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ABSTRACT

Certain manufacturing facilities formerly used large quantities of polychlorinated biphenyl (PCB) fluids in heat transfer operations. At many of these locations, operations have also involved PCB-containing electrical equipment. Commonly, over many years of plant operations, spills and leaks have resulted in PCB soil contamination. Dioxins and furans have been associated with PCB contamination in both the technical and popular press. Consequently, the need for analyses for dioxins and furans must be evaluated at locations where soils are contaminated with PCBs. This report presents an evaluation of potential dioxin and furan soil contamination based on heat transfer operations and spills from electrical equipment. The following five scenarios were examined for dioxin and furan contamination: (1) impurities in heat transfer fluids, (2) formation during heat transfer operations, (3) pyrolysis of heat transfer fluids, (4) impurities in dielectric fluids, and (5) pyrolysis of dielectric fluids. The potential contamination with dioxins and furans was calculated and compared with a 20 ppb guideline that has been used by the Centers for Disease Control for dioxin in subsoil. The results demonstrated that dioxins are formed only under pyrolytic conditions and only from the trichlorobenzenes present in dielectric fluids. Furans are found as impurities in PCB fluids but, as with dioxins, are not formed in significant quantities except during pyrolysis. Fortunately, pyrolytic conditions involving PCB fluids and soil contamination are unlikely; therefore, analyses for dioxin and furan contamination in soils will rarely be needed.

1. INTRODUCTION

The purpose of this report is to evaluate whether the determination of polychlorinated dibenzodioxins (dioxins) and polychlorinated dibenzofurans (furans) is necessary at polychlorinated biphenyl (PCB) investigation sites at industrial facilities where heat transfer operations employed PCB fluids. Consultants collecting environmental samples at such facilities have raised this issue as a safety concern. Because of the great expense involved in performing the analyses, Oak Ridge National Laboratory's Pollutant Assessment Group (ORNL/PAG) in Grand Junction, Colorado, reviewed the pertinent literature to determine when dioxin and furan analyses are necessary.

Consideration was given to the following questions in determining the need for dioxin and furan analyses: (1) What concentrations of dioxins/furans were and are contained in the PCB fluids used in heat transfer operations? (2) Did the operating conditions of the heat transfer systems produce additional dioxins/furans? (3) Under what conditions are significant concentrations of dioxins and furans formed in PCB fluids?

1.1 BACKGROUND

PCB oil was a commonly used heat transfer media for the molding and fabrication of plastic products from the early 1960s to the mid-1970s. Typically, heat transfer systems serviced various high-temperature, hydraulic press, and molding operations used in the fabrication of plastic products. Such systems often had fluid capacities of several thousand gallons. After 1975 most such systems were drained and filled with non-PCB heat transfer fluids.

Heat transfer systems had the potential of leaking because of failures of expansion joints, pumps, and heat exchangers. Consequently, site investigations are being conducted at facilities where such spills occurred. Because these same locations generally had or have PCB-containing dielectric fluids, it is necessary to evaluate dioxin and furan soil contamination from both sources.

1.2 PCBs

PCBs are a class of chlorinated, aromatic compounds that have found widespread application because of their thermal stability and inertness as well as their excellent dielectric properties (Hutzinger et al. 1979). The basic biphenyl structure is shown in Fig. 1. PCBs are formed by substituting chlorine atoms for hydrogen atoms at one or more of the numbered positions of the biphenyl structure (Griffin and Chian 1979). There are 209 possible chlorinated biphenyls. These are collectively referred to as PCBs, although many are not actually polychlorinated. Only half of this number have actually been identified in commercial formulations (Lloyd et al. 1976).

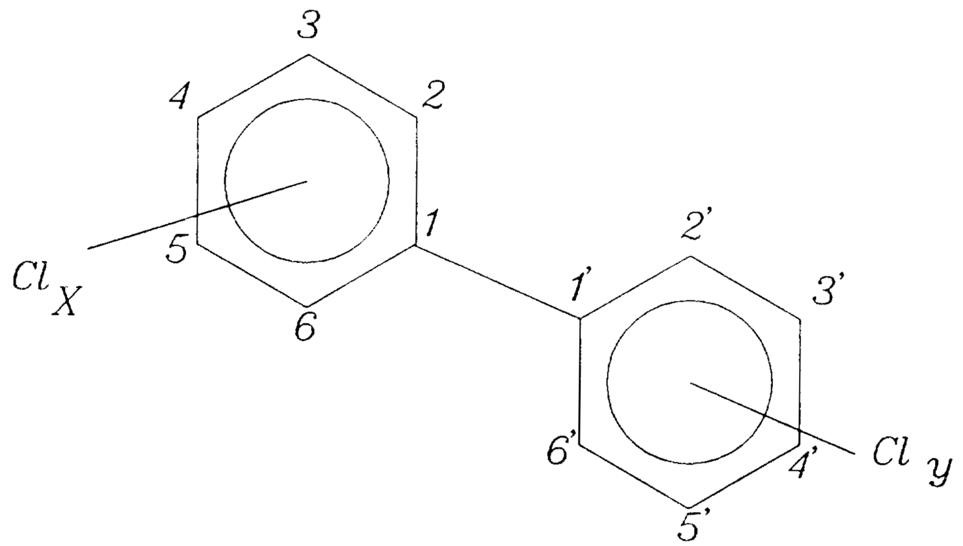

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Fig. 1. Structural formula for chlorinated biphenyl, where X + Y = 1–10.

