in drums to Idaho and therefore could be subtracted from the atmospheric source term.

For the Phase I estimates, 903 Pad carbon tetrachloride was not explicitly accounted for, neither subtracted nor added to the release estimate ([ChemRisk](#) 1994). ChemRisk used the lower number of 3,500 barrels, apparently assuming that only plutonium-containing barrels contained carbon tetrachloride. Although uranium may have required less machining and cleaning, there are reports that uranium and beryllium processes used carbon tetrachloride and it is likely that these other barrels also contained carbon tetrachloride and some unknown amount of carbon tetrachloride in the drums was released by leaking.

In 1959, a recommendation was made to construct a still for the separation, purification and reuse of carbon tetrachloride and shell vitrea. The process was set up in Building 771 using surplus stainless steel equipment. Test runs were begun in May of 1960. In June of 1960,

corrosion of the stainless steel equipment caused by hydrochloric acid, a hydrolysis product of carbon tetrachloride, became a problem and the process was shut down in September of 1960 (Plock 1972).

In 1966 another process to recover plutonium from the oil was developed and processing of the stored oil began (Joshel 1970). Spent organic liquids were filtered and then solidified for disposal (Joshel 1970; Crisler 1991). The waste was filtered then fed into a open steam distillation column to separate the oil and carbon tetrachloride. Overhead vapors were condensed into a water-cooled surface condenser. The carbon tetrachloride was put into a separator tank for gravity separation of water and carbon tetrachloride, then pumped into one of two 400-gallon epoxy-lined steel storage tanks. After analytical analysis the carbon tetrachloride was returned for reuse.

Some waste was transferred to a process evaporator and concentrated by evaporation which led to atmospheric releases of carbon tetrachloride (Plock 1972). Plock (1972) reported that aqueous waste was discharged to holding ponds, the Building 774 evaporator and the solar evaporation ponds. These disposal practices would be expected to lead to the evaporation of carbon tetrachloride contained in the liquid waste. The evaporator salts were drummed for shipment to Idaho (Anderson et al. 1970).

Contaminated lathe oil coolant, oil bottoms from the evaporators and other organic solutions from throughout the plant were mixed with a calcium silicate and absorbent to form a solid known as 'grease' (Ryan et al. 1965). The grease was packaged in 55-gallon drums and eventually shipped to Idaho (Plock 1972). In fiscal year 1969, about 78,000,000 gallons of organic liquids were converted to about 5,300 cubic feet of grease (Anderson et al. 1970).

Information available about early solid waste disposal is limited to the number of containers and the volume and weight of material shipped rather than reliable measurements of concentrations of materials. It is unclear from the descriptions of waste processing in various documents, how much of the waste grease and sludge, both before and after processing, was carbon tetrachloride.

CARBON TETRACHLORIDE IN WASTE SHIPPED TO IDAHO

From 1954 to 1971, a volume of about 59,558 m³ of waste in an estimated 4344 55-gallon drums and 579 4' x 4' x 7' boxes was shipped from the Rocky Flats Plant to the Idaho National Engineering Laboratory (INEL), in southeast Idaho (EG&G Idaho 1994). Most barrels included cutting oil and carbon tetrachloride which had been turned into grease or sludge (ChemRisk 1992). No liquid was shipped to Idaho for burial (Joshel 1970). The majority backlog of stored organic chemicals was processed into sludge and shipped to Idaho between 1966 and 1969. All radioactive waste sent from RFP to the INEL from 1954 to 1970 was buried at the Radioactive Waste Management Complex (RWMC). In 1994, EG&G, Idaho published a comprehensive inventory of waste buried at the RWMC for use in a baseline risk assessment under CERCLA. The disposal area was large and the waste was very heterogeneous. A drilling and sampling campaign was not expected to yield a good inventory, and would have been hazardous. Although some of the waste was retrieved as a part of two retrieval programs conducted in the late 1970s, the hazardous nature of the waste severely limited the information gained about its characteristics.

