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Polychlorinated Dibenzofurans (PCDF) and Polychlorinated Dibenzo-p-Dioxins (PCDD) in Utility Transformers and Capacitors

Volume 1:
Formation of PCDF and PCDD in Askarels and Contaminated Mineral Oil Equipment

Prepared by
General Electric Company
Pittsfield, Massachusetts

MONS 018463

REPORT SUMMARY

SUBJECTS: Hazardous/toxic substances / Transmission: Substations / Distribution: Substations

TOPICS: PCB; Capacitors; Chemical analysis; PCDF-PCDD; Transformers; Insulating oil

AUDIENCE: Environmental managers / Distribution engineers

Polychlorinated Dibenzofurans (PCDF) and Polychlorinated Dibenzo-p-Dioxins (PCDD) in Utility Transformers and Capacitors

Volumes 1–3

Many health effects originally attributed to PCBs appear to result from their pyrolysis and combustion by-products, PCDF and PCDD. This study developed improved techniques for characterizing these products and showed that PCDF and PCDD do not form during catastrophic arcing failure in transformers and capacitors.

BACKGROUND Partial oxidation of askarels—mixtures of polychlorinated biphenyls (PCB) and tri- and tetrachlorobenzenes—produces polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD). However, analytic techniques for separating the active components in these mixtures are not yet mature. Information is also sparse on the quantity and types of PCDF and PCDD in as-manufactured PCB and on their formation during normal operation or arcing failure in utility equipment. Because of these uncertainties, utilities and regulators assume the worst-case PCDF-PCDD formation when there is a PCB-related accident and thereby overstate potential toxicity.

OBJECTIVE To improve techniques for measuring PCDF-PCDD in the presence of PCB and in utility transformers and capacitors.

APPROACH Researchers developed a rationale for selecting transformers and capacitors to be sampled for PCDF-PCDD content. They also simulated catastrophic transformer failure through arcing in askarel and contaminated mineral oil to investigate PCDF-PCDD formation. Several laboratories then performed round-robin gas chromatography–mass spectrometry analyses of PCDF-PCDD samples using specially prepared carbon-13 (^{13}C) PCDF spiking compounds. After the first set of analyses, each laboratory modified its techniques and analyzed a larger group of samples from utility equipment. Another organization statistically analyzed all laboratory results.

RESULTS These three volumes are the first release in a six-volume report of PCDF-PCDD analytic findings. Results from all participating laboratories correlated remarkably well. Some of those results follow.

MONS 018464

- Making use of the ^{13}C compounds, researchers successfully separated the components in several closely eluting pairs of physiologically active PCDF and less-active components.

- The researchers found *no* PCDF or PCDD in the arcing of PCB, tri- and tetrachlorobenzene, or contaminated mineral oil.

- Analyses of samples from utility equipment suggested that the PCDF–PCDD present did not result from high-load, high-temperature operation.

Volume 1 presents researchers' sampling recommendations for investigating PCDF–PCDD in utility equipment. It also describes arcing simulations and results. Volumes 2 and 3 describe several analytic techniques, with volume 3 including a report on the synthesis of new PCDF spiking compounds. Later volumes will complete the descriptions of laboratory techniques, present comprehensive statistical analyses, and provide an executive summary.

EPRI PERSPECTIVE

This project appears to be a landmark in PCDF–PCDD analysis. One important result is the synthesis of new PCDFs for use as spiking compounds in gas chromatography–mass spectrometry analysis. The ability to separate many of the active PCDF compounds from more-innocuous materials is also of great value. The fact that laboratory results correlated so well indicates that researchers can have great flexibility in selecting techniques and developing facilities.

Utilities benefit from this work in several ways. The study provides data showing that little or no PCDF–PCDD forms in electrical equipment either during normal operation or during arcing failure. Moreover, improved analytic techniques make it clear that past predictions of toxicity have been unnecessarily high.

PROJECTS

RP2028-5, RP2028-8, RP2028-9
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Electrical Systems Division; Energy Analysis and Environment Division
Contractors: Radian Corporation; General Electric Company; Illinois Institute of Technology Research Institute

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Polychlorinated Dibenzofurans (PCDF) and Polychlorinated Dibenzo-p-Dioxins (PCDD) in Utility Transformers and Capacitors

Volume 1: Formation of PCDF and PCDD in Askarels and Contaminated Mineral Oil Equipment

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General Electric Company
Pittsfield, Massachusetts

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ABSTRACT

Concern about the health effects of polychlorinated biphenyls (PCBs) led to a ban on their production and to regulation of their continued use and their disposal. Specific regulations deal with PCBs in electrical equipment. Many of these health effects now appear to be associated with polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD). The Electric Power Research Institute has sponsored work to establish the levels of PCDF and PCDD in dielectric fluids used in electrical equipment and to examine the factors leading to their formation in dielectric liquids containing PCBs. This report describes two contributions to this work.

The first provides a rationale for the gathering of samples from equipment in normal service for chemical analysis. The intent here was to select transformers and capacitors with diverse service histories in order to develop an acceptable broad overview of the occurrence of PCDF and PCDD, while minimizing the number of samples and costly analyses. The second was a study of the formation of PCDF and PCDD in controlled simulations of equipment in abnormal service -- electrical breakdown ("arcing"). Little or no formation PCDF or PCDD was found as a result of arcing in askarels containing large amounts of PCBs and TCBs or of mineral oils containing small amounts of PCBs and TCBs.

MONS 018468

ACKNOWLEDGMENTS

The contributions of many people have been invaluable in meeting the objectives of this project. Two particularly stand out. Bob Koch of the High Voltage Laboratory of General Electric was the planner and overseer of the electrical breakdown testing. Fred DeRoos of Battelle-Columbus Laboratories provided the PCDF and PCDD analysis. Bill Fessler of the General Electric Materials Laboratory provided continual aid and support.

Gil Addis and Jacques Guertin of EPRI provided expert guidance of the project. They also made it a pleasure to be a part of the larger Electric Power Research Institute enterprise.

MONS 018469

CONTENTS

Section		Page
1	INTRODUCTION	1-1
	General	1-1
	PCDF and PCDD Formation	1-4
	References	1-8
2	SELECTION OF SAMPLES FROM ELECTRICAL EQUIPMENT FOR PCDF AND PCDD ANALYSIS	2-1
	Transformers	2-1
	Capacitors	2-5
	Summary	2-6
	References	2-7
3	FORMATION OF PCDF AND PCDD IN ELECTRICAL DISCHARGES	3-1
	Experimental	3-1
	Results	3-2
	Discussion	3-5
	References	3-6

MONS 018470

ILLUSTRATIONS

Figure		Page
1-1	Pyrolysis of PCBs to PCDF	1-5
3-1	Relation of Arc Energy to Pressure in Spiked Oil and Askarel	3-4

MONS 018471

TABLES

Table		Page
1-1	Composition of Askarel Components	1-2
1-2	Compositions of Askarels	1-2
1-3	Trade Names of Askarels	1-3
1-4	Formation of PCDF From Pyrolysis of Aroclors	1-6
2-1	Equipment Recommended for Sampling for PCDF and PCDD Analysis	2-6
3-1	Arcing Tests Oils Containing Askarels	3-3
3-2	PCDF and PCDD Content of Askarels - Before and After Arcing	3-4
3-3	PCDF Content of Mineral Oil Containing PCBs - Before and After Arcing	3-5

MONS 018472

EXECUTIVE SUMMARY

Polychlorinated biphenyls (PCBs) were widely used in electrical equipment until the late 1970's. Concern for their environmental persistence and biological response led to a ban on additional use and to regulation of disposal and maintenance in continuing application. Attention is now shifting to the products of partial oxidation of PCBs, the polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD). The levels at which PCDF and PCDD occur in electrical equipment filled with PCBs or with mineral oils containing traces of PCBs is not well known. The project reported here has had two aims. The first has been to develop a rationale for the selection of transformers and capacitors to be sampled for PCDF and PCDD analysis. The analysis is time consuming and difficult and the intention has been to choose a small number of samples, which will give the greatest amount of information about the large population of equipment in use. Specifically, it has been recommended that 8 to 10 load center/network askarel filled transformers, 2 rectifier transformers, 2 precipitator transformers, 4 load center transformers containing PCB contaminated mineral oil and 4 PCB filled capacitors be sampled.