PCBs have been manufactured in the United States since 1929 by the Monsanto Chemical Company under the trade name Aroclor (Griffin and Chian 1979). Each Aroclor is a complex mixture of chlorobiphenyls (Erickson 1985). Aroclor products are characterized by a four-digit number. The first two digits represent the type of molecule; the number 12 for example, indicates that the molecule is a biphenyl. The last two digits are the weight percentage of chlorine (e.g., A-1254 contains 54% chlorine) (Hutzinger et al. 1979). In 1970, the year of peak production, more than 85 million pounds of PCBs were produced in the United States alone, 57% of which were in the form of Aroclor 1242 (HEW 1972). Beginning in 1971 Monsanto voluntarily restricted its domestic sales of PCBs to closed system dielectric applications (capacitors and transformers) because of environmental concerns (Lloyd et al. 1976).

Monsanto's PCB heat transfer fluid was known as Therminol FR-1. According to Monsanto, Therminol FR-1 was 100% Aroclor 1242 [telephone conversation between P. Michael, Monsanto Chemical Corporation, St. Louis, and D.W. Greene, Oak Ridge National Laboratory (ORNL), Grand Junction, Colorado, March 1989]. Aroclor 1242 is a colorless liquid and was used primarily as a heat transfer media because of its thermal stability (Geiringer 1962). Distribution of PCB components in Aroclor 1242 is shown in Table 1.

1.3 DIOXINS/FURANS

Contamination of the environment by dioxins and furans has become a major concern in recent years. Incidents in Times Beach, Missouri, and Seveso, Italy, have heightened public interest in the environmental and public health effects of these compounds.

Dioxins and furans are not intentionally created but are produced as trace contaminants from various combustion processes (Smith et al. 1990) and in the manufacture of such industrial chemicals as chlorophenols and their derivatives (Buser 1979). Trace quantities of furans have also been reported as contaminants in commercial PCB mixtures (Roach and Pomerantz 1974; Bowes et al. 1975; Morita et al. 1977). Increased levels of furans have been observed in PCBs and chlorobenzenes that have been subjected to extreme temperatures. Additionally, the formation of dioxins from the pyrolysis of chlorobenzenes has been reported (Buser et al. 1978a,b; Buser 1979). Thus, dioxins and furans are secondary contaminants where PCBs are found.

Dioxins and furans are tricyclic aromatic compounds with similar chemical, physical, and toxicological properties. Structural formulas are shown in Fig. 2. Furans differ in basic structure from PCBs by the addition of one oxygen atom joining the pair of benzene rings, whereas dioxins differ by the addition of two oxygens between the rings. In all, there are 75 dioxin and 135 furan isomers ranging from the mono- to the octa-chloro compounds. Some of these compounds are extremely toxic. Toxicity seems to depend on the number and position of the chlorine substituents, with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and the corresponding dibenzofuran analogue (2,3,7,8-tetra-CDF) being the most toxic isomers (Buser 1979). Although a previous study suggested that the toxic effects of all furan and dioxin isomers are similar to those of TCDD (Moore et al. 1976), recent studies have shown that furans and other dioxin isomers are 2 to 1,000 times less toxic (Table 2 and 3; Van Zorge et al. 1989; Kutz et al. 1990). The OCDD isomer, for example, is the least toxic dioxin. It is also the most abundant in the environment (Reed et al. 1990).

Table 1. Distribution of PCB components in Aroclors

Components	Aroclor 1242 (%)	Aroclor 1260 (%)
Biphenyl	<0.1	---
Monochlorobiphenyls	1	---
Dichlorobiphenyls	16	---
Trichlorobiphenyls	49	---
Tetrachlorobiphenyls	25	---
Pentachlorobiphenyls	8	12
Hexachlorobiphenyls	1	38
Heptachlorobiphenyls	<0.1	41
Octachlorobiphenyls	none detected	8
Nonachlorobiphenyls	---	1

Source: Lloyd et al. 1976.