During the period of interest, emphasis was not placed on documenting the nonradiological hazards in the waste because current requirements for characterizing and reporting hazardous chemicals did not exist. Knowledge of the processes, operating logs, inventory related documents, shipping records, information databases and interviews with personnel having knowledge of facility operations were used to try to close the gaps in the shipping records. The documentation found on the RFP waste was quite general. Most of the knowledge of RFP processes used by EG&G was derived from ChemRisk Task 3&4 and 5 Reports from Phase I of the Rocky Flats Dose Reconstruction.

Tables I and II from a letter from the RFP by [Lee](#) (1971), provide an estimate of the volume of waste shipped annually to the RWMC from 1954 to 1970. No documents could be identified that would supply information on the amount of nonradioactive contaminants in the buried waste from the RFP. Waste received after 1970 had more specific information related to RFP content codes, such as the average weight of each container, a description of where the waste was generated and how it was packaged and the type and estimated quantities of nonradiological contaminants per container ([Kudera 1987; 1989](#)).

Consistent with the RFP reports, the records found by EG&G, Idaho stated that the organic sludge waste stream from the RFP (called RFO-DOW-15 in INEL documents) was produced by the treatment of liquid organic waste generated by various operations. The organic waste, largely carbon tetrachloride mixed with Texaco Regal oil, was mixed with calcium silicate to form the paste-like material called 'grease'. Small amounts of oil-Dri absorbent were also mixed with the waste. Detailed annual data were available on this waste stream. The quantities of carbon tetrachloride in this waste stream were obtained by reviewing RFP Waste Management Monthly Reports ([Cadre 1987](#)). These monthly reports contained data on the amount of lathe coolant and oil, which was about 40% carbon tetrachloride, received for processing each month. These reports also reported the total volume of oil, trichloroethylene, trichloroethane and perchloroethylene that was received for treatment each month. It is unclear whether or not these reports were used in Phase I. Other waste streams such as paper, plastics and clothing, glovebox materials, shipped to the INEL, may also have been contaminated with carbon tetrachloride.

Nonradiological contaminants were identified as accompanying shipments of radioactive waste to the INEL. A rather complex approach of relating total waste streams to plutonium waste streams was used to estimate the quantities of nonradiological contaminants in the waste. The ratio of each hazardous chemical to the quantity of plutonium in each combined waste stream was determined. Then the total quantity of each hazardous chemical in the waste was obtained by multiplying the total amount of plutonium in each buried waste stream by the ratio of the quantity of each hazardous chemical to quantity of plutonium in each contaminated waste stream.

The INEL estimates of the amount of carbon tetrachloride buried at the RWMC from 1952 to 1983 are:

Best estimate 1.2×10^8 g

Lower bound 1.0×10^8 g

Upper bound 1.4×10^8 g

which can be converted to the following:

Best estimate 132.3 metric tons

Lower Bound 110.2 metric tons

Upper bound 154.3 metric tons.

The estimated quantities of volatile organic chemicals are expected to be conservatively high because of unknown losses to evaporation before the waste was packaged and shipped. The best estimate is taken to be 3/4s of the upper bound. The INEL Comprehensive Inventory report states that “it was the professional judgment of the lead RFP data gatherer that the reported value for volatile contaminants, arrived at through the extrapolation process described in Section 2.4.6 is actually an upper bound” . The three-quarter value was taken to account for evaporation and other losses during processing ([EG&G Idaho](#) 1994). Theoretically, a value of 132 tons could be subtracted from the total carbon tetrachloride release from Rocky Flats for all years.

UNCERTAINTY

Phase I Estimates of Uncertainty

The type of data used to make the Phase I estimates of carbon tetrachloride air emissions is shown in Table 1.0 for Buildings 776/777 and 707. The largest range of estimates differed by a factor of six. Although estimates of uncertainty were included in the Phase I Task 8 Report final risk estimates, quantification of the uncertainties associated with carbon tetrachloride release estimates was not specifically addressed in the Phase I Task 5 report. The range of estimates is said to “have been established with the intent of ensuring that the range encompasses the actual value for any one year” ([ChemRisk](#) 1994). In the response to comment 76 on the Draft Task 5 Report, ChemRisk stated that inventory reports and purchasing records were not extensive or complete enough to support a quantitative uncertainty analysis of these information sources.

