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4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

4.1 PRODUCTION

CDDs are not manufactured commercially in the United States except on a small scale for use in chemical and toxicological research. CDDs are unique among the large number of organochlorine compounds of environmental interest in that they were never intentionally produced as desired commercial end products (Zook and Rappe 1994). Typically, CDDs are unintentionally produced during various uncontrolled chemical reactions involving the use of chlorine (EPA 1990c) and during various combustion and incineration processes (Zook and Rappe 1994). In the process of making white paper products, for example, chlorine or chlorine derivatives are often used as the primary bleaching agent. As a result, several chlorinated organic compounds are formed, including small amounts of CDDs (EPA 1990c). These chlorinated compounds not only leave the mills in the pulp and paper products, they are also released through waste waters (effluents from the mills) and sludge produced as a result of waste water treatment (EPA 1990c). CDDs are also produced as undesired by-products during the manufacture of chlorinated phenols such as pentachlorophenol, 2,4,5-trichlorophenol, and related chemicals, and during incineration of chlorinated wastes (IARC 1977; NTP 1989; Podoll et al. 1986). By far the greatest unintentional production of CDDs occurs via various combustion and incineration processes including all forms of waste incineration (municipal, industrial, and medical), many types of metal production (iron, steel, magnesium, nickel, lead, and aluminum), and fossil fuel and wood combustion (Czuczwa and Hites 1986a, 1986b; Oehme et al. 1987, 1989; Zook and Rappe 1994). More extensive information on sources of CDDs released to the environment can be found in Chapter 5.

In general, there are two conventional methods for the preparation of CDDs for research purposes: condensation of a polychlorophenol and direct halogenation of the parent dibenzo-*p*-dioxin or a monochloro-derivative. For example, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) is generally synthesized by the condensation of two molecules of 2,4,5-trichlorophenol in the presence of a base at high temperatures or by chlorination of dibenzo-*p*-dioxin in chloroform in the presence of iodine and ferric chloride (EPA 1987k; IARC 1977). Other methods of 2,3,7,8-TCDD synthesis include the following: pyrolysis of sodium α -(2,4,5-trichlorophenoxy) propionate at 500 EC for 5 hours; reaction of dichlorocatechol salts with *o*-chlorobenzene by refluxing in alkaline dimethyl sulfoxide; ultraviolet irradiation of CDDs of high chlorine content; Ullman reaction of chlorinated phenolates at 180–400 EC;

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pyrolysis of chlorinated phenolates and chlorinated phenols; and heating 1,2,4-trichloro-5-nitrobenzene and 4,5-dichlorocatechol in the presence of a base (EPA 1984a; IARC 1977).

1,2,3,4-TCDD has been prepared by refluxing a mixture of catechol, potassium carbonate, pentachloronitrobenzene and acetone in nitrogen (IARC 1977).

DCDD can be synthesized by two methods. In the first method, 2-bromo-4-chlorophenol and potassium hydroxide are dissolved in methanol and evaporated to dryness. The residue is then mixed with bis(2-ethoxyethyl) ether, ethylene diacetate, and a copper catalyst; and then heated, cooled, and eluted from a chromatographic column with chloroform. This residue is evaporated and then sublimed. DCDD can also be synthesized by heating the potassium salt of 2,4-dichlorophenol in the presence of copper powder in a vacuum sublimation apparatus (IARC 1977).

1,2,4,6,7,9-HxCDD has been made by heating the potassium salt of 2,3,5,6-tetrachlorophenol with powdered copper and potassium carbonate in a vacuum sublimation apparatus (IARC 1977).

1,2,3,4,7,8-HxCDD has been prepared by mixing 1,2,3,4-TCDD, ferric chloride, chloroform, and a crystal of iodine and then adding a solution of chlorine in carbon tetrachloride (IARC 1977).

OCDD has been synthesized by the following methods: irradiation of aqueous solutions of CDD-free sodium pentachlorophenol with ultraviolet light; heating the potassium salt of pentachlorophenol; heating pentachlorophenol in the presence of an initiator, such as chlorine, bromine, iodine, or 2,3,4,4,5,6-hexachloro-2,5-cyclohexadienone; and heating hexachlorocyclohexadienone in an atmosphere of carbon dioxide for 30 minutes (Crosby and Wong 1976; EPA 1984a; IARC 1977).