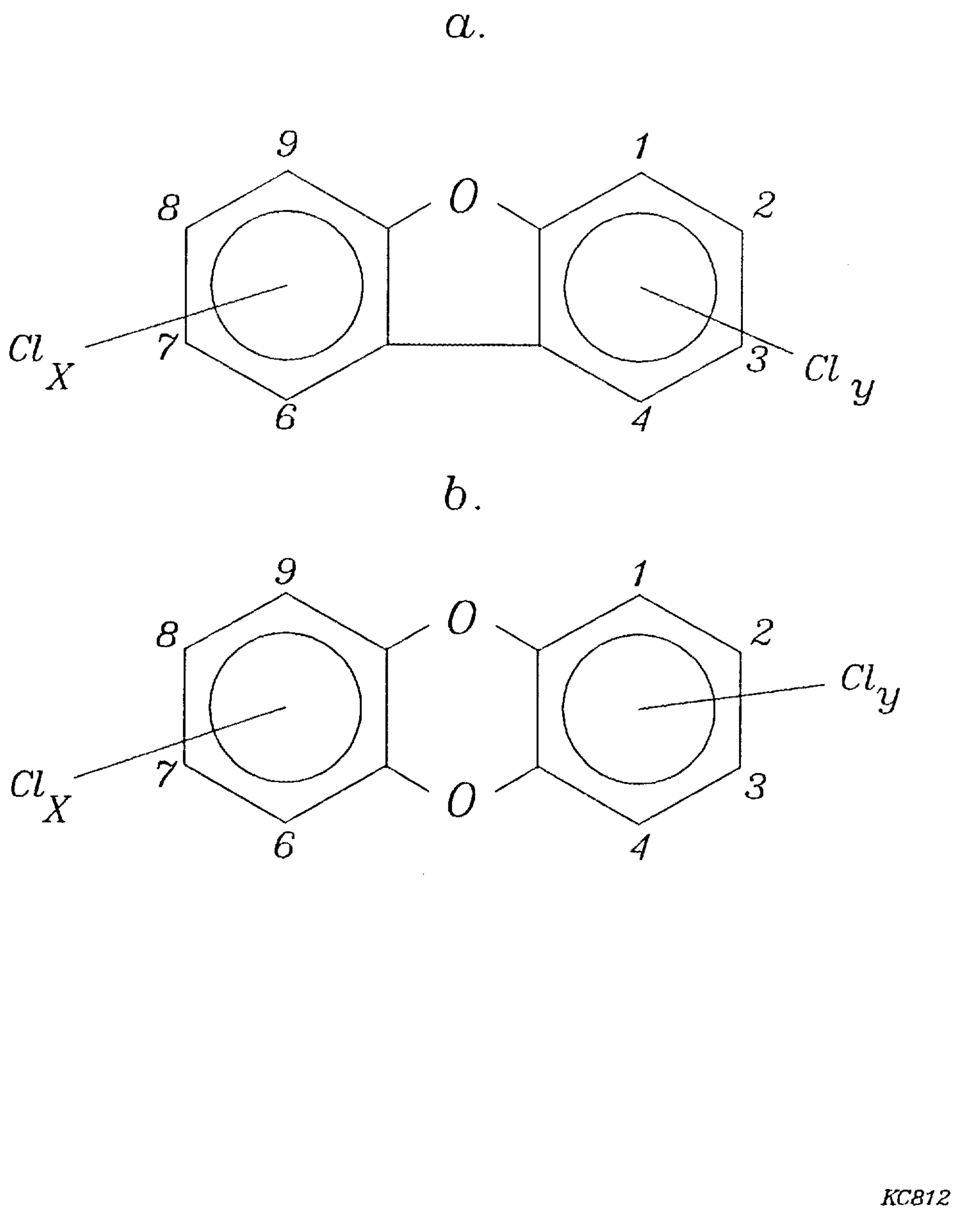

Fig. 2. Structural formulas for (a) chlorinated dibenzofurans and (b) chlorinated dibenzodioxins where X + Y = 1–8.

Table 2. [a]International toxicity equivalency factors for dioxin (CDD) isomers[b]

CDD isomer	1-TEF value
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,6,7,8-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.001

[a]From Kutz et al. 1990.

[b]All other CDDs have a zero value.

Table 3. [a]International toxicity equivalency factors for furan (CDF) isomers[b]

CDF isomer	1-TEF value
2,3,7,8-TCDF	0.1
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	
1,2,3,7,8,9-HxCDF	0.1
1,2,3,6,7,8-HxCDF	
2,3,4,6,7,8-HxCDF	
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	
OCDF	0.001

[a]From Kutz et al. 1990.

[b]All other CDFs have a zero value.

Laboratory tests of TCDD show that different species exhibit a wide range of sensitivity. For example, a hamster can tolerate doses of TCDD up to 5,000 times higher than that which would kill a guinea pig (Stolzenburg and Sullivan 1983). However, on the basis of studies of organisms that are acutely sensitive, the dioxins and furans are among the most toxic compounds known (Poland and Kende 1976).

As with PCBs, the only proven effect of dioxins and furans on humans is chloracne, a temporary skin condition (Cheremisinoff 1989). Chloracne is a skin eruption resembling acne that is caused by exposure to certain chlorinated organic chemicals (Tschirley 1986). In most instances of chloracne, a variety of signs and symptoms accompany the appearance of the skin lesions and persist for different lengths of time (National Institute of Occupational Safety and Health [NIOSH] 1984). Other transitory symptoms attributed to exposure to dioxins and furans include weight loss, insomnia, muscle pain, digestive disorders, increased weariness, decreased libido, and tender and enlarged livers (Arthur and Frea 1989). However, there is no evidence linking serious long-term health effects of these compounds to human beings (Tschirley 1986).