In planning Phase II, it was thought that further analysis of uncertainty, to the extent feasible, could be useful for setting better lower and upper bounds on the estimate ranges and for determining how conservative the estimates may be.

PHASE II ESTIMATES OF UNCERTAINTY

Many factors contribute to the source term estimates and their associated uncertainty. Much of the uncertainty comes from assumptions which are based on little or no factual data. These factors, assumptions and unknown variables are listed and described below.

Carbon Tetrachloride Inventory Amounts and Usage Information

- It was assumed that the reported inventory amount was directly related to the amount used.
- A linear decrease in usage was presumed to occur after 1971. The actual rate of solvent replacement and reduction in carbon tetrachloride use is unclear.
- The estimates of the amount used and released per year depend on assumptions regarding the average length of the workweek, workshift, holiday schedule and hours of operation each year.

Carbon Tetrachloride in Air

- It was assumed that all important sources and release points were accounted for.

- It was presumed that the air monitoring sampling periods were representative of usual working conditions and typical usage, the air monitoring measurements reported were correct, and that the assumptions made about flows of the building effluent were correct and representative of typical conditions.
- For the Phase I estimates, a reduction of 28% was applied for good practices, which would have limited solvent evaporation. To what extent the practices were adhered to is unknown.
- Evaporative losses due to nonroutine events which have not been reported such as leaks, spills, etc. are unascertained.

Carbon Tetrachloride in Surface Water

- The concentrations of carbon tetrachloride in the liquid effluent releases can not be calculated based on process knowledge. Carbon tetrachloride released to surface water from waste holding ponds was not monitored and the amount released is not known.
- The transit time of water from effluent discharge through retention ponds and to sources of domestic water, like Great Western Reservoir, has not been measured and was extrapolated from limited hydrogeological studies of similar areas.
- The hydrogeological characteristics of Walnut Creek were taken to be similar enough to Woman Creek that the USGS flow data could be applied to both.
- Surface water flow around Rocky Flats is extremely variable and is dependent on the season and weather conditions. This variability was not accounted for in estimating transit times.
- Whether or not carbon tetrachloride reached domestic water supplies depends on how rapidly it evaporated from surface water. The evaporation rate of carbon tetrachloride from surface water is variable and depends on turbulence, temperature and other factors, for which little or no information is available.
- There is uncertainty in the estimate of the total Walnut Creek water inflow to Great Western Reservoir. The estimate of 2% to 4% is based on one estimate published in the literature.
- Bioconcentration factors from fish species different that that used in the [Zillich](#) study (1974) were used to estimate water concentrations. This study used a small number of fish exposed to creek water for a short time. The calculations were based on the assumption that equilibrium conditions exist between the fish and water concentrations.

Carbon Tetrachloride in Groundwater

- The volume of ground water was estimated using uncertain assumptions about saturated thickness, surface areas, porosity and conductivity.
- The carbon tetrachloride concentrations in ground water were estimated using isoconcentration maps and data from several different well monitoring studies. Groundwater concentrations varied by several orders of magnitude, perhaps due to pockets of carbon tetrachloride under waste burial areas or leaking storage tanks.
- There is no information on the amount of carbon tetrachloride released directly to the soil or leached from solvent burning grounds or other disposal areas.
- The transit time for discharged carbon tetrachloride moving through the soil into groundwater and whether the carbon tetrachloride in groundwater has reached maximum concentrations are unknown.