Establishing the amounts of PCDF and PCDD in electrical equipment in typical service has been one goal. The second here has been to determine if PCDF and PCDD are formed in electrical breakdown in electrical equipment. It was not practical to attempt to do controlled experiments on actual apparatus because of the hazards of spills and splashes. Therefore, controlled arcs were generated in a fuse tube configuration at the General Electric High Voltage Laboratory facility. The PCDF and PCDD content of the PCB or chlorobenzene containing askarel or contaminated mineral oil was measured by the Battelle-Columbus Laboratory. The simulation in this geometry was as near to the reality of a transformer failing through arcing as possible. No PCDF or PCDD formation was found.

MONS 018473

Section 1

INTRODUCTION

GENERAL

Concerns about the health effects of polychlorinated biphenyls (PCBs) led to a ban on their production and to regulation of their use and their disposal. Specific regulation deals with PCBs in electrical equipment. Many of these adverse health effects now appear to be attributable to polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD) in the PCBs. Attention is shifting to the presence and formation of PCDF and PCDD in electrical insulating liquids. The first section of this report discusses the types of transformers and capacitors which could be sampled to determine the levels of PCDF and PCDD present in equipment in a variety of normal modes of operation. The second section describes a study of the transformer insulation system in an abnormal situation; namely, an electrical arc in which PCDF and PCDD might form.

Mixtures of PCBs have been used in capacitors and transformers, often combined with chlorinated benzenes (TCB - primarily tri-, T_3, and tetra-, T_4). High dielectric constant is important in the first application; low flammability in the second. These mixtures were called "askarels"; defined as non-flammable synthetic chlorinated aromatic hydrocarbons. The primary producer of PCBs in the United States was the Monsanto Industrial Chemicals Company who labeled their PCB products - Aroclor®. Aroclors used as electrical insulating oils were 1260 (60% chlorine by weight), 1254 (54% Cl), 1242 (42% Cl) and 1016 (a narrow boiling cut of 1242). Typical compositions (by homolog) of the Aroclors used in electrical equipment are given in Table 1-1 (1). Typical compositions (by isomer) for electrical grade chlorobenzene mixtures are also given in Table 1-1 (2). Typical compositions for askarels described by ASTM are given in Table 1-2 (3). Askarel A formulation (transformers) was introduced in the 1930's and used into the 1960's. Askarel B was in use from the early 1950's to the early 1970's. In the 1940's, tin tetraphenyl was introduced in small quantities (0.15%) as a chloride ion scavenger. It was replaced by one or another epoxide, usually 3,4-epoxy cyclohexylmethyl - (3',4'-epoxy cyclohexane) carboxylate, in the 1950's.

TABLE 1-1

COMPOSITION OF ASKAREL COMPONENTS

PCB Isomer	No. Cl	Polychlorinated Biphenyls Amount in Aroclor [%] (1) 1016	1242	1254	1260
Mono-	1	2	1.1		
Di-	2	19	16.9		
Tri-	3	57	39.2		
Tetra-	4	22	31.6	13.8	
Penta-	5		9.6	61.9	11.5
Hexa-	6		0.5	23.3	46.2
Hepta-	7			1.0	30.7
Octa-	8				8.8

TCB Isomer	No. Cl	Chlorinated Benzenes Amount in Mixture [%] (2) 1,2,4	1,2,3	1,2,3,4	1,2,4,5	Other
Mono-	1					
Di-	2					
Tri-	3	49	13			5
Tetra-	4			28	3	
Penta-	5					4

TABLE 1-2

COMPOSITION OF ASKARELS (3)

Application	Component 1016	1242	1254	1260	T_3CB	T_3,T_4CB
Capacitors						
A		100				
B			100			
C				75	25	
D	100					
Transformers						
A				60	40	
B				45		55
C		80				20
D			70		30	
E		100				
F			45			55
G			60		40	

MONS 018475

The other formulations came into use for various periods in the 1960's and 1970's. Production of new electrical apparatus filled with PCBs containing askarels ended in 1978. It should be emphasized that the compositions listed in Table 1-2 are typical, but not definitive. There were over twenty producers of askarel containing electrical apparatus in the US, each freely using its own formulation at any time. The apparatus included transformers, power capacitors used in transmission and distribution systems and several types of industrial capacitors used in motor starting, lights, etc. A partial listing of producers of transformers and larger capacitors is given in Table 1-3 (4). The distribution of any PCDF and PCDD congeners formed by partial oxidation is related to the distributions of PCBs and TCB congeners in the precursor askarel. The diversity of the sources and types of askarels argues that there will be substantial variations in the distributions of PCDF and PCDD found in equipment in use.

TABLE 1-3

TRADE NAMES OF ASKARELS

Manufacturer	Trade Name
Allis-Chalmers	Chlorextol
Ferranti-Packard	Askarel
General Electric	Pyranol
Hevi-Duty Electric	
ITE Circuit Breaker	Non-Flammable Liquid
Kuhlman Electric	Saf-T-Kuhl
McGraw Edison	Elemex
Niagara Transformer	EEC-10, Askarel
H. K. Porter	
Power Zone Transformer	EEC-10
Research-Cottrell	Askarel
Sangamo Electric	Diaclor
Standard Transformer	
R. E. Uptegraff Manufacturing	
Van Tran Electric	
Wagner Electric	No-Flamol
Westinghouse Electric	Inerteen

MONS 018476

PCDF AND PCDD FORMATION

PCDF and PCDD are products of partial oxidation of PCBs and TCBs. Complete oxidation results in carbon dioxide and hydrogen chloride. The best evidence to date (5) indicates that pyrolysis of PCBs results in minor amounts of PCDF; little PCDD formation occurs. Pyrolysis of TCBs results in the formation of both PCDF and, to an order of magnitude less, PCDD. PCBs and TCBs give comparable amounts of PCDF when pyrolyzed under similar conditions. PCDF then are the primary products of partial oxidation of askarels

There are 209 different congeners in the PCB chemical class. Not all are present in any one Aroclor. There are 135 congeners of PCDF and 75 congeners of PCDD. Formation of PCDF from PCBs involves elimination of adjacent hydrogen or chlorine atoms ortho to the biphenyl bond and insertion of an oxygen atom. The four reaction paths which have been established (5) are shown in Figure 1-1. None include random rechlorination around the biphenyl rings. Therefore, particular PCDF congeners formed by a given PCB can be predicted. The PCDF mixture formed by partial oxidation of a given Aroclor then also should be predictable from a knowledge of the specific PCB composition of the Aroclor.

This is not the case for PCDF (or PCDD) formation from chlorobenzenes. That process includes oxidative dechlorination followed by bimolecular reactions of chlorobenzene fragments and randomized final products. Further, rechlorination by the eliminated chlorine atoms appears to occur. This leads to PCDF more highly chlorinated than would be predicted from reactions involving simply T_3- and T_4CBs.