2. POTENTIAL SOURCES OF DIOXINS/FURANS

Five potential sources of dioxin/furan contamination were evaluated: (1) contamination as impurities in the Therminol FR-1 (Aroclor 1242), (2) formation as a result of the operating conditions of the Therminol system, (3) formation as pyrolysis products from Therminol FR-1, (4) contamination as impurities in PCB fluids in transformers and capacitors, and (5) formation as pyrolysis products from PCB/chlorobenzene mixtures in the transformers and capacitors.

2.1 DIOXINS/FURANS AS IMPURITIES IN THERMINOL

A sample of unused Therminol FR-1 analyzed by Midwest Research Institute (MRI) contained furans in trace quantities (Table 4). The table also includes other results of analyses for American-produced Aroclors. Levels of furan impurities in the Aroclors range from 0.7 to 5.6 ppm. The maximum concentration reported for A-1242 or Therminol FR-1 was 4.5 ppm. Of the literature reviewed on the subject, dioxins have not been reported as contaminants in commercial PCB mixtures.

2.2 DIOXINS/FURANS FORMED DURING HEAT TRANSFER OPERATIONS

In heat transfer operations, Therminol FR-1 oil was heated by a gas furnace and then circulated to various parts of the processing system for use in plastics molding operations. Such systems consisted of a "hot side" (260-288°C) and a "cold side" (232-260°C), which were mixed to achieve the desired critical temperature for heating the molds. Temperatures of the fluid at the furnace could have reached 343°C. The systems were continuously heated and removed from service only in the case of malfunction or scheduled maintenance. Morita and coworkers (1977) reported that when PCBs (A-1260) were sealed with air in a glass tube and heated at 300°C for 2 weeks, increased amounts of furans were found (quantities were not reported). The same study also analyzed a PCB fluid (A-1248) used for 2 years as a heat transfer media in a chemical factory (operating conditions were not specified). Analyses revealed a total furan concentration of 12.4 ppm, which represents more than a fourfold increase above the 2.8 ppm furan concentration found in an unused A-1248 sample. No mention of dioxin formation was made, but as noted previously, the literature suggests that dioxins are not readily formed from PCBs.

2.3 DIOXINS/FURANS FROM THERMINOL PYROLYSIS

A third source of furan contamination is from the pyrolysis of Therminol FR-1. Buser and coworkers have documented the formation of furans from the pyrolysis of PCBs (1978a,b 1979). At temperatures of 550-650°C, the total yield of furans from A-1254 ranged from 3-25% with mono- to penta-furans being formed. These temperatures, however, are 50-100% higher than those used in heat transfer systems.

Table 4. Furan contamination (ug/g) in commercial PCB mixtures

(Bowes et al. 1975)

	Aroclor 1248	Aroclor 1254	Aroclor 1260
μg/g	2.0	1.7	1.0

(Morita et al. 1977)

	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
μg/g	4.5	2.8	5.6	2.2

(Midwest Research Institute)

	Aroclor 1242 (Therminol FR-1)
μg/g	0.7

Pyrolysis of individual PCB isomers revealed that the tetra-furans were formed from the tetra-, penta-, and hexachlorobiphenyls; however, the specific 2,3,7,8-tetra-furan isomer was produced only from the penta- and hexachlorobiphenyls in small amounts (quantities not given). The penta- and hexachlorobiphenyls comprise ~9% of A-1242 (see Table 1). Dioxins are apparently not formed in significant quantities under these conditions.

2.4 DIOXINS/FURANS AS IMPURITIES IN DIELECTRIC FLUIDS

Another potential source of furan contamination is impurities in the PCB oil contained in electrical transformers and capacitors. Two common PCB containing dielectric fluids are known by the trade names Pyranol and Inerten. These fluids are mixtures of A-1260 (60-70%) and trichlorobenzenes (30-40%). Studies report furan impurities in A-1260 at levels similar to those found in A-1242. Furans, as impurities in A-1260, range from 1.0 to 2.2 ppm (Table 4). There is no indication in the literature reviewed that dioxins are found in these fluids.

2.5 DIOXINS/FURANS FROM PYROLYSIS OF DIELECTRIC FLUID

A fifth potential source of dioxin/furan contamination is through pyrolysis of the PCBs and trichlorobenzenes contained in electrical transformers and capacitors. This scenario represents the only process that could result in significant dioxin formation from a PCB-containing fluid. Buser (1979) has shown that both dioxins and furans form from the pyrolysis of trichlorobenzenes in the presence of air. At temperatures of 620°C trichlorobenzene produced dioxin and furan quantities equivalent to 0.03% and 1.05%, respectively. The tetra-dioxins represented ~45% of the total dioxins detected, whereas the tetra-furans represented 20% of the total furan content. In both cases, the 2,3,7,8-tetra isomers were detected but not as primary components (quantities not given).