At present, the only reported producers of CDDs are Eagle Picher Industries, Inc., located in Lenexa, Kansas, and Cambridge Isotope Laboratories, located in Andover, Massachusetts. Eagle Picher Industries produces 2,3,7,8-TCDD and OCDD for research purposes (SRI 1991). Cambridge Isotope Laboratories produced unlabeled chlorodioxin standards (TCDD through HpCDD) and C¹³ labeled chlorodioxin standards (DCDD through OCDD) for use in chemical analyses and in toxicological research (Cambridge Isotope Laboratories 1995).

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Since CDD releases are not required to be reported under Superfund Amendments and Reauthorization Act (SARA) Section 313, there are no data on CDDs in the 1994 Toxics Release Inventory (TRI) (EPA 1995g).

4.2 IMPORT/EXPORT

2,3,7,8-TCDD is not imported into the United States (NTP 1989). There were no data located pertaining to the export of 2,3,7,8-TCDD or any other CDD for research purposes.

4.3 USE

The only reported use of CDDs/CDFs is as research chemicals (NTP 1989). A large diversified group of researchers use various CDDs in studies of toxicology, environmental fate, transformation, and transport, and in residue analysis of a variety of contaminated media. CDDs have been tested for use in flame-proofing polymers such as polyesters and against insects and wood-destroying fungi; however, there are no data reporting its commercial production or use for these purposes (IARC 1977).

4.4 DISPOSAL

The 1994 estimates on the degree of TCDD contamination in the environment indicated that approximately 500,000 tons of soil and sediment in the United States were contaminated with 2,3,7,8-TCDD (Hilarides et al. 1994). The development of treatment technologies for CDD-contaminated soils and wastes needed to address unique problems associated with CDDs: for example, they are insoluble in water, only slightly soluble in organic solvents, have a strong affinity for adsorption on organic matter, and are biologically and environmentally stable (U.S. Congress 1991). In order to meet the clean-up standards established for CDDs, the treatment system must be capable of removing the CDDs from the contaminated matrix (U.S. Congress 1991). Several treatment or disposal methods for CDDs and CDD-contaminated materials have been investigated, including land disposal, thermal destruction, and chemical and biological degradation. Each of these methods has limitations regarding economics, technical feasibility, and acceptability (HSDB 1995).

Land disposal of CDD-containing wastes is currently prohibited (EPA 1986f, 1988f). The Toxic Substances Control Act (TSCA) regulates the use, disposal, and distribution in commerce of process waste water treatment sludges intended for land application from pulp and paper mills employing chlorine or

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chlorine derivative-based bleaching processes (EPA 1991b, 1991c). Also, under the Marine Protection Research and Sanctuaries Act, ocean dumping of CDD-containing wastes is prohibited except when only trace amounts are present (EPA 1977a, 1977b).

Thermal destruction technologies offer the most straightforward approach to treating or disposing of CDD-contaminated materials because under the appropriate conditions the breakdown of the CDDs is assured (U.S. Congress 1991). The thermal treatment technologies that are currently used to treat waste containing hazardous or toxic constituents and that have demonstrated potential use toward the treatment of CDD-contaminated waste include rotary kiln incineration, liquid injection incineration, fluidized-bed incineration, advanced electric reactor (AER), infrared incineration, plasma arc pyrolysis incineration, supercritical water oxidation, and *in situ* vitrification (U.S. Congress 1991). In addition to kiln incinerators, the technologies that have been field-tested for treating CDD-contaminated media under EPA's Superfund Innovative Technology Evaluation (SITE) program include dechlorination, stabilization, and *in situ* vitrification (U.S. Congress 1991). Although some alternatives look promising and have been shown effective in the laboratory or in application to other pollutants, more development and testing is needed to demonstrate viability for large-scale treatment of CDD contamination.