PCDD congeners have been shown to differ markedly in biological activity. The most active are those having the 2,3,7,8 substitution pattern; the 2,3,7,8 tetra- isomer, the 1,2,3,7,8 and the 2,3,4,7,8 penta- isomers and the 1,2,3,4,7,8, the 1,2,3,6,7,8 and the 1,2,3,7,8,9 hexa- isomers. Comparable LD_{50} data on PCDF in guinea pigs are scarce. The 2,3,7,8 tetra- and the 2,3,4,7,8 penta- isomers do show a high activity. A reasonable working hypothesis is that the 2,3,7,8 congeners will give the strongest biological responses in the PCDF series.

The relative amounts of the PCB congeners have been measured in typical samples of Aroclors (5). Utilizing these results and the reaction routes shown in Figure 1-1, estimates can be made of the relative formation of the several 2,3,7,8 congeners through partial oxidation of the Aroclors. Table 1-4 lists the various 2,3,7,8

MONS 018477

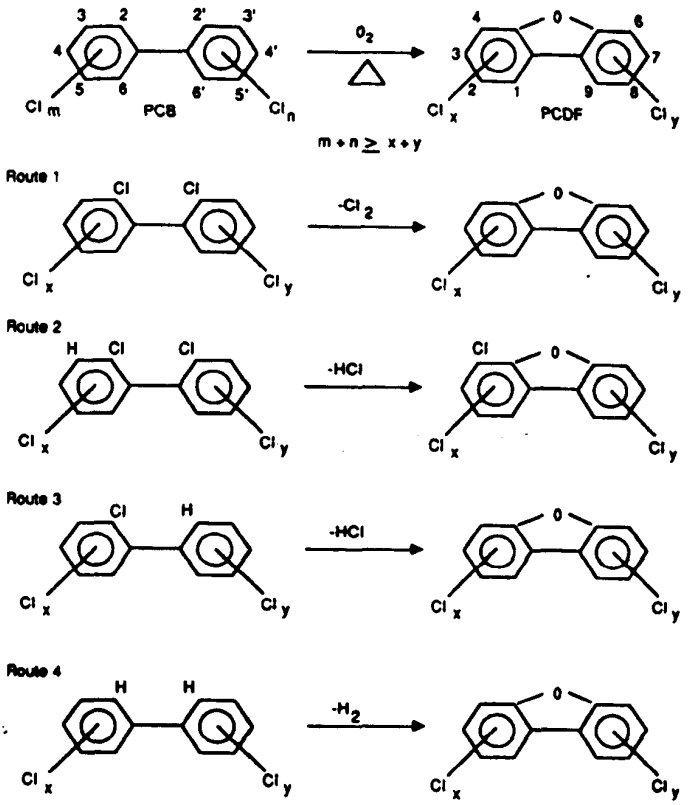

Figure 1-1. Pyrolysis of PCBs to PCDF

MONS 018478

PCDF congeners of concern, the PCB congeners found in either Aroclor 1254 or 1260 (§) which form one of these PCDF compounds, the reaction path by which it can be formed, the relative peak area associated with that PCB isomer and an estimate of the relative amounts of the PCDF congeners found in the pyrolyzed Aroclors (§). (It is assumed here that the response factors for the several PCB congeners are much the same and that the associated peak areas are an acceptable estimate of the relative amounts of these PCB isomers).

TABLE 1-4

FORMATION OF PCDF FROM PYROLYSIS OF AROCLORS

2,3,7,8 PCDF	PCB Precursor	Reaction Path	Aroclor 1254		Aroclor 1260	
			PCB	PCDF	PCB	PCDF
-	2,2',3,3'	4	VS	Sig	VS	Sig
	2,2',3,4,4'	2	Sig		Min	
	2,3',4,4',5	3	Sig		ND	
	2,2',4,4',5,5'	1	Sig		Sig	
1,	2,3,3',4,4'	4	Sig	Sig	ND	Sig
	2,2'3,4,4',5	3	Min		Sig	
	2,3,3',4,4',6	3	ND		Min	
,4,	2,2',4,4',5,5'	2	Sig	Sig	Sig	Sig
	2,3',4,4',5,5'	3	Min		Sm	
	2,2',3,4,4',5,5'	1	Sm		Sig	
,4,6,	2,3,3',4,4',5,5'	3	ND	NR	VS	Min
	2,2',3,4,4',5,5'	2	Sm		Sig	
	2,2',3,3',4,4',5,5'	1	ND		Sm	
1,9	2,2',3,3',4,4',6	3	ND	NR	Sm	NR
	2,2',3,3',4,4',6,6'	1	ND		Sm	
1,4,	2,3,3',4,4',6	4	ND	NR	Sm	NR
	2,2',3,4,4',5,5',6	1	ND		VS	
1,6,	2,3,3',4,4',5	4	ND	NR	Sm	NR
	2,3,3',4,4',5',6	3	ND		Min	

Sig - Significant
Min - Minor
Sm - Small
VS - Very Small
NR - Not Reported, presumed absent
ND - Not Detected

Several points stand out. Only three PCDF congeners were found on pyrolyzing Aroclor 1254; the 2,3,7,8 tetra-, and the 1,2,3,7,8 and 2,3,4,7,8 penta- species. The four hexa- isomers were not found and the possible precursors are virtually absent. The tetra- and the two penta- isomers were found on pyrolyzing Aroclor 1260, as was a minor amount of the 2,3,4,6,7,8 hexa- species. The other three

MONS 018479

hexa- isomers were not reported and their possible precursors are present in only small amounts. The relation between the several 2,3,7,8 PCDF formed and the presence or absence of an appropriate precursor does seem to hold. All of the significant 2,3,7,8 PCDF formation reported in the pyrolysis of Aroclors can be attributed to just six PCBs (2,2',3,4,4'-; 2,3,3',4,4'-; 2,3',4,4',5-; 2,2',4,4',5,5'-; 2,2',3,4,4',5-; 2,2',3,4,4',5,5'-). If appreciable amounts of the hexa-PCDF isomers are found in pyrolysis products of askarels containing Aroclor 1260 and 1254, it is likely that T_3-, T_4CBs are involved, rather than PCBs.

The only 2,3,7,8 precursors present in Aroclor 1242 are the 2,2',3,3'- and the 2,2',3,4,4'- PCB. Presumably none of the penta- and hexa- PCDF isomers would be found in the pyrolysis of Aroclor 1242 alone. The higher boiling components found in Aroclor 1242 have been substantially reduced in Aroclor 1016. Aroclors 1016 and 1242 were used without chlorobenzenes in many capacitors (and a few transformers). It may well be that little if any 2,3,7,8 and none of the more highly substituted 2,3,7,8 PCDF congeners would be formed in the pyrolysis of Aroclor 1242 filled capacitors and transformers and none in the Aroclor 1016 filled capacitors.

The above discussion is based on results reported for moderate temperature reactions with oxygen. Conditions in transformers and capacitors are much more anaerobic. Capacitors are well sealed and transformers are opened only occasionally for servicing. Simple oxidation may have little effect on PCB and TCB in electrical equipment operating normally. Small quantities of water are present, both as residue from the manufacturing or filling operation and as a product of cellulose degradation. Reaction of PCBs with water does not appear to have been examined in detail and it is not at all clear that oxygenated products will be formed from water in electrical apparatus. (There are non-oxygenated toxic products, the polychlorinated biphenylenes - for example, which also may be formed in anaerobic conditions). In any case, large quantities of PCDF and PCDD are unlikely to be formed. Total concentrations of PCDD of a few ppm (μg/g) or less have been found in unused Aroclors (5) (see also Section 3-3 below). The available findings in Aroclors taken from transformers are similar (8).