3. BACKGROUND CONCENTRATIONS

Dioxin and furan contamination of the environment is widespread, particularly in industrialized nations. The compounds are present as impurities in the manufacture of certain chlorinated phenolic compounds, particularly that of 2,4,5-trichlorophenol (2,4,5-TCP). 2,4,5-TCP has been used as the basic ingredient in the manufacture of a wide variety of pesticides and herbicides. Additionally, contamination has been found in such related chemicals as pentachlorophenol and 2,4-D (Stolzenburg and Sullivan 1983).

The primary source of dioxins and furans in the environment appears to be myriad combustion processes (Travis and Hattemer-Frey 1989). These include high-temperature industrial processing plants, municipal solid waste and hazardous waste incinerators, motor vehicle emissions, and even forest fires. Many of these combustion products have as their precursors chlorinated phenolic compounds such as PCBs, chlorobenzenes, or 2,4,5-TCP from which the chemical formation of dioxins and furans is understood. However, dioxins and furans may also be routinely formed from the burning of wood and fossil fuels or from any fire that involves a source of chlorine and hydrocarbons (Bumb et al. 1980; Deutsch and Goldfarb 1988). Travis and Hattemer-Frey report total dioxin/furan levels in background soil samples from the suburban United States as 1.32 ng/g (ppb).

Dioxins and furans, like PCBs, are persistent environmental pollutants that have a strong affinity for soil particles, especially clay and organic matter (Kearney et al. 1973). Photodegradation is the major environmental degradative mechanism for these compounds, but the rate varies widely among different environments. Compared with photodegradation, such processes as volatility and degradation by chemical or biological means, appear to be relatively minor fate paths. The half-life for dioxin in soils is estimated to range between 1 and 10 years (Arthur and Frea 1989).

4. ESTIMATED PRESENCE OF DIOXINS AND FURANS IN SOIL

This section provides calculations of potential dioxin and furan soil contamination at facilities that employed heat transfer operations with PCB fluids. These calculations are based on an assumption that PCB soil contamination is rarely as high as 10,000 ppm. The majority of PCB-contaminated samples are assumed to contain less than 100 ppm PCBs.

4.1 DIOXINS/FURANS AS IMPURITIES IN UNUSED THERMINOL FR-1

If a Therminol FR-1 spill resulted in soil contaminated with 10,000 ppm PCBs, the following is predicted on the basis of the expected concentrations of dioxin/furan impurities. Dioxins are not contaminants in commercial PCB mixtures; therefore, no dioxins will be present in the soil. On the basis of data in Table 4, furans are present in A-1242 at 4.5 ppm, which would contribute 45 ng/g (ppb) to the soil for the given scenario (10,000 ppm PCBs in soil). Therefore, 100 ppm PCB contamination would result in 0.45 ng/g furans in soil (Appendix A).

4.2 DIOXINS/FURANS FORMED DURING HEAT TRANSFER OPERATIONS

Dioxins are not present in A-1242, neither are they formed from the heating of A-1242. The operating conditions of Therminol systems, however, may have led to increased levels of furans. A fourfold increase of furans in A-1242 is assumed (Morita et al. 1977). This fourfold increase of furans over the amount found as impurities in unused A-1242 would result in a 180 ng/g (ppb) concentration of furans in soil contaminated with 10,000 ppm PCBs and 1.8 ng/g (ppb) in soil with 100 ppm PCBs (Appendix A).

4.3 DIOXINS/FURANS FROM THERMINOL PYROLYSIS

Soil contamination in conjunction with pyrolysis of Therminol FR-1 entails a complicated set of circumstances. A combination of the following is needed: (1) a fire involving Therminol FR-1 and (2) PCB-contaminated soil. In order for these conditions to be met one of the following must take place: (a) a Therminol spill onto the ground with a subsequent or concurrent fire or (b) a Therminol fire inside the building with the resulting residues being deposited on the ground. Although these events are unlikely, this situation must be given consideration because of the high levels of furans produced. Dioxins are not formed from PCBs; therefore, none are predicted. On the basis of the previously discussed work of Buser and coworkers, pyrolysis of A-1254 yields 3-25% furans. Given a 10,000 ppm PCB soil content, furan concentrations in the soil would range from 300 to 2,500 μg/g (ppm). The furan concentration levels for a contaminated soil registering 100 ppm PCBs would range from 3 to 25 μg/g (ppm) (Appendix A).

4.4 DIOXINS/FURANS AS IMPURITIES IN DIELECTRIC FLUID

Some dielectric fluids contain 60-70% A-1260 and 30-40% trichlorobenzenes. Furans as impurities in A-1260 are listed in Table 4. Given a soil contaminated with 10,000 ppm PCBs plus trichlorobenzenes and an A-1260/trichlorobenzene ratio of 65/35, the following is predicted. If the highest reported value for furan impurities in A-1260 (2.2 ppm) is used, the furan concentration in soil would be ~14 ng/g (ppb). If a site is contaminated with 100 ppm PCBs plus trichlorobenzenes, the predicted furan concentration is 0.14 ng/g (ppb) (Appendix A). As in the previous situations, no dioxins are expected from this scenario. Additionally, no dioxin or furan contamination is expected from the trichlorobenzenes.