Carbon Tetrachloride in Waste

- No information is available on the amount of carbon tetrachloride disposed of in sludge pits, chemical burial sites, and the solvent burning ground.
- Estimates of the number of barrels at the 903 Pad, burial mound and other areas which were recovered and shipped to Idaho vary.
- Estimates of the amount of oil which leaked from the barrels are uncertain.
- The number of barrels that contained carbon tetrachloride and the amount of carbon tetrachloride in each barrel is uncertain. Estimates of the amount of carbon tetrachloride in buried waste depend on assumptions about the concentration of carbon tetrachloride in waste oil. Estimates of the concentration of carbon tetrachloride in the drums range from 13% ([ChemRisk 1992](#)) to 40% ([EG&G Idaho 1994](#)). The oil used for the machining of uranium was reported to be formulated at a ratio of 1:15 carbon tetrachloride to oil.
- The amount of carbon tetrachloride remaining in the oil and placed into barrels after waste processing is not known.

The list above was developed with the intent to try to assign uncertainty values to the various parameters used to estimate the source term. We thought it might have been possible to analyze individual reports and datasets used to derive the release estimates and determine some levels of uncertainty associated with each parameter. If this information could have been extracted, a range, a distribution of probable values and a best estimate might have been developed for each uncertain term. An overall uncertainty value for the estimates could have been calculated by the propagation of errors or a more complex method of uncertainty analysis. Unfortunately, for most of the parameters, little or no data exists with which to complete this task. The documentation available does not allow reliable quantitative ranges or best estimates of these parameters to be determined.

[Hobbs \(1982\)](#) discussed some of the limitations of the 1974 monitoring data ([Johnson et al. 1974b](#)) and reported uncertainty estimates of $\pm 10\%$ for carbon tetrachloride concentration fluctuations and $\pm 12\%$ for questionable air flow measurements during monitoring. It is unclear how these error estimates were determined. With the exception of the estimates in [Hobbs \(1982\)](#) and several rough and variable estimates of the percentage of carbon tetrachloride in waste oil ([ChemRisk 1992](#); [EG&G Idaho 1994](#)), no quantitative data to help define uncertainty appear to be at hand.

The largest sources of uncertainty come from uncertainties in the monitoring data, inventory amounts and usage information that were used to develop the release estimates. The amount of carbon tetrachloride in waste and groundwater is very small compared to the total atmospheric source term, so their contribution to the overall uncertainty is small as well.

The amount of carbon tetrachloride discharged to surface water is unknown. Effluent discharges were not described nor measured and carbon tetrachloride in drinking water was not measured until the late 1980s, at which time it was below the practical detection limit. Although carbon tetrachloride in surface drinking water could have been an important exposure pathway we can not make reliable estimates of exposure based on the information available.

Additional sources of uncertainty in the estimation of exposure and risk from carbon tetrachloride exist. For example, the cancer potency factors used to calculate risk are uncertain and

controversial for carbon tetrachloride, which has been shown to cause cancer in laboratory animals but not in humans. It will be beneficial to remain aware of the largest sources of uncertainty and important gaps in the data. Having at least a qualitative idea of the uncertainty associated with the most sensitive components of the source term estimates, the exposure estimates, and the risk estimates, will help to keep the certainty of the final estimates in perspective.

CONCLUSIONS

Although the Phase I assumption of complete evaporation of all carbon tetrachloride used at the Rocky Flats Plant seems justified for determining a conservative, upper bound estimate for atmospheric releases, this approach ignores potential releases to surface water. The Phase I estimates did not account for carbon tetrachloride which moved into the ground water or was a part of waste material shipped off-site, both of which could be subtracted from the total amount which might have evaporated.

No significant historical process changes which would alter the carbon tetrachloride usage data or better refine release estimates have been identified. Carbon tetrachloride use and release were not directly proportional to production because solvent baths were changed out, and carbon tetrachloride was used to clean equipment and work surfaces during periods of no production. Although the assumption that 100% of all carbon tetrachloride used evaporated led to conservative estimates of atmospheric releases, we have found no evidence that the upper bound release estimates are incorrect.