Incineration, involving the high-temperature oxidation of CDD molecules, is the most extensively tested method for disposal of CDDs. CDDs such as TCDD, PeCDD, and HxCDD are classified by EPA as Principal Organic Hazardous Constituents (POHCs) and are required to be incinerated under conditions that achieve a destruction and removal efficiency of 99.99% (EPA 1990b; Sedman and Esparza 1991). Incinerator operating conditions currently considered adequate for destruction of 2,3,7,8-TCDD and most other chlorinated organics require a temperature of at least 1,500–2,600 °F, with residence times of at least 30 minutes (although 1.5 hours is a more common residence time) to ensure complete destruction (EPA 1990a). Thermal destruction of CDDs that are adsorbed on fly ash can be accomplished through the use of a rotary kiln furnace combined with a baghouse filter for the recycling of entrained fly ash and an activated carbon filter for adsorption of CDD traces transported in the gas phase. This method is capable of destroying 99.5% of CDDs in fly ash, which is considered a high level of efficiency (Kahr et al. 1990). EPA's Mobile Incineration System, a transportable rotary kiln system, was judged to be more than adequate for detoxifying CDD-contaminated solids and liquids after it was performance-tested with a variety of uncontaminated soils and other solid wastes, and thus could be expected to accomplish a successful CDD trial burn. The system, which has been extensively modified for field use, consists of a

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rotary-kiln, a secondary combustion chamber, an air pollution control unit, and separate continuous stack-gas analysis capabilities (HSDB 1995). In 1977, the U.S. Air Force disposed of Agent Orange contaminated with 2,3,7,8-TCDD by high temperature incineration at sea (Bumb et al. 1980). The high flame temperature reached 1,500 EC in the incinerator, and EPA determined a combustion efficiency of 99.9% for 2,3,7,8-TCDD.

Kiln incinerators have been used to treat a variety of containerized and noncontainerized solid and liquid wastes. Since the waste can be treated individually or simultaneously, the versatility of this technology has made it popular in the United States for disposing of hazardous waste. For the disposal of CDD-containing waste, however, kiln incineration is more commonly practiced in Europe than in the United States (U.S. Congress 1991). Although liquid injection incineration has been used for ocean-based incineration of Agent Orange, certain limitations must be considered before applying the technology to treating CDD contamination. These limitations include the applicability of the technology only to combustible low-viscosity liquids and slurries that can be pumped; atomizing the waste prior to injection into the combustor; and the importance of particle size because burners are susceptible to clogging (U.S. Congress 1991). Fluidized-bed combustion (FBC) systems have traditionally been used to treat the sludge produced by municipal waste treatment plants and waste generated from oil refineries, pulp and paper mills, and the pharmaceutical industry. The system consists of a vertical refractory-lined vessel which holds a perforated plate. A bed of granular material, usually sand, is placed on the perforated plate. The system uses forced hot air to fluidize the bed and cause a highly turbulent zone that ensures the mixing of the waste with bed particles and the combustion air. Combustion is facilitated by an overhead burner (U.S. Congress 1991). The type and size of materials to be treated are critical because variations in gravity and density could be deleterious to the process (U.S. Congress 1991). Modification of the traditional FBC system for treatment of chlorinated wastes continues to be investigated by researchers in the private sector. A modified system designed by Waste-Tech Services, Inc. uses a granular bed composed of a mixture of combustion catalyst and limestone. The results of the trial burn for the Waste-Tech Services system which used chlorinated waste containing carbon tetrachloride, tetrachloroethane, p-dichlorobenzene and some CDDs and CDFs, showed no measurable amount of any of the chlorinated pollutants treated and no 2,3,7,8-TCDD in any of the samples tested (U.S. Congress 1991). *In situ* vitrification (ISV), which treats waste in place, solidifies all materials not volatilized or destroyed. Bench-scale testing of ISV on soils containing 10 ppb CDDs showed destruction removal efficiency (DRE) values of 99.9999% (U.S. Congress 1991).

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Since the early 1970s, several chemical methods have been investigated for the degradation of CDDs. Treatment of CDD-contaminated materials with alkali polyethylene glycolate (APEG) reagents at hazardous waste sites has been demonstrated to successfully destroy CDDs in liquid wastes and to be viable even under difficult circumstances. This method involves the reaction of potassium hydroxide with polyethylene glycol to form an alkoxide that reacts with one of the chlorine atoms on the CDD to produce an ether and potassium chloride. Bioassays indicate that the by-products produced by treating 2,3,7,8-TCDD with APEG reagents do not bioaccumulate or bioconcentrate, do not cause mutagenicity, and are far less toxic than 2,3,7,8-TCDD (Klee 1988). Cleavage of the ether linkages with the formation of halophenols may be achieved by treatment with strong acids or quaternary ammonium salts, but the dibenzodioxin nucleus is resistant to chemical attack. Oku et al. (1995) investigated the dechlorination of polychlorinated dibenzo-p-dioxins (CDDs) and polychlorinated dibenzofurans (CDFs) using a modified alkali-metal hydroxide method. The destruction reagent, prepared by dissolving either potassium hydroxide or sodium hydroxide in 1,3-dimethyl-2-imidazolidinone (DMI) destroyed all components regardless of the difference in the number of chlorine atoms or isomers of CDDs and CDFs (Oku et al. 1995). The efficiency of the methods was evaluated under varying conditions; in the presence and absence of water, at 90 and 50 EC, for 0.5 and 5 hours. Although the degree of CDD destruction (99.95–99.80%) was less than that for CDFs (99.99–99.98%), overall, the investigators considered the DMI reagent to be more useful than the polyethylene glycols because of its stability under strongly basic conditions and its efficiency in the presence of water (Oku et al. 1995).