4.5 DIOXINS/FURANS FORMED FROM PYROLYSIS OF DIELECTRIC FLUID

Pyrolysis of the A-1260 and trichlorobenzenes contained in a dielectric fluid is the most complex scenario. This scenario requires the combination of a fire and PCB contamination in the soil. Increased furans will result from the pyrolysis of the PCBs, and both furans and dioxins are produced from the pyrolysis of the trichlorobenzenes.

Data from Buser et al. (1978a, 1978b) and Buser and Rappe (1979) demonstrate that the conversion of PCBs to furans will occur at a rate of 3-25%. The conversion of trichlorobenzenes to dioxins and furans occurs at a rate of 0.03% and 1.05%, respectively (Buser 1979). Approximately 45% of the dioxins and 20% of the furans formed from trichlorobenzenes are the highly toxic tetra-substituted compounds.

When these data and soil contamination with 10,000 ppm of a 65/35 mixture of PCBs and trichlorobenzenes are considered, 195 to 1,625 μg/g (ppm) furans are contributed by the PCBs and 37 μg/g (ppm) by the trichlorobenzenes. Of those furans contributed by the trichlorobenzenes, ~15-20% (6-7 ppm) are tetra-furans. Predicted furan levels for a 100 ppm spill of a 65/35 mixture of PCBs and trichlorobenzene are 2.3-16.6 ppm total furans and 55 to 74 ppb tetra-furans.

Because of the presence of trichlorobenzenes, the pyrolysis of a dielectric fluid represents the only potential source of significant dioxin formation. For soil contaminated with 10,000 ppm PCBs plus trichlorobenzenes, a total dioxin concentration of ~1.05 ppm is predicted. This result was obtained from an estimated rate of dioxin formation of 0.03% during pyrolysis of trichlorobenzenes, again assuming a 65/35 mixture of PCBs and trichlorobenzenes. The tetra-dioxins comprise ~45% (or 472 ppb) of the total dioxins produced (Buser 1979). For soil contaminated with 100 ppm PCBs plus trichlorobenzenes, total dioxins are 10 ppb and tetra-dioxins 5 ppb (Appendix A).

5. COMPARISONS TO CLEANUP STANDARDS

The only relevant cleanup standard was obtained from the Centers for Disease Control (CDC), who advised Missouri officials dealing with dioxin contamination at Times Beach that surface soils containing more than 1 ppb 2,3,7,8-tetra-dioxin (TCDD) must be removed from residential areas (Stolzenburg and Sullivan 1983). Concentrations as high as 20 ppb are allowed at soil depths of 1 ft or greater. As shown by Tables 2 and 3, the next most toxic dioxin isomer and the most toxic furan isomer are only half as toxic as TCDD. All other isomers are 10 to 1,000 times less toxic. The 1 ppb TCDD standard is too conservative for comparing the mixtures of dioxins and furans potentially produced. Thus, the 20 ppb standard for depths of 1 ft provides a conservative target soil contamination level for total dioxins and furans. The PCB soil concentrations that could result in dioxin and furan concentrations that exceed the 20 ppb target concentration are presented in Table 5.

For a spill of new or unused Therminol FR-1, a PCB soil concentration of 4440 ppm is required to exceed the 20 ppb guideline. If increased furans resulting from the operating conditions of the Therminol system are assumed, a concentration of more than 1100 ppm would be required to exceed the 20 ppb guideline. Because of the 3-25% conversion rate described previously it can be assumed that soil contaminated as a result of Therminol pyrolysis would always exceed the 20 ppb guideline.

Contamination as the result of a dielectric fluid spill would require a PCB concentration of ~14,300 ppm to exceed the Times Beach standard. Once again, for soil contamination as a result of dielectric fluid pyrolysis, furan concentrations would exceed the 20 ppb guideline at very low concentrations of PCBs. Dioxins are also produced in this situation because of the presence of trichlorobenzenes.

Table 5. PCB soil concentration at which 20 ppb of furans and/or dioxins would be present

Scenario	PCB soil concentration needed to exceed 20 ppb furans/dioxins
Furans as impurities in Therminol	4,440 ppm
Furans formed by the heat transfer process	1,100 ppm
Furans from Therminol pyrolysis	80 ppb
Furans as impurities in dielectric fluids	14,300 ppm
Furans from pyrolysis of dielectric fluids	120 ppb
Dioxins[a] from pyrolysis of dielectric fluids	1,000 ppm

[a] Dioxins are not formed from any other scenario.

6. DISPOSAL AND TREATMENT CONSIDERATIONS

Disposal and treatment regulations for dioxins and furans are found in 40 CFR 268. These regulations apply to commercial processes that produce dioxins and furans.