Over the years, there has been considerable inadvertent mixing of askarels with the mineral oil more commonly used in transformers. There are on the order of 100 million gallons of transformer oil containing 500 ppm or less of PCBs. PCDF and PCDD formation in contaminated mineral oil is also a complicated situation, but the PCBs and TCBs are present in much lower quantities and the rates of reaction

MONS 018480

(the product of concentration and rate constant) should be much less (1). Moreover, the hydrocarbon molecules of the mineral oil, and the paper insulation will compete in reacting with any available oxygen. (It has also been found in earlier work here on electron irradiation of oil containing PCBs that the hydrocarbons are a sink for chlorine atoms stripped from the biphenyl structure. If rechlorination is diverted by hydrocarbons, the distribution of PCDD and PCDF isomers from partial oxidation of an askarel in oil may differ from that of oil alone.) The likelihood that PCDF and PCDD are formed in contaminated mineral oil must be substantially less than in askarels.

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Section 2

SELECTION OF SAMPLES FROM ELECTRICAL EQUIPMENT FOR PCDF AND PCDD ANALYSIS

This section describes a rationale for the gathering of samples for analysis from equipment in normal service. The intent here has been to consider transformers and capacitors in diverse applications so that an acceptably broad overview of the occurrence of PCDF and PCDD can be developed with a minimum number of samples and costly analyses.

TRANSFORMERS

Transformers are used to change electrical voltage and to control current. They consist of a core and coil structure immersed in a dielectric fluid. The fluid insulates against electrical breakdown and also serves to carry away the heat generated by electrical losses in the transformer. A modern transformer operating at its rated current load is designed so that the average temperature in the coil winding is 65°C above ambient. The temperature at the top of the liquid in the transformer is perhaps 15°C lower at this load and that at the most constricted and hence hottest spot within the winding is perhaps 15°C higher. Temperatures in normally operating transformers then will rarely be much above 100°C. Transformers are sometimes overloaded and higher temperatures can occur. This can result from an abrupt and usually brief emergency demand for power. This also can result from irregular and periodic needs such as air conditioning on summer afternoons. In extreme cases, hot spot temperatures of 180°C can occur in applications such as railroad transformers. Higher local temperatures can be reached in the vicinity of corona and other electrical discharges, and the liquid can be damaged by the electronic processes in the discharge. The fluids also are in contact with cellulose, metals, elastomers and a variety of materials of construction. Air is usually excluded during operation, but not all units are welded and some are initially filled under air. Limited oxidation is possible and there is some prospect that PCDF and PCDD will form in askarel filled transformers.

It has been estimated that as many as 30 million distribution transformers and 5 million other larger units of various kinds are in use (10). Many are owned by utilities but most belong to industrial and governmental organizations. Some

MONS 018483

140,000 are filled with askarels, all of which contain ~50% PCB, and are, by US regulation, "PCB" transformers. These askarel units were generally used in circumstances where there was a high risk of fire and, in many cases, the National Electric Code specified their use. Askarel transformers also developed an excellent reputation for reliability and were sometimes used where trouble-free operation, rather than fire resistance, was the prime concern.

The majority of the transformers in use today are insulated with hydrocarbon oils refined from petroleum crude oils. The mineral oils are specified to have flash points above 145°C (in earlier years - 135°C). Oil filled units are used where the hazard of fires is small or has been minimized by vaulting, sprinklers, or other external protections. A number of these oil filled transformers contain measurable PCBs. Fresh transformer oil does not normally contain PCBs on arrival from the refinery and PCBs were not added deliberately to oil. The presence of PCBs in oil filled transformers then is due to the inadvertent mixing of askarels with oil during manufacture, installation, or servicing. In this writer's experience, some 25% of the mineral oil samples being commercially analyzed for PCBs contain 50 to 500 ppm PCB and 1-2% contain over 500 ppm PCB. This is not to argue that 25% or 1% of the 30 million small units are "PCB contaminated" or "PCB" transformers respectively. Many smaller distribution transformers were produced in plants where PCBs were never used; small transformers arrive filled with oil at the site of installation; and many have not required service during their life. The possibility that PCBs will be found in these small transformers is relatively low. Further, selection for sampling for analysis implies a degree of concern for a particular transformer that would be rare for any given small transformer. The distribution of samples arriving for analysis will be skewed toward those from larger transformers. Perhaps 1% of the 5 million larger oil-filled transformers also fall into the "PCB" transformer category. In this project, twenty or less units will be sampled and analyzed for PCBs, TCBs, PCDD and PCDF. It can only be hoped that the results will be representative for some 200,000 "PCB" transformers (140,000 askarel filled and ~50,000 "PCB" oil-filled) in use.

There are two general classes of transformers, power and distribution. Power transformers include those that step voltage up from generation levels to transmission levels and those that step voltage down to subtransmission, load center and motor-circuit use. High voltages range to 800 kV and low voltages are typically 2.4 to 22 kV. The low voltage of some transmission line interties, however, may be as high as 345 kV. Generator step-up transformers operate at rather steady loads under continual supervision. Substation transformers have associated switch

MONS 018484

gear and protective equipment and, as the voltage and kVA rating goes down, are increasingly dispersed. They also are increasingly subjected to erratic overloading to meet local demands within the system. The design average winding temperature may be 105°C with a corresponding hotspot temperature of 120°C. Under overload conditions, these temperatures will be higher and the thermal degradation processes will be hastened.

The distinction between power and distribution transformers is somewhat imprecise but generally is taken to be at about 500 kVA. Distribution transformers step down voltage for the end use. They typically have input voltages to 14.4 kV and output voltages which can be used directly by the customer, 600 or 480 V for the industrial user and 240 or 120 for the commercial and residential user. Distribution transformers can be categorized as pole mounted, pad-mounted, or subsurface (underground). The 30 million small transformers discussed earlier are pole mounted distribution units. Pad mounts are typically installed outdoors on concrete pads and are enclosed in one way or another to avoid hazard to humans.

Subsurface units are installed in manholes, under streets and buildings, and occasionally in buildings. Askarel filled pole mounted transformers are rare, but askarels have been used extensively in the "underground" application. Distribution networks often are formed by connecting the low voltage windings of several of these transformers to a common bus. This allows a sharing of load and a redundancy of capacity to minimize local outages. It also results in more frequent overloading of an individual unit during the outage of a companion or during short term fault clearing.

Network and smaller substation power transformers are examples of honest, hard working ordinary transformers. Several other types are used in applications which provide more severe conditions for possible askarel decomposition. Furnace and rectifier transformers are power transformers which produce high current, low voltage DC power for electric furnaces, rolling mills, etc. They are operated rather continuously at high loads in hot ambient conditions and prolonged periods. Hot spots of 110 - 120°C are not impossible. Furnace and rectifier transformers may be utility owned, but many are the property of the industrial concern in whose plant or mill they are located.

Smaller DC rectifier transformers are used in electrostatic precipitators for particle removal from stack gases. Together with a rectifier, they convert 480 V

AC to 50 - 120 kV DC and there is the possibility that the askarel in them can be subjected to degradation by DC breakdown.

Two general types of railroad transformers are in service. Transformers mounted on locomotives provide power for the traction motors pulling the train. Transformers for multiple unit (MU) cars are mounted underneath passenger cars. Compactness is important and units are designed for somewhat higher operating temperatures. Short time (2-5 min) overloads for high motor torque during starts can result in hotspot temperatures of 180°C. Further, while most transformers are equipped with pressure relief valves, the large temperature swings suggest that valves will operate more frequently on railroad transformers and thereby provide a greater opportunity for inadvertent oxygen pick up through leaks. Railroads own virtually all transformers in this class.

In order to obtain a cross section of the typical and extreme (both low and high) PCDF and PCDD contents of transformers, it is recommended that some three dozen samples be gathered. These should be obtained from several different utilities.

Samples should be taken with normal precautions, preferably with the transformers de-energized, and be a minimum of one liter in volume. A copy of the information given on the nameplate of the transformer should accompany the sample along with any available information on operation and service history. These samples should be analyzed for PCB and TCB content and a selection of a dozen askarel and four "PCB" mineral oil samples should be made (Table 2-1). An effort should be made to choose askarel samples with a variety of compositions from transformers made by a number of manufacturers.

