# 5. POTENTIAL FOR HUMAN EXPOSURE

## 5.1 OVERVIEW

Titanium tetrachloride is an inorganic compound that undergoes rapid hydrolysis upon contact with water. On contact with moist air, it produces a heavy, dense white smoke composed of fine particles of hydrochloric acid, titanium oxychloride, and titanium dioxide. It may be released to air during production and/or use, or as a result of chemical spills. Because it hydrolyzes upon contact with water, it is unlikely to be transported significant distances in any environmental media. However, one of its hydrolysis products, titanium dioxide, may persist in soils or sediments. The other hydrolysis product, hydrochloric acid, dissociates in water and air.

Exposure to titanium tetrachloride is primarily occupational, with titanium industry workers having the greatest potential exposure. Exposure to fumes and vapors can occur during handling of titanium tetrachloride and may also occur in the chlorinating department during production of titanium dioxide. Exposure can also occur by the dermal route, particularly in cases of occupational spills. Members of the general population are not likely to receive significant exposure to titanium tetrachloride except in the case of a spill or accident.

No analytical methods are currently available for measuring concentrations of titanium tetrachloride directly in any environmental medium, although methods are available for determining the concentrations of several of its hydrolysis products. As a result of the absence of detection methods for this compound, coupled with the compound's rapid rate of hydrolysis, titanium tetrachloride concentrations have not been reported in air, water, soil, sediments, or in food products.

Titanium tetrachloride has not been identified at any of 1,416 hazardous wastes sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 1995). However, the number of sites evaluated for titanium tetrachloride is not known.

## 5.2 RELEASES TO THE ENVIRONMENT

Table 5-l summarizes data on industrial releases of titanium tetrachloride reported to the EPA (TR193 1995). These data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

### 5.2.1 Air

According to the Toxic Chemical Release Inventory (TR193 1995), an estimated total of 24,722 pounds of titanium tetrachloride, amounting to 99.6% of the total environmental release, was discharged to the air from 38 large manufacturing and processing facilities in the United States in 1993. Table 5-l lists the amount of titanium tetrachloride released from each of these facilities.

### 5.2.2 Water

No information was found regarding releases of titanium tetrachloride to surface water or groundwater via underground injection. However, assuming titanium tetrachloride spills may be dispersed with large amounts of water into a sewer system using recommended clean-up procedures (ITII 1984), runoff contaminated with titanium tetrachloride hydrolysis products could reach surface waters.

### 5.2.3 Soil

According to the Toxic Chemical Release Inventory (TR193 1995), an estimated total of 100 pounds of titanium tetrachloride, amounting to 0.4% of the total environmental release, was discharged to land from 38 large manufacturing and processing facilities in the United States in 1993. Table 5-l lists the amount of titanium tetrachloride released from each of these facilities.