Ruthenium tetroxide treatment can cause oxidative degradation of CDDs. This method can be used for detoxification of glassware and artifacts, or for the periodic purging of industrial reactors to counteract the accumulation of CDD residues (HSDB 1995). There is no available evidence on the nature of fragments formed during oxidation of the CDDs; however, the related chlorophenols undergo extensive decomposition to yield chlorine ions and no significant levels of organic products (HSDB 1995). Other chemical methods of detoxification include exposure to ultraviolet light or gamma radiation, the use of ozone or special chloriodide compounds, and the use of solvents or adsorbents to concentrate CDDs into smaller volumes for final disposal by incineration (HSDB 1995).

Dougherty et al. (1993) conducted a theoretical analysis of a proposed *in situ* method for decontaminating soil by photodegradation. Up to 86% of TCDD in the soil can be degraded by this process (Zhong et al. 1993). Because of its extremely low water solubility and volatility, TCDD is a very persistent soil contaminant. With the method, based on the physical properties that facilitate photolysis of TCDD by

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sunlight, an organic solvent mixture (2:1 w/w) of tetradecane and 1-butanol is applied to the contaminated soil (Dougherty et al. 1993). The controlling factors in TCDD photodegradation are desorption of the compound from the soil, the transport mechanism to the soil surface, and the availability of sunlight. As the solvents remove the tightly bound TCDD from the soil, convective upward movements of the compound are caused by the evaporation of the solvent (Dougherty et al. 1993; Zhong et al. 1993). The effectiveness of the process also depends on a balance between the convective movement and sunlight availability for degradation (Dougherty et al. 1993). Modeling conducted by Zhong et al. (1993) identified and quantified the controlling factors governing the TCDD photodegradation process. Following the concentration variation of TCDD in the top 2 mm of soil through sunlight/night cycles over an exposure period of 15 days, the model showed that during the daytime of the first few days, there is little accumulation of TCDD as the losses due to photodegradation were almost equal to the convective flux in magnitude but with different signs. Although the losses due to photodegradation drop to zero at night, the convective flux effected a build-up of TCDD. The losses due to photodegradation held steady while the convective movements decreased as evaporation slowed down (Zhong et al. 1993). A balance between the build-up of TCDD concentration at night and the drop in concentration during the day did not occur until the eleventh day of exposure (Zhong et al. 1993).

Hilarides et al. (1994) investigated degradation of TCDD in the presence of surfactants. Their results indicated that radiolytic destruction of TCDD using γ radiation can be achieved. Greater than 92% of the TCDD was destroyed in soils amended with 100 ppb TCDD, 25% water, and 2% nonionic surfactant using ^{60}Co at high radiation doses (800 kGy or 80 Mrad). The use of ^{60}Co as a source avoids the temperature increases and power requirements of other sources of ionizing radiation such as an electron beam. It is also better suited for soil application because of its greater penetration depths (Hilarides et al. 1994).

Biotreatment systems which use microorganisms for degradation of refractory organopollutants, like CDDs, are also being considered. *Phanerochaete chrysosporium*, a white rot fungus, has shown the ability to slowly degrade 2,3,7,8-TCDD in the laboratory (Bumpus et al. 1985; Des Rosiers 1986). The ability of this fungus to metabolize 2,3,7,8-TCDD is thought to be related to its extracellular lignin degrading enzyme system (Bumpus et al. 1985; Des Rosier 1986).

Other proposed methods of disposal are burial in salt mines and inclusion of these chemicals with nuclear fission by-products in secured cavities (HSDB 1995).