The majority of these dozen samples should be load center and/or network transformers which represent a range of loading histories and utility practices. It would be desirable for two or three of these samples to come from spare or very lightly loaded units. In assessing the formation of PCDF and PCDD in operating transformers, it is useful if some estimate of the background levels in the unused askarel be available. Askarels were often treated with fuller's earth before introduction into a transformer and any PCDF or PCDD content originating in the manufacture of the Aroclors or T_3- and T_4CBs may have been reduced. Analysis of reserved stocks of only the untreated starting materials could lead to an erroneously high estimate. One or two utility owned and heavily used rectifier transformers should be included to provide samples with maximum thermal exposure of the askarel. Steel mills and aluminum producers should be sources of samples.

MONS 018486

Finally, at least two precipitator transformer samples are useful in determining if unusual PCDF and PCDD formation occurs in units with high DC voltage available. The "PCB" oil samples should be from oil-filled substation or network transformers. Installation and servicing of these transformers was quite similar for oil and askarel units and was, at times, done with the same equipment. Overloading practices should be much the same for the two types in this size range.

The PCBs found in oil probably will be from Aroclor 1260, but it is desirable that at least one sample containing relatively large amounts of the lower chlorinated Aroclors be selected. It is likely that transformers meeting these needs will already have been identified by analysis as part of normal servicing and the initial round of selection may not be needed for the oil samples. PCB and TCB analyses should be repeated.

CAPACITORS

Askarels were used in power capacitors because of their high dielectric constant, rather than because of their lack of flammability. A much smaller unit can be made for a given capacitance with askarel rather than mineral oil as the impregnant in the paper or film insulation. Initially in the 1930's, Aroclor 1254 alone or, mixed with T_3CB for low temperature applications, was used. Aroclor 1242, which has a higher dielectric constant, came into use, followed by Aroclor 1016. Aroclor 1016 is somewhat less viscous than 1242 because it lacks the high boiling congeners, but otherwise its properties are much the same. Capacitor askarels were thoroughly treated with fuller's earth to reduce the power factor of the capacitor and residual PCDF also may have been reduced. Capacitors are well sealed from the atmosphere. Voltages, physical sizes and capacitance vary, but voltage stress is relatively comparable from unit to unit and the temperature of operation is ambient.

It was estimated that there were some 5 to 10 million PCB filled power capacitors in service. In view of the relatively benign and more or less common operating conditions for capacitors, it is recommended that samples from only four power capacitors be obtained. They should represent four different manufacturers. They should be large enough to provide 25 ml or more of askarel. Three should have been in use for over 15 years and a general description of service conditions should accompany the capacitors to the laboratory for disassembly. One of these should have failed in service. The fourth sample could usefully be an unused unit

MONS 018487

of the same age. PCB and TCB analyses should be made prior to analysis for PCDF and PCDD.

SUMMARY

Samples of liquid from three dozen "PCB" transformers should be obtained and analyzed for PCB and TCB content. From these, a dozen askarel and four mineral oil samples should be selected for PCDF and PCDD analysis. The samples should be selected to cover a broad spread of initial composition and of service conditions. The service conditions should range from very mild to heavy overloading.

Four askarel filled capacitors should be randomly selected from utility sources. They should be disassembled to obtain their liquid contents and the liquids should be analyzed for PCBs TCBs, PCDFs and PCDDs.

These recommendations are summarized in Table 2-1.

TABLE 2-1

EQUIPMENT RECOMMENDED FOR SAMPLING FOR
PCDF AND PCDD ANALYSIS

Askarel Filled	
Load Center/Network Transformers	8-10 (2-4)*
Rectifier Transformers	1-2
Precipitator Transformers	2
Capacitors	4
PCB Oil Filled	
Load Center/Network Transformers	4

*Spare or lightly loaded

Note: These recommendations were made at an early stage of the overall EPRI program to evaluate PCDF and PCDD in equipment. They will not have been completely implemented by the conclusion of the program. Their completion is still a desirable goal.

MONS 018488

REFERENCES

10. EPA Report No. 560 6-77 - 035, p. 47, May 1978; See also EPRI FP 1207. Disposal of Polychlorinated Biphenyls and PCB Contaminated Materials, Vol. 1. SCS Engineers, 1979.

Section 3

FORMATION OF PCDF AND PCDD IN ELECTRICAL DISCHARGES

Failure of transformers or capacitors can result in degradation of the insulating liquid in at least two ways. One is explosion of liquid into the surroundings where it may catch fire itself or become involved in a fire resulting from nearby materials. A second is degradation of the liquid in the heated zone of the electrical breakdown within the equipment. PCDF and PCDD formation in fires is being studied widely. Their formation in the dielectric liquid in and near the vicinity of an electrical breakdown has not been examined. Electrical breakdown represents a malfunction in a transformer which is neither readily controlled nor reproduced and occasionally cannot be contained. Electrical failure of actual transformers then is not an acceptable approach to examining PCDF and PCDD formation. This section describes studies of the formation of PCDF and PCDD in controlled simulations of high energy electrical breakdown - "arcing" - in transformers. Askarels alone and mineral oil containing low concentrations of askarels have been examined.

EXPERIMENTAL

Test cells were capped, glass filament wound epoxy fuse tubes (6.8 cm ID x 40 cm L) containing 1.35 liters of liquid, with a wrap of 0.23 mm thick electrical insulating Kraft paper inside the tube. Both were half saturated with water and the oil was fully saturated with air. The air space over the oil was 17% of the oil volume.

Electrodes were radiused 1.5 cm diameter aluminum (6061) rods with a 1.27 cm gap, initially bridged by a small diameter low carbon steel (0.3% Mn, 0.1% Cu, 0.1% Ni) wire to start the arc. Each cell was provided with a connection to a pressure gauge, a pressure transducer, and a gas sampling container. Current, arc voltage, duration and pressure excursions were recorded; $I^2 \cdot t$ products and arc energies were integrated automatically.

Askarels tested were electrical grade trichlorobenzene (Hooker Chemical) and Aroclors 1254 and 1260 (PCB mixtures made by Monsanto Company). TCB and 1:1 mixture of TCB and Aroclor 1254 were each treated twice with 3% of their mass of

activated fuller's earth, a normal manufacturing practice in removing polar impurities prior to filling askarel transformers. One component usually added to askarels was 0.15% of 3,4-epoxy cyclohexylmethyl-(3',4'-epoxy cyclohexane) carboxylate as a scavenger for chlorine or water. The possibility of its halogenation, dehydrogenation, and rearrangement to form PCDF and PCDD is remote and it was omitted here to simplify the testing. Oil samples were made from commercially available, fuller's earth treated transformer oil and Aroclor 1254 (50 ppm, 500 ppm, 3 part per thousand [ppt], 10 ppt wgt/wgt), Aroclor 1260 (10 ppt) or TCB (10 ppt). PCDF, PCDD and some PCBs were separated from the sample matrixes after arcing using silica and activated alumina. Analysis was done by capillary column GC/MS with ^{13}C-PCDF and ^{13}C-PCDD spikes (11).

Several unsuccessful attempts were made to generate repetitive corona discharges in these insulation systems. Tapered and radiused (0.08 cm) rod-to-rod gaps flashed over before reliable corona occurred. Rod-to-ground plane geometry gave intermittent and erratic bursts in gaps ranging from 0.02 to 1.78 cm rather than the continuous level hoped for. Tests were made with electrical grade insulating paper or Nomex® bonded to the plane electrode. Again, corona bursts were intermittent and erratic, and the integrated charge level was low. The final attempt to produce continuous high levels of corona in the gap was to bond a disk of unmetallized zinc oxide to the ground plane electrode. In dried degassed test oil, corona levels of 50,000 to 100,000 pico-Coulombs were maintained while energized for 50 hours over a six day elapsed period. The oil then was half saturated with water and fully saturated with air. The corona discharges generated in this configuration were erratic and often very low in magnitude. Attempts to evaluate PCDF and PCDD formation in low energy electrical breakdowns were abandoned.