The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

## Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Titanium Tetrachloride

| State[a] | City | Facility | Reported amounts released in pounds per year | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Air | Water | Land | Underground injection | Total environment[b] | POTW transfer | Off-site waste transfer |
| AL | AXIS | DU PONT | | | | | | | 2,380,000 |
| CA | ANTIOCH | DU PONT | 1,140 | | | | 1,140 | | |
| CT | NA | PFIZER INC. | | | | | | | |
| DE | EDGEMOOR | DU PONT | 549 | | | | 549 | | |
| GA | SAVANNAH | KEMIRA INC. | 2,600 | | | | 2,600 | | |
| KY | LOUISVILLE | AMERICAN SYNTHETIC RUBBER | 5 | | | | 5 | | |
| LA | LAKE CHARLES | HIMONT USA INC. | 100 | | | | 100 | | |
| LA | NORCO | SHELL NORCO MFG. COMPLEX | 3,702 | | | | 3,702 | | 272,000 |
| LA | WESTLAKE | LOUISIANA PIGMENT CO. L.P. | 474 | | | | 474 | | 169 |
| MD | BALTIMORE | SCM CHEMICALS | 47 | | | | 47 | | |
| MI | ADRIAN | ANDERSON DEVELOPMENT CO. | 22 | | | | 22 | | |
| MI | WESTON | AKZO CHEMICALS INC. | 10 | | | | 10 | | |
| MS | HAMILTON | KERR-MCGEE CHEMICAL CORP. | 1,500 | | | | 1,500 | | |
| MS | PASS CHRISTIAN | DU PONT DELISLE | 3,070 | | | | 3,070 | | |
| NJ | EDISON | AKZO NOBEL CHEMICALS INC. | 1,100 | | | | 1,100 | | |
| NJ | NA | E. I. DU PONT DE NEMOURS & | | | | | | | |
| NJ | WEST DEPTFORD TWP. | HUNTSMAN POLYPROPYLENE | 1 | | | | 1 | | |
| NV | HENDERSON | TITANIUM METALS CORP. | 400 | | | | 400 | | |
| NY | NA | CORNING INC. | | | | | | | |
| NY | NIAGARA FALLS | TAM CERAMICS INC. | 23 | | | | 23 | | |
| OH | ASHTABULA | SCM CHEMICALS | 162 | | | | 162 | | |
| OH | ASHTABULA | SCM CHEMICALS AMERICAS | 100 | | | | 100 | | |
| OK | BARTLESVILLE | PHILLIPS RESEARCH CENTER | 1 | | | | 1 | | |
| OR | ALBANY | OREGON METALLURGICAL | 500 | | | | 500 | | |
| PR | NA | PFIZER INC. | | | | | | | |
| TN | NEW JOHNSONVILLE | DU PONT | 2,250 | | | | 2,250 | | |
| TX | CHEEK | GOODYEAR TIRE & RUBBER | 1 | | 100 | | 101 | | |
| TX | LONGVIEW | TEXAS EASTMAN DIV. | 2,105 | | | | 2,105 | | |
| TX | NA | AMOCO CORP. | | | | | | | |
| TX | NA | SOLVAY AMERICA INC. | | | | | | | |

## Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Titanium Tetrachloride (continued)

| State[a] | City | Facility | Reported amounts released in pounds per year | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Air | Water | Land | Underground injection | Total environment[b] | POTW transfer | Off-site waste transfer |
| TX | NA | CHEVRON CORP. | | | | | | | |
| TX | NA | NA | | | | | | | |
| TX | NA | OCCIDENTAL PETROLEUM | | | | | | | |
| TX | NA | E. I. DU PONT DE NEMOURS & | | | | | | | |
| TX | PASADENA | CATALYST RESOURCES | 500 | | | | 500 | | 422 |
| TX | PASADENA | ETHYL CORP. | 4,248 | | | | 4,248 | | |
| TX | WADSWORTH | OCCIDENTAL CHEMICAL CORP. | 10 | | | | 10 | | 306,409 |
| WV | GALLIPOLIS FERRY | AKZO NOBEL CHEMICALS INC. | 2 | | | | 2 | | |
| | | Totals | 24,622 | | 100 | | 24,722 | | 2,959,000 |

Source: TRI93 1995

POTW = Publicly Owned Treatement Works

[a] Post office state abbreviations used
[b] The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

## 5.3 ENVIRONMENTAL FATE

### 5.3.1 Transport and Partitioning

Titanium tetrachloride hydrolyzes rapidly upon contact with moist air to form a vapor of hydrochloric acid, titanium dioxide, and titanium oxychloride (Whitehead 1983; Wilms et al. 1992). Consequently, environmental transport of this compound is negligible; however, the atmospheric transport of the resulting hydrolysis products may be significant.

No data were located to estimate the residence time for titanium tetrachloride in air or water; however, based on the compounds rapid hydrolysis, residence times are expected to be short (in the order of hours).

### 5.3.2 Transformation and Degradation

#### 5.3.2.1 Air

Upon contact with moist air, titanium tetrachloride rapidly hydrolyzes with fuming into hydrogen chloride, titanium dioxide, and titanium oxychloride (Whitehead 1983; Wilms et al. 1992).

#### 5.3.2.2 Water

When titanium tetrachloride is released to water it rapidly hydrolyzes to hydrochloric acid, titanium oxychloride, and titanium dioxide. Titanium oxychloride usually further hydrolyzes to hydrochloric acid and titanium dioxide (Wilms et al. 1992). In water, hydrochloric acid dissociates to the hydrogen and chloride ions. Titanium dioxide is insoluble in water and may settle out into the sediments.