The documents used to derive Phase I carbon tetrachloride release estimates were not complete or extensive enough to support a quantitative uncertainty analysis. The range of estimates that was established (1,100–5,400 tons) was thought to be sufficiently large to encompass the actual release to the atmosphere ([ChemRisk 1994](#)).

Discharge to domestic water sources was probably reduced by holdup in retention ponds and by the volatility of carbon tetrachloride. The transit time of effluent in surface water from the RFP to Great Western Reservoir was likely to have been on the order of days or weeks rather than months. Carbon tetrachloride readily volatilizes from surface water and would be expected to have evaporated from creeks and reservoirs within weeks of its release. The estimated transit time and evaporation time are similar and the amount of carbon tetrachloride remaining in the water when it reached the reservoir can not be predicted based on this information.

Carbon tetrachloride concentrations in effluent and surface water were not measured. Calculations based on a single study of several fish exposed to water from Walnut Creek suggest that carbon tetrachloride concentrations in the creek were above background levels. Based on bioconcentration factors published in the literature we estimated the creek water concentrations were on the order of 22 $\mu\text{g L}^{-1}$. If the creek contributed 4% of the volume to Great Western Reservoir, concentrations in the reservoir, which supplied drinking water to the City of Broomfield, may have approached 0.8 $\mu\text{g L}^{-1}$. The current drinking water standard is 5 $\mu\text{g L}^{-1}$.

Discharges of carbon tetrachloride to surface water may warrant further study. More information on effluent treatment and discharge and an in-depth analysis of surface water flow from the site to drinking water sources would be required in order to better resolve this issue. We have conducted a search for additional information and have been unable to locate any new documents which could be used to better quantify or characterize the releases to surface water.

The amount of carbon tetrachloride which spilled, leaked, leached or otherwise reached ground water is difficult to estimate. Although of concern when compared to drinking water standards, the amount in groundwater is likely to be a small amount relative to atmospheric emissions, on the order of less than 0.1 ton. Carbon tetrachloride has not been carried beyond the site boundary in groundwater.

An estimated 110–150 tons of carbon tetrachloride may have been shipped to Idaho. This amount was from carbon tetrachloride in waste stored in liquid form at the burial mound and 903 Pad in the 1950s and 1960s, This waste was then processed and shipped to Idaho in the mid 1960s. This estimate is uncertain due to a lack of process information and uncertainties in estimates of the carbon tetrachloride content of the waste, which was not measured.

The estimated amount of carbon tetrachloride lost to ground water (less than 0.1 ton) and the amount shipped to Idaho (110–150 tons) seems quite meager when compared to the ChemRisk release estimates of 1,100–5,400 tons total from 1953–1989. The small size and uncertainty of these estimates suggest these amounts do not need to be subtracted from the Phase I atmospheric source term estimates.