RESULTS

Two or more samples of each liquid were subjected to arcing and at least one of each pair was analyzed for PCDF and PCDD. Arc currents ranged from 700 to 750 amps rms and durations from 48 to 96 msec. The intent was to control the arc energy to less than 10 kJ. The energy dissipated in an actual transformer arc might reach 100 kJ. However, actual transformer arcs are not confined to volumes as small as that of these test cells and the test conditions are considered to be more severe. Arcing parameters are listed in Table 3-1.

The pressure buildup in the cells was proportional to the arc energy (Figure 3-1) and in two cases, it pegged the pressure gauge at 60 psig. Gas analyses (12) were

MONS 018491

made on the contents of four mineral oil filled test cells after arcing under these conditions. Nitrogen, oxygen and CO_2 levels were not affected and no CO appeared. Little or no decomposition of the paper occured. The primary decomposition product was, as expected, acetylene (0.43 ± 0.03 m moles/kJ). The ratios of the other fault gases were about as expected for a high energy breakdown in oil:

H_2/C_2H_2 - 0.78 ± 0.20 CH_4/C_2H_2 - 0.29 ± 0.07

C_2H_4/C_2H_2 - 0.46 ± 0.07 C_2H_6/C_2H_2 - 0.04 ± 0.01

TABLE 3-1

ARCING TESTS OILS CONTAINING ASKARELS

Tube Number	Dielectric Liquid	Arc Parameters: Current (Amp)	Time (ms)	Charge (Coul)	Energy (kJ)	Pressure (psig)
2	TCB	745	48	36	4.3	12
	TCB/1254					
4	1:1	735	90	66	11.5	>60
5	1:1	725	55	40	3.7	13
	Oil/1254					
6	50 ppm	730	72	53	6.5	29
7	500 ppm	715	80	57	9.4	52
8	3.0 ppt	705	46	33	3.1	10
9	10.0 ppt*	715	53	45	6.4	30
	Oil/1260					
10	10.0 ppt	745	48	36	3.7	14
	Oil/TCB					
11	10.0 ppt	730	88	65	15.6	>60

* - part per thousand (mg/g)

The concentrations of PCDF and PCDD in the TCB and TCB/1254 mixture before (B) and after (A) arcing are given in Table 3-2 (11). A good deal of carbonaceous residue was formed in the liquids. A portion of this was filtered from a TCB sample, washed with methanol, extracted with benzene and analyzed. The results of these analyses are also given in Table 3-2. The results of analysis of the mineral oil samples before and after arcing are given in Table 3-3 (Note - Analysis of the unarced 10 ppt Aroclor 1254 in oil sample - tube 9 - was not done.)

The concentration of PCDF in the Aroclor 1254 was estimated from the analysis of the TCB/1254 mixture and the TCB itself. The concentration in the unarced Tube 9 sample was then calculated from the dilution factor. As a check, this same procedure was followed for the 3 ppt 1254 sample - tube 8. The calculated and measured values are in reasonable agreement. PCDF content of the 50 and 500 ppm Aroclor 1254 samples were below the limit of detection both before and after arcing, as was the PCDD concentration in all oil samples.

MONS 018492

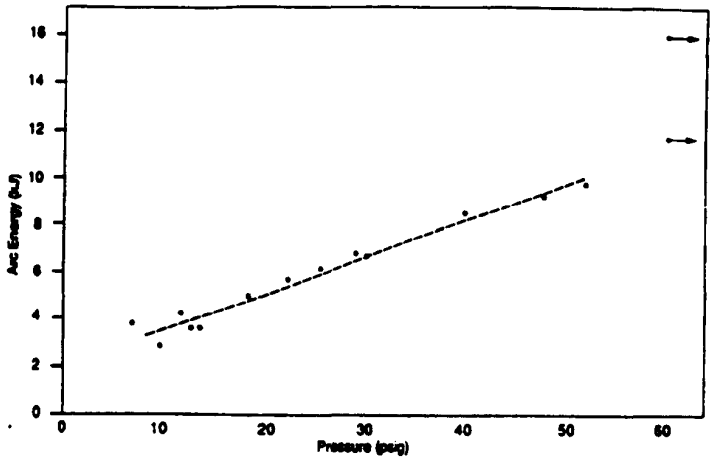

Figure 3-1. Relation of ARC Energy to Pressure in Spiked Oil and Askarel

TABLE 3-2

PCDF AND PCDD CONTENT OF ASKARELS - BEFORE AND AFTER ARCING

Isomer	PCDF or PCDD Content - ng/g (ppb)			
	TCB		50:50 TCB/Aroclor 1254	
	Tube 2		Tube 4	Tube 5
	B/A	Particles	B/A	B/A
PCDF				
Tetra-	200/270	100	367/173	230/96
Penta-	2000/2500	990	1850/1740	1200/340
Hexa-	1700/2000	1500	1790/1180	1300/310
Hepta-	930/1000	1100	2960/1360	520/29
Octa-	170/150	560	217/171	100/0
Total	5820/5920	---	7184/4624	3350/783
PCDD				
Tetra	33/29	40	21/24	20/6
Penta-	11/16	ND	ND/12	1/1
Hexa-	4/2	ND	ND/2	2/ND
Hepta-	ND/ND	ND	ND/ND	ND/ND
Octa-	ND/ND	ND	ND/ND	ND/ND
Total	48/47	---	21/38	23/7

ND - Not Detected

MONS 018493

TABLE 3-3

PCDF CONTENT OF MINERAL OIL CONTAINING PCBS - BEFORE AND AFTER ARCING

PCDF ISOMER	PCDF Content - ng/g (ppb) Aroclor - mg/g (ppt)				
	1254			1260	TCB
	Orig 1000 ppt	Tube 8 3 ppt B/A	Tube 9 10 ppt B/A	Tube 10 10 ppt B/A	Tube 11 10 ppt B/A
Tetra-	-- (180)	0.1/ND (0.5)	--/11 (2)	1/1	ND/ND
Penta-	-- (400)	3/0.5 (4)	--/4 (4)	3/2	0.4/ND
Hexa-	-- (900)	1/1 (3)	--/2 (9)	4/3	1/ND
Hepta-	-- (110)	6/ND (0.3)	--/ND (ND)	6/7	ND/ND
Octa-	-- (30)	ND/1 (0.1)	--/ND (ND)	23/15	ND/ND
Total	-- (1620)	11/2 (8)	--/7 (15)	37/29	1/ND

( ) - calculated values, see text.

DISCUSSION

The TCB and Aroclors used here were retained samples from the mid-1970's. After a laboratory treatment with fuller's earth similar to that done on a larger scale in the manufacture of transformers and capacitors, measurable PCDF and PCDD remain. It therefore seems probable that, if unused transformers and capacitors could be found and askarel samples taken and analyzed, measurable PCDF and PCDD could be found. This, in turn, suggests that the interpretation of analyses of samples from functioning transformers and other sources will be complicated by the presence of an unmeasured and variable background.

It also appears that arcing TCBs and PCBs under the conditions here does not result in the formation of PCDF and PCDD. The reliability of the analytical method is still under study, but clearly there is no major increase in the concentrations found in the liquids after arcing. If anything, there appears to have been a reduction in the solution concentrations. This, in part, might be due to adsorption of the pre-existing furans and dioxins on the carbonaceous material forming in the discharge. No attempt was made to recover all of this finely divided powder. It is a minor, but very visible, amount. Extraction with benzene did not reveal any PCDF or PCDD. Unless the extraction with benzene is very inefficient, the powder is not a sink for any major quantity of PCDF and PCDD which may have been formed in the discharge.