#### 5.3.2.3 Sediment and Soil

No information was located on the degradation of titanium tetrachloride released to soils or sediments; however, based on the rapid hydrolysis of this compound in moist air or in water, it may be expected that titanium tetrachloride will also hydrolyze upon contact with moisture in the soil and sediment. Residues of titanium dioxide, a very inert compound, are likely to remain in the soil or settle out to the sediment.

## 5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

No methods are currently available for measuring concentrations of titanium tetrachloride directly in any environmental medium. Methods are available for determining concentrations of several of its hydrolysis products (see Section 6).

### 5.4.1 Air

No information was located on concentrations of titanium tetrachloride in air.

### 5.4.2 Water

No information was located on concentrations of titanium tetrachloride in surface water or groundwater.

### 5.4.3 Sediment and Soil

No information was located on concentrations of titanium tetrachloride in sediment or soil.

### 5.4.4 Other Environmental Media

No information was located on concentrations of titanium tetrachloride in any other environmental media.

## 5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Information on the potential for general population exposure to titanium tetrachloride as a result of its manufacture, use, disposal, or presence at a hazardous waste site was not located. The lack of data on concentrations of titanium tetrachloride in air, water, soil, food, and other sources of general population exposure, coupled with the rapid rate of hydrolysis of titanium tetrachloride in all environmental media, suggest that such exposure is probably limited. Members of the general population are not likely to receive significant exposure to titanium tetrachloride except in the case of a spill or accident.

Workers who are involved in the manufacture, processing, handling, and disposal of titanium tetrachloride are likely to be exposed to higher concentrations by dermal exposure and inhalation than the general population. Occupational exposure to titanium tetrachloride may be significant for workers in titanium industries. Preliminary data from a workplace survey, the National Occupational Exposure Survey (NOES), conducted by the National Institute for Occupational Safety and Health (NIOSH) from 1980 to 1983, indicated that 2,107 workers, including 131 women, were potentially exposed to titanium tetrachloride in the workplace in 1980 (NIOSH 1993).

NIOSH (1992) does not provide recommendations for occupational exposure levels to titanium tetrachloride, but does provide a recommendation for occupational exposure levels to titanium dioxide, a hydrolysis product, of 0.2 mg/m$^3$. However, two independent limit setting organizations have recommended exposure limits for titanium tetrachloride. The American Industrial Hygiene Association's Workplace Environmental Exposure Limits (WEEL) Committee has recommended an S-hour TWA for chronic exposure of 0.5 mg/m$^3$ for titanium tetrachloride (AIHA 1994). In addition, the American Industrial Hygiene Association's Emergency Response Planning Guidelines Committee has recommended short-term (<1 hour) emergency limits (ranging from 100 mg/m$^3$ to 5 mg/m$^3$) (AIHA 1992).

## 5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers in the titanium processing industry have the greatest potential for exposure to titanium tetrachloride during its production, processing, handling, and disposal. Workers who are involved in the process of producing titanium metal from titanium tetrachloride receive the most exposure, particularly those involved in the reduction process where they are exposed to vapors of titanium tetrachloride, titanium oxychloride, and titanium dioxide particulates (Garabrant et al. 1987). Maintenance and repair workers at these facilities also are exposed to high concentrations of titanium tetrachloride vapors containing its hydrolysis products, titanium oxide and hydrochloric acid (Mogilevskaja 1983). Workers who may use titanium tetrachloride for examining welding machinery also may be exposed as a result of occupational spills (Ross 1985).

Other than individuals who are occupationally exposed to titanium tetrachloride, no members of the general population are likely to receive high exposures except as a result of an accidental spill. Because of its rapid hydrolysis and because it has not been identified at any NPL hazardous waste site

(HazDat 1995), individuals living near these sites are unlikely to be exposed to any significant concentrations of titanium tetrachloride.

## 5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of titanium tetrachloride is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of titanium tetrachloride.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

### 5.7.1 Identification of Data Needs

**Physical and Chemical Properties.** Although it has been determined that titanium tetrachloride hydrolyzes rapidly upon contact with water in all environmental media, it is not a well-defined chemical in terms of its physical and chemical properties (Merck 1989). Because of its rapid hydrolysis, information on some of its other chemical and physical properties would be difficult if not impossible to measure.