REFERENCES

- Anderson D.M., Putzier, E.A. and D.L. Ziegler. 1970. Sorting of Radioactive Waste at Rocky Flats. 326-74-A009. February 11.
- Barrick, C.W. 1974. Harmful and Potentially Harmful Materials Inventory. With transmittal memo to J.B. Owen.. Dow Chemical, Golden, Colorado. January 25.
- Barrick, C.W. 1981. *Past Accidental Releases of Radioactivity from the Rocky Flats Plant*. Dow Chemical, Golden, Colorado.
- ChemRisk. 1994. Project Task 5 Report. Estimating Historical Emissions from Rocky Flats. ChemRisk, A Division of McLaren/Hart, Alameda, California. March.
- ChemRisk. 1992. *Reconstruction of Historical Rocky Flats Operations and Identification of Release Points*. Project Tasks 3&4 Final Draft Report. ChemRisk, A Division of McLaren/Hart. Alameda, California. August.
- ChemRisk. 1991. Project Task 2 Report. Selection of the Chemicals and Radionuclides of Concern. June 1991. ChemRisk, A Division of McLaren/Hart, Alameda, California.
- City of Westminster. 1988-1991. Radiation Data Monthly Report. Volatile Organic Analysis Summaries. Westminster, Colorado.
- City of Broomfield. 1989-1991. Radiometric Monitoring Report. Monthly Information Exchange Meeting. Organic Analysis Summaries.
- Crisler, L.R. 1991 "A History of Rocky Flats Plutonium/Actinide Recovery Plant 1962-1991". Draft. Dow Chemical company, Golden, Colorado. October 30.
- DOE (U.S. Department of Energy). 1980. *Final Environmental Impact Statement, Rocky Flats Plant*. DOE/EIS-0064. April.
- EG&G Rocky Flats. 1990. Buildings 707, 559, 777, Air Pollution Emissions Notice (APEN) Log Book April 5, 1990 - December 7, 1990. EG&G Rocky Flats, Inc., Golden, Colorado.
- EG&G Rocky Flats. 1994. Environmental Technology Site HHRA Chemicals of Concern Identification, TM 4 for Operable Unit 3. September 23.
- EG&G Idaho, Inc. 1994. *A Comprehensive Inventory of Radiological and Nonradiological Contaminants in Waste Buried in the Subsurface Disposal Area of the INEL RWMC during the Years 1952 - 1983*. Volume 1. EGG-WM-10903. EG&G Idaho, Inc., Idaho Falls, Idaho. June.
- Ferrera, K.P. 1988. Monthly Status Report—Halogenated Solvents. Rockwell International, Golden, Colorado. December 8.
- Fruehof, V. and T. Richter. 1974. Handling and Monitoring of Carbon Tetrachloride. Dow Chemical Company, Golden, Colorado. January 8.
- Grogan, H.A., K.R. Meyer, P.G. Voillequé, S.K. Rope, M.J. Case, H.R. Meyer, R.E. Moore, T. Winsor, and J.E. Till. 1994. *Phase II Final Task 2 Report. Verification of Phase I Source Term and Uncertainty Estimates*. Radiological Assessments Corporation, Neeses, South Carolina. September.
- Hamilton, T.H. and L.V. Moser. 1990. *Volatile Organic Emission Report for the US DOE Rocky Flats Plant*. K/QT-359, Volume 1. Martin Marietta Energy Systems Inc. March 29.
- Hobbs, F.D. 1970. "A Survey of Potential Solvents to Replace Carbon Tetrachloride for Degreasing Plutonium. PRD 940477-104. Rockwell International, Golden, Colorado