MONS 018494

REFERENCES

11. Fred L. DeRoos, Battelle-Columbus Laboratories. EPRI 2020-6.

12. Annual Book of ASTM Standards. Vol. 10.03; D3612-85 and D3613-82.

MONS 018495

LABORATORY INVESTIGATION OF THE HIGH TEMPERATURE FORMATION AND DESTRUCTION OF PCDFs

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The formation of polychlorinated dibenzofurans (PCDFs) as a result of the thermal degradation of polychlorinated biphenyls (PCBs) has become an area of intense interest due to the reported toxicity of these partial oxidation products. Reports of their formation as a result of fires in PCB containing transformers, has caused the United States Environmental Protection Agency (US-EPA) to consider expanded regulations to reduce the risk of accidental combustion of PCB containing material.

Most previous studies of the formation of PCDFs have been concerned with the optimization of conditions for their formation from PCBs. In this study, we have investigated the effect of temperature and oxygen concentration on the rate of formation and destruction of PCDFs as well as the thermal stability of the parent PCB. Additional objectives were to identify other degradation products and provide some information to elucidate the mechanism of PCB destruction and PCDF formation in a flow reactor system.

The thermal degradation of a single PCB isomer was conducted under four reaction atmospheres at a constant gas phase residence time of 2.0 seconds. The isomer selected for study was 2,3',4,4',5-pentachlorobiphenyl (2,3',4,4',5-PCB). The oxygen availability in the reaction atmosphere is described using the equivalence ratio, phi. Phi is defined as the ratio of fuel to oxygen actually in the reactor divided by the ratio of fuel to oxygen required for complete combustion. The values of phi used in this study were 3.0, 1.0, 0.2, and 0.05 which range from oxygen starved to very oxygen rich conditions as the values of phi become progressively smaller. A phi of 1.0 means there is exactly enough oxygen available for complete combustion; thus, the percent excess air is zero. Thermal degradation experiments were conducted at various temperatures ranging from 500-1000C.

MONS 018496

The thermal decomposition profiles and reaction products were determined using the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) system and the Thermal Decomposition Analytical System (TDAS). Both pieces of laboratory instrumentation are closed continuous systems that contain a narrow-bore quartz tubular reactor which is capable of subjecting gaseous species to controlled thermal exposures with precise control of residence time and other reaction variables. Mixtures of oxygen and nitrogen were used to obtain the various reaction atmospheres tested in this study. A 40ug sample of 2,3',4,4',5-PCB was used in all experiments.

Following thermal exposure, the remaining parent material and the various thermal reaction products were cryogenically trapped. The numerous trapped samples were subjected to in-line chromatographic analysis using a capillary column, 15 m length by 0.25 mm ID and possessing a 0.25 micron DB-5 film thickness. On the TDU-GC, a hydrogen flame ionization detector was used for detection of the various solutes, and the data were processed and displayed using a Varian CDS 401 chromatographic terminal. The identities of the thermal reaction products from the decomposition of the PCB were tentatively determined from their electron impact ionization mass spectra obtained on the TDAS which incorporates an LKB 2091 GC/MS. The reaction products examined were generated from the degradation of the PCB at 800C and phi = 0.2. Sample handling and chromatographic conditions were the same as those used for the TDU-GC testing.

Table 1 lists the major thermal reaction products tentatively identified for the thermal degradation of 2,3',4,4',5-PCB. A variety of pyrolysis and partial oxidation products have been formed, with PCDF congeners representing the majority of the oxidative products. Significant quantities of partially dechlorinated biphenyl congeners are formed along with dichlorobenzenes and trichlorobenzenes. Tetrachlorobiphenylene isomers were also observed. These are of particular interest due to their suspected toxicity. The formation of tetrachloronapthalene is important because of its apparent thermal stability. At 1000C for phi = 1.0, the reaction product tentatively identified as tetrachloronapthalene exceeded the concentration of the parent PCB. As one might expect, the yield of pyrolysis products decreased with increasing oxygen levels. However, the increase in PCDF concentration with increase in oxygen concentration was far more striking.

MONS 018497

Table 2 presents the yields of observed PCDFs at various equivalence ratios. As the oxygen concentration increased by a factor of 60, the yield of total PCDFs increased by a factor of 10. The percentage of total PCDFs identified as tetra isomers ranged from 62-72%. Thermal formation/destruction profiles for observed PCDFs for phi=1.0 are depicted in Figure 1.

TABLE 1

MAJOR THERMAL REACTION PRODUCTS TENTATIVELY IDENTIFIED FROM THE THERMAL DEGRADATION OF 2,3',4,4',5-PENTACHLOROBIPHENYL

Product Class	Number of Major Peaks
Tetrachlorodibenzofurans	2
Trichlorodibenzofurans	2
Pentachlorodibenzofurans	1
Tetrachlorobiphenyls	5
Trichlorobiphenyl	1
Trichlorobenzene	1
Dichlorobenzene	1
Trichloronaphthalene	1
Tetrachloronaphthalene	1
Trichlorophenylethyne	2
Dichlorophenylethyne	1
Tetrachlorobiphenylenes	2
C_9H_8OCl	1
$C_{10}H_3Cl_3$	1

TABLE 2

MAXIMUM WEIGHT % YIELD OF PCDFs AS A FUNCTION OF REACTION ATOMSPHERE

ϕ	TEMPERATURE OF MAXIMUM YIELD (C)	WEIGHT % YIELD			
		TRI-CDFS	TETRA-CDFS	PENTA-CDFS	TOTAL-PCDFS
0.05	750	0.66	4.3	2.0	6.9
0.2	800	0.34	1.7	0.56	2.6
1.0	900	0.13	1.3	0.25	1.7
3.0	850	0.068	0.71	0.21	0.99

The relative yields predicted for PCDF isomer production may be estimated by examination of the reaction enthalpies for the global reactions. Calculations reveal that an overall reaction involving elimination of a hydrogen atom and a chlorine atom from ortho positions to form either 2,3,7,8-TCDF or 2,3,6,7-TCDF and HCl, has a reaction enthalpy of -29.7 kcal/mole. Elimination of ortho hydrogens to form either 1,3,4,6,7-PCDF or 1,3,4,7,8-PCDF and H_2 has a reaction enthalpy of -14.2 kcal/mole. Using these values as a "zeroth" order approach to the reaction kinetics of PCDF formation, one would predict that the two tetra isomers would be the predominant reaction products. Two major TCDF peaks were, in fact, observed that accounted for 60-70% of the total PCDF formation. Further isomer specific identification work is strongly indicated.

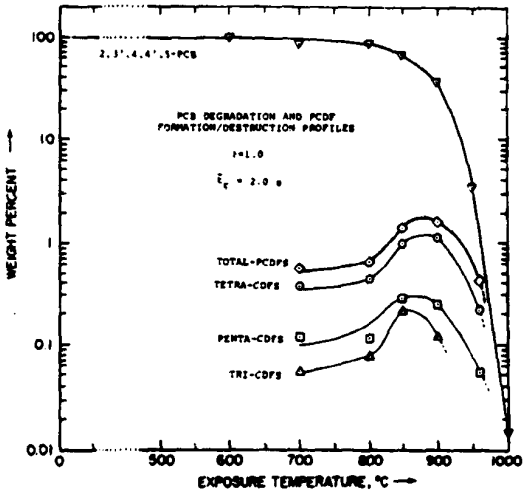

Figure 1. PCDF Formation/Destruction Profiles.