Dioxin-containing wastes (F020, F021, F022, F023, F026, F027, and F028) were prohibited from land disposal effective November 8, 1990, unless the wastes meet the standards in Subpart D. The standard from Subpart D for dioxin-containing wastes is <1 ppb for wastewater or nonwastewater. Some specific dioxin compounds are listed and have different concentrations.

Wastes that are otherwise prohibited from land disposal in Part 268 may be treated in a surface impoundment according to the restrictions in 268.4. Sampling and testing are required and removal is necessary if residues do not meet treatment standards in Subpart D or prohibition levels in Subpart C. Prohibitions on storage of restricted wastes are listed in 268.50.

Furans (Waste #U-124) are "first-third" wastes listed in 268.10. Sect. 268.33 (c) indicates that contaminated soil and debris containing furans were prohibited from land disposal effective August 8, 1990, unless the wastes meet the standards of Subpart D. Subpart D lists specific furans and the allowable wastewater and nonwastewater concentrations.

In essence, if an industrial process results in soil contamination with dioxins or furans, the waste will be listed and the treatment standard prescribed in the regulations will apply. Although in this case, the generator still maintains the option of applying for a variance as described in 260.22. To obtain a variance, however, it is probably necessary to demonstrate that the concentrations are background and not the result of a local spill. In instances where traces of dioxins or furans are found and their source is unknown, proper disposition is up to the site owner. Although consultation with the EPA region should be considered, it is not mandatory in those instances.

7. CONCLUSIONS

There is some potential for dioxin and furan contamination as a result of PCB usage at facilities where PCB-containing heat transfer fluids were used. However, the amount of contamination possible is dependent upon the source of the PCB materials and the conditions to which they have been subjected. This report has shown the following:

- The toxicological properties of dioxins and furans differ significantly.
- Dioxin formation from PCBs is relatively insignificant.
- Furan contamination was present in commercially produced PCB materials such as Therminol FR-1.
- Additional furans are produced when PCB fluids are subjected to elevated temperatures (300°C) for extended periods of time.
- Much greater quantities of furans are produced from PCBs in pyrolytic conditions.
- Dioxins may be formed when trichlorobenzenes in PCB-dielectric fluids are subjected to pyrolytic conditions.

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APPENDIX A

CALCULATIONS OF FURAN AND DIOXIN CONTENT IN SOILS CONTAMINATED WITH POLYCHLORINATED BIPHENYLS AT FACILITIES WHERE POLYCHLORINATED BIPHENYLS CONTAINING HEAT TRANSFER OPERATIONS WERE CONDUCTED

Appendix A
Calculations

This appendix presents the calculations used to estimate the concentrations of dioxins and furans for the various scenarios.

FURANS AS IMPURITIES IN THERMINOL

Assuming furan contamination of 4.5 ppm for a 100% A-1242 fluid, a spill resulting in a PCB soil contaminant concentration of 10,000 ppm would result in the following total furan concentration:

$$\frac{4.5\ \mu g/g\ \text{furan}}{10^6\ \mu g/g\ \text{PCB}} = \frac{x\ \mu g/g\ \text{furan}}{10^6\ \mu g/g\ \text{PCB}}$$

$$\frac{4.5\ \mu g/g\ \text{furan} \times 10^4\ \mu g/g\ \text{PCB}}{10^6\ \mu g/g\ \text{PCB}} = 0.045\ \mu g/g\ \text{furan}$$

$$0.045\ \mu g/g\ \text{furan} = 45\ ng/g\ \text{or}\ 45\ ppb\ \text{furan.}$$

It may then be assumed that if a 10,000 ppm spill results in a furan concentration of 45 ppb, a 100 ppm spill would result in 1/100th the concentration, or 0.45 ppb furan in soil.

FURAN FORMATION DURING HEAT TRANSFER OPERATIONS

Assuming a furan impurity concentration of 4.5 ppm for a 100% A-1242 fluid and a fourfold increase in furan concentration as a result of heat transfer operations, a spill resulting in a PCB soil contaminant concentration of 10,000 ppm would result in the following total furan concentration:

$$4.5\ \mu g/g\ \text{furan} \times 4 = 18.0\ \mu g/g\ \text{furan}$$

$$\frac{18.0\ \mu g/g\ \text{furan}}{10^6\ \mu g/g\ \text{PCB}} = \frac{x\ \mu g/g\ \text{furan}}{10^4\ \mu g/g\ \text{PCB}}$$

$$\frac{18.0\ \mu g/g\ \text{furan} \times 10^4\ \mu g/g\ \text{PCB}}{10^6\ \mu g/g\ \text{PCB}} = 0.18\ \mu g/g\ \text{furan}$$

$$0.18\ \mu g/g\ \text{furan} = 180\ ng/g\ \text{or}\ 180\ ppb\ \text{furan.}$$

It may then be assumed that if a 10,000 ppm PCB spill results in a 180 ppb furan concentration, a 100 ppm PCB spill would result in 1/100th the concentration, or 1.8 ppb furans in soil.