- Hobbs F.D. 1982. "Carbon Tetrachloride Emissions from Production Area, Buildings 707 and 776/777." Rockwell International, Golden, Colorado. October 14.
- Howard, P.H., editor. 1990. *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, Volume II. Lewis Publishers, Inc. Chelsea, Michigan.
- Hurr, T.R. 1976. Hydrology of a Nuclear-Processing Plant Site, Rocky Flats, Jefferson County, Colorado. US Geological Survey. Report 76-268. Denver, Colorado. March.
- Johnson, T.C. 1971. Memo to B.L. Kelchner, "Carbon Tetrachloride Vapor Emission from Building 774." Dow Chemical, Golden, Colorado. March 1.
- Johnson, C.M. 1973. Monthly Environmental Progress Report—Stack Emissions Monitors, Report Index C-37. Dow Chemical, Golden, Colorado. August.
- Johnson, C.M., L.H. Faber, and J.L. Lawless. 1974a. Internal Report—Hydrocarbon Emissions Booster No. 1. CRDL 950373-104. Dow Chemical, Rocky Flats Colorado. August 12.
- Johnson, C.M., L.H. Faber, and J.L. Lawless. 1974b. Monthly Report. RFP-2200-A. Dow Chemical, Golden, Colorado.
- Joshel, 1970a. The Environmental Effect of the Rocky Flats Plant. Draft Number 2. Dow Chemical, Golden, Colorado. December 11.
- Joshel, L.M. 1970b. TWX to H.C. Donalley re:Chronological History Regarding Leakage in Drum storage area. February 17.
- Kudera, D.E. 1987 "Estimate of Rocky Flats Plant Organic Wastes Shipped to the RWMC" internal note, EG&G Idaho, Inc., Idaho Falls, Idaho. July 24.
- Kudera, D.E. 1989. Hazardous Waste Constituents of INEL, Contact-Handled Transuranic Waste. Engineering design file RWMC-369. Idaho National Engineering Laboratory, Idaho Falls, Idaho. May.
- Lee, W.H. 1971. The Dow Chemical Company. Letter to H.F. Soule, Atomic Energy Commission, Washington. Subject: Rocky Flats Solid Wastes Shipped to NRTS. 10 June.
- Love, C.M. 1970. *Report of the Task Force on Potential Offsite Contamination*. Dow Chemical, Golden, Colorado. June 1.
- Meyer, K.R. and J.E. Till. 1999. *Characterization of Surface Water Releases at the Rocky Flats Plant*. RAC Report No. 7-CDPHE-RFP-1996-FINAL(Rev.1). *Radiological Assessments Corporation*, Neeses, S.C. August.
- Musgrave, L.E. 1975. *Possible Uses of 1,1,1 Trichloroethane in Fabrication and Metallurgical Operations*. FET 950896-121. Dow Chemical, Golden, Colorado. January 10.
- National Academy of Sciences. 1978. *Report of the Panel on Low Molecular Weight Halogenated Hydrocarbons of the Coordinating Committee for Scientific and Technical Assessments of Environmental Pollutants*. Scientific and Technical Assessments of Environmental Pollutants, Chapters 4 and 5.
- Ofte D., F. Coffman and D. Elle. 1974. Investigation of a Tritium Release Occurring in Building 777 on September 3-4, 1974. Rocky Flats Plant, Golden Colorado.
- Pottorff, E.T. 1995. Water Quality Control Division, Colorado Department of Public Health and Environment. Personal communication with Patricia D. McGavran, consultant to RAC, September.
- Plock, C.E. 1972. "Survey of Rocky Flats Division Waste Streams". CRDL-950351-009. Dow Chemical, Golden, Colorado. June 30.

- Roberts, B. 1995. Rocky Mountain Remedial Services, Rocky Flats Personal communication with Patricia D. McGavran, consultant to RAC. October.
- Rockwell. 1988. *Solar Evaporation Ponds Closure Plan*. Rockwell International, Golden, Colorado.
- Rockwell. 1989. Internal Letter from C.R. Hodgkin to Distribution. "Scoping Analysis - Environmental/Health Impacts from Routine Atmospheric Releases of Carbon Tetrachloride from the Rocky Flats Plant." CRH-12/1.
- Ryan, E.S., Vance, J.N. and N.E. Maas. 1965. *Aqueous Radioactive Waste Treatment Plant at Rocky Flats*. RFP-638. Dow Chemical, Golden, Colorado.
- Seed, J.R., Calkins K.W. and F.J. Miner. 1970. *Status Report of Committee on Plutonium in Soil*. Dow Chemical, Golden, Colorado.
- Seed, J.R., Calkins K.W., Illsley C.T., Miner F.J. and J.B. Owen. 1971. *Committee Evaluation of Plutonium Levels in Soil Within and Surrounding USAEC Installation at Rocky Flats - Colorado*. RFP-INV-10. Dow Chemical, Golden Colorado. July 9.
- Siders, M. 1995. Rocky Mountain Remedial Services, Rocky Flats. Personal communication with Patricia D. McGavran, consultant to RAC, October.
- EPA (U.S. Environmental Protection Agency). 1985. *Compilation of Air Pollution Emissions Factors, EPA Office of Air Quality Planning and Standards*. AP-42. Research Triangle Park, North Carolina. September.
- Zillich, J.A. 1974. *Biological Impacts of Rocky-Flats Wastes Discharged to Surface Waters*. RFP. 2210. Rockwell International, Golden, Colorado. April 9.