In summary, the results of this study show that the yields of PCDFs formed from the thermal degradation of 2,3',4,4',5-PCB are on the order of a few percent; and these yields increase as the oxygen concentration increases (ϕ=3.0→ϕ=0.05). The predominant mechanism for their formation is HCl elimination. For equivalent combustion conditions, it appears that PCDFs can be destroyed at temperatures that are sufficient to destroy the parent PCB. However, there is evidence for formation of pyrolysis products such as tetrachlorobiphenylenes and chlorinated polynuclear aromatics that are major reaction products at very high temperatures.

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MONS 018499

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Topics:
PCB
Chemical analysis
Fires
Transformers
Pollution control
Insulating oils

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Workshop Proceedings: PCB By-product Formation

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Electric Power Research Institute
Palo Alto, California

MONS 018500

REPORT SUMMARY

SUBJECTS: Transmission: Substations / Distribution: Substations / Hazardous/toxic substances

TOPICS: PCB; Chemical analysis; Fires; Transformers; Pollution control; Insulating oils

AUDIENCE: Environmental scientists and managers

Workshop Proceedings: PCB By-product Formation

Fires involving PCB-filled transformers occur infrequently, but concern exists about the release of potentially toxic combustion by-products. Responding to proposed EPA regulations on PCB-filled building transformers, experts gathered to review current information on the partial-oxidation products of PCB.

BACKGROUND

In March 1984, EPA announced its intention of drawing up regulations to cover polychlorinated biphenyl (PCB) fires in electric transformers. A preliminary version of the proposed EPA rules was prepared, and public hearings were scheduled for January 1985. Before final regulations were determined, EPRI sponsored a workshop to make available the most current knowledge on PCB fires and research.

OBJECTIVES

To compile the latest information and review the current research on the effects of fires in PCB-filled transformers—including PCDF formation, chemical analyses, risk assessment, and cleanup techniques.

APPROACH

Twenty-seven papers dealing with PCB conversion were presented at the EPRI workshop in December 1984. The agenda called for three background presentations and four half-day sessions focusing on (1) analysis of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs); (2) pyrolysis and combustion; (3) fires, spills, and cleanup; and (4) risk assessment. More than 70 representatives of EPA, EPRI, the chemical industry, major equipment manufacturers, utilities, research organizations, and universities participated in the meeting.

RESULTS

The presentations covered a wide range of PCB conversion subjects, including improved approaches to sample preparation and PCDF analysis; advances in decontamination techniques and preventive measures that would decrease accident response time and costs; and the implementation of risk assessment and risk minimization techniques. There was agreement that an improved understanding of PCB pyrolysis and combustion under varying conditions would provide insight into designing installations for minimum risk. Participants also agreed that better methods of assessing risk would lead to the establishment of more realistic risk levels. As a result, substantial cost reductions could be achieved.

MONS 018501

EPRI PERSPECTIVE

This workshop provided a useful opportunity for experts in PCDF analysis, PCDD analysis, and PCB combustion problems to exchange current, reliable information that should be of significant value to those charged with the responsibility of establishing PCB regulations. The discussions indicated that there is a need for more accurate chemical analyses, more realistic risk assessments, and more timely and efficient decontamination and cleanup following spills and fires.

A new report on a related EPRI project is now available: CS-4094, *Design Manual for Reducing Airborne PCB Contamination.*

PROJECT

RP2028
EPRI Project Managers: Ralph Y. Komai; G. Addis
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For further information on EPRI research programs, call EPRI Technical Information Specialists (415) 855-2411.

MONS 018502

Workshop Proceedings: PCB By-product Formation

CS/EL-4104
Research Project 2028

Proceedings, July 1985

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December 4–6, 1984

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MONS 018503

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MQNS 018504

ABSTRACT

The EPRI PCDF workshop was held to assemble current data on PCB fires, a subject of vital interest to the Electric Utility Industry. It was timed to precede the public hearings on the EPA's proposed regulation on PCB fires. It is hoped that some of the ideas expressed were useful input to those active at the hearing.

Four half-day sessions covered Analysis, Pyrolysis and Combustion, Documentation of Fires, Spills and Clean-up, and Risk Assessment.

MONS 018505

ACKNOWLEDGMENTS

We would like to acknowledge the help of our session chairmen, Jacques Guertin, Marcus Cooke, Brian West and Vic Niemeyer. Ellen Lanum provided excellent meeting arrangements. Other EPRI personnel who helped were:

Gary Cobbley
Barbara Cole
Eleanor Keith
Kay Kidd

Thanks to all.

MONS 018506

CONTENTS

Section		Page
PART 1:	BACKGROUND	
1.	EPRI's PCB Interdivisional Task Force - Narain Hingorani (EPRI) (no paper available)	1-1
2.	Regulation Development Process as it Applies to PCB - Denise Keehner (USEPA) (no paper available)	1-3
3.	Cost-Effectiveness Analysis of the Proposed Rule For Indoor PCB Transformers - Amy Moll	1-5
PART 2:	ANALYSIS - JACQUES GUERTIN - MODERATOR	
4.	Factors Affecting the Reliability of Quantitative Analyses for Chlorinated Dibenzodioxins and Dibenzofurans in PCB-Containing Transformer Fluids and Their Products of Combustion - T. O. Tiernan, M. L. Taylor, J. H. Garrett, H. G. Solch, G. F. Vanness, D. J. Wagel, T. Mazer and B. Ramalingam	2-1
5.	Mathematical Modeling of the Physical Properties Used in the Analysis of PCDFs - F. D. Hileman, M. D. Hale, T. Mazer and R. W. Noble	2-9
6.	Formation of PCDD and PCDF in Askarel and Contaminated Mineral Oil Equipment - Fred L. De Roos, Marcus Cooke, Gil Addis, Ralph Komai and Jacques Guertin	2-12
7.	Chlorodibenzofuran Analysis Using Two-Dimensional Gas Chromatography-Mass Spectrometry - Woodfin V. Ligon, Jr. and Ralph J. May	2-16
8.	PCDF Isomers and Isomer Levels Found in PCBs - Christoffer Rappe, Lars-Owe Kjeller and Stellan Marklund	2-20
PART 3:	PYROLYSIS AND COMBUSTION - MARCUS COOKE - MODERATOR	
9.	Formation of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans From Burning of Silicone Dielectric Fluid Spiked with Polychlorinated Biphenyls - Jon W. Swanson and Thomas O. Tiernan	3-1

MONS 018507

Section		Page
10.	Simulated Building Fire Study Using Retrofilled Transformer Dielectric Coolant - Marcus Cooke, Fred L. De Roos, Bruce Rising, William H. Martin, Christoffer Rappe and John Slayback	3-9
11.	Formation of PCDFs under "Optimized" Combustion Conditions From Low-Level PCB Dielectric Fluids - Mitchell D. Erickson, Christopher J. Cole, Jairus D. Flora, Jr., Paul G. Gorman, Clarence L. Haile, Gary D. Hinshaw, Fred C. Hopkins, Stephen E. Swanson and Daniel T. Heggem	3-13
12.	Laboratory Investigation of the High-Temperature Formation and Destruction of PCDFs - Barry Dellinger, Wayne A. Rubey, Douglas L. Hall and Sueann L. Mazer	3-17
13.	Products of Incomplete Combustion of Dielectric Fluids - C. Clair Claiborne	3-21
14.	Pyrolysis and Combustion of Mineral Oil, Tetrachlorethylene and Silicone Oil Mixtures Containing Arocior 1254 - George Eadon	3-24
15.	Formation of PCDFs From PCBs - Christoffer Rappe, Stellan Marklund and Lars-Owe Kjeller	3-28
PART 4:	DOCUMENTATION OF FIRES, SPILLS AND CLEAN-UP - BRIAN WEST - MODERATOR	
16.	Decontamination of Fire Fighters' Protective