**Production, Import/Export, Use, Release, and Disposal.** According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1993, became available in May of 1995. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

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The available use, production, and release information for titanium tetrachloride is insufficient to determine the amount of titanium tetrachloride that hydrolyzes (CICIS 1993; OHM/TADS 1992; Whitehead 1983). In addition, there is a lack of data on how much titanium tetrachloride may be stored at waste sites, current methods of industrial disposal, and environmental releases that may result from its use as a dye, as a catalyst, and in the titanium metal industry. This information would be useful in determining whether significant releases of titanium tetrachloride occur, what disposal methods are available, and the potential of its hydrolysis products for environmental contamination.

**Environmental Fate.** Titanium tetrachloride readily hydrolyzes upon contact with moisture to form hydrochloric acid, titanium dioxide, and titanium oxychloride (Whitehead 1983; Wilms et al. 1992). Information on the degradation rates, persistence, and fate of these degradation products would be helpful in determining levels of titanium tetrachloride that may have an impact on various environmental media. This is particularly true for releases of titanium tetrachloride to soil as a result of spills.

**Bioavailability.** Available information regarding the rate of titanium tetrachloride absorption following inhalation, oral, and dermal contact has been discussed under Toxicokinetics (see Section 2.3) (Elo et al. 1972; Lee et al. 1986; Ophus et al. 1979; Redline et al. 1986). Information is lacking on the Bioavailability of titanium tetrachloride from environmental media as there is no information available on titanium tetrachloride concentrations in environmental media. Because of the physico-chemical properties of titanium tetrachloride, the major route of occupational exposure is by inhalation and the major target organ is the lung. Exposure can also occur by the dermal route particularly in cases of occupational spills. The rapid hydrolysis of titanium tetrachloride in water (Wilms et al. 1992) suggests that human exposure via contaminated drinking water or surface waters is unlikely, and no further studies on the bioavailability of this compound in water are indicated.

**Food Chain Bioaccumulation.** No information was found on the Bioaccumulation potential of titanium tetrachloride in aquatic or terrestrial ecosystems. However, its rapid hydrolysis upon contact with moisture (Wilms et al. 1992) suggests that there is little potential for Bioaccumulation or biomagnification in aquatic or terrestrial organisms. Further studies on the Bioaccumulation or biomagnification of this compound are not required.

5. POTENTIAL FOR HUMAN EXPOSURE

**Exposure Levels in Environmental Media.** No data were located on the concentration of titanium tetrachloride in ambient air or in occupational settings, therefore no estimate of inhalation exposure to titanium tetrachloride can be obtained for the general population or for any occupationally exposed groups. No data on the concentration of titanium tetrachloride in drinking water, surface water, or groundwater were located. However, because of its physico-chemical properties, titanium tetrachloride is expected to undergo rapid hydrolysis (Wilms et al. 1992) and would not be expected to be present in these environmental media.

Reliable monitoring data for the levels of titanium tetrachloride in contaminated media at hazardous waste sites are needed so that the information obtained on levels of titanium tetrachloride in the environment can be used in combination with the known body burden of titanium tetrachloride to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** Most human exposures to titanium tetrachloride occur in the workplace as a result the production of titanium or because of accidental spills. No data on titanium tetrachloride concentrations in various human tissues and body fluids of unexposed populations, populations living near hazardous waste sites, or occupationally exposed groups are available. Because of its tendency to undergo rapid hydrolysis in aqueous environments, titanium tetrachloride is not likely to be detected in human tissues although particles of titanium dioxide, a hydrolysis product, have been detected in the lungs of occupationally exposed individuals (Elo et al. 1972; Ophus et al. 1979; Redline et al. 1986). Data on workplace exposures do exist (Garabrant et al. 1987; Ross 1985); however, exposure levels for the general population or persons living near hazardous waste sites are not available. Additional data on the concentrations of titanium tetrachloride hydrolysis products in body tissues and fluids are needed to estimate the extent of occupational exposure to this compound and in determining whether there is a health risk to occupationally exposed populations. Members of the general population are not likely to be exposed to titanium tetrachloride except in the case of a spill or accident.

This information is necessary for assessing the need to conduct health studies on these populations.

**Exposure Registries.** No exposure registries for titanium tetrachloride were located. This substance is not currently one of the compounds for which a subregistry has been established in the

National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

### 5.7.2 Ongoing Studies

No ongoing studies on the potential for human exposure to titanium tetrachloride were located.