FURANS FROM THERMINOL PYROLYSIS

Assuming furan production by Therminol pyrolysis of 3%-25%, an A-1254 spill that resulted in a soil contamination level of 10,000 ppm which had been subjected to the temperatures necessary for pyrolysis of the entire contaminated deposit, the following concentrations of furan can be expected:

10,000 ppm PCB x 0.03 = 300 ppm furan

10,000 ppm PCB x 0.25 = 2500 ppm furan.

It may then be assumed that if a 10,000 ppm spill of pyrolyzed Therminol yields a furan contaminant level of between 300 and 2500 ppm, a 100 ppm spill of pyrolyzed Therminol would result in 1/100th the concentration or 3-25 ppm furan contamination in soil.

FURANS AS IMPURITIES IN DIELECTRIC FLUIDS

Assuming from Table 3 that the furan impurity of A-1260 in pure form is 2.2 ppm and also assuming that dielectric fluids are composed of 65% A-1260, a spill of dielectric fluid that contaminated the soil to 10,000 ppm of PCBs plus trichlorobenzenes would result in the following concentration of furan in soil:

10,000 ppm spill of dielectric fluid = 6.5 x 10^3 PCB in spill.

$$\frac{2.2\ \mu g/g \text{ furan}}{10^6\ \mu g/g \text{ PCB}} = \frac{x\ \mu g/g \text{ furan}}{6.5 \times 10^3\ \mu g/g \text{ PCB}}$$

$$\frac{2.2\ \mu g/g \text{ furan} \times 6.5 \times 10^3\ \mu g/g \text{ PCB}}{10^6\ \mu g/g \text{ PCB}} = 0.014\ \mu g/g \text{ furan}$$

or
14 ppb

It may then be assumed that if a 10,000 ppm spill of dielectric fluids would result in a furan contamination level of 14 ppb, a 100 ppm spill would result in 1/100th of the furan concentration in soil, or 0.14 ppb.

PYROLOSIS OF DIELECTRIC FLUID

Pyrolysis of a dielectric fluid with a PCB/trichlorobenzene ratio of 65/35% and soil contaminated with 10,000 ppm of this mixture results in the following concentrations of dioxins and furans:

Assuming PCBs produce 3-25% furans under conditions of pyrolysis (Buser 1979), the following furan soil contamination results from the pyrolysis of A-1260:

10,000 ppm (dielectric fluid) x 65% = 6500 ppm PCBs.

6500 ppm (PCBs) x 0.03 = 195 ppm furans.

6500 ppm (PCBs) x 0.25 = 1625 ppm furans.

Therefore, the range of furan contamination generated by the pyrolysis of the PCBs can be expected to range from 195 ppm to 1625 ppm.

When the 35% trichlorobenzene content of the dielectric fluid is pyrolyzed, 1.05% and 0.03% is expected to be converted to furans and dioxins respectively. Therefore, the following concentrations of furans and dioxins can be expected as a result of the trichlorobenzene pyrolysis:

10,000 ppm x 35% = 3,500 ppm trichlorobenzene.

3,500 ppm (TCB) x 0.0105 = 36.75 ppm furans.

3,500 ppm (TCB) x 0.0003 = 1.05 ppm dioxins.

According to Buser's studies (1979), ~20% of the furans and 45% of the dioxins produced by the pyrolysis of the trichlorobenzene will be of the highly toxic tetra-furan and tetra-dioxin variety. Therefore, 7 ppm of the furans will be tetra-furans, whereas 472 ppb of the dioxins will be tetra-dioxins.

When the furan and dioxin contribution from the pyrolysis of the PCBs and the trichlorobenzenes are combined, the level of furan/dioxin contamination in a 10,000 ppm deposit of pyrolyzed dielectric fluid will range from ~232 ppm to 1,662 ppm for furans while containing ~1 ppm dioxin.

Assuming a 100 ppm spill of pyrolyzed dielectric fluid, the furan concentration can be expected to range from 2.3 ppm to 16.6 ppm, with a total dioxin concentration of ~10 ppb.

Table A-1. Summary of calculated concentrations of dioxins and furans

Potential source	Expected dioxins (ppm) for 10,000 ppm PCBs	Expected dioxins (ppm) for 100 ppm PCBs	Expected furans (ppm) for 10,000 ppm PCBs	Expected furans (ppm) for 100 ppm PCBs
Impurities in Therminol	—	—	4.5×10^{-2}	4.5×10^{-4}
Formation during heat transfer operations	—	—	1.8×10^{-1}	1.8×10^{-3}
Therminol pyrolysis	—	—	300 to 2,500	3 to 25
Impurities in dielectric[a] fluids	—	—	1.4×10^{-2}	1.4×10^{-4}
Pyrolysis of dielectric[a] fluids	1.05	1×10^{-2}	230 to 1,660	2.3 to 16.6

[a] For dielectric fluids, ppm refers to the combined concentrations of trichlorobenzenes and PCBs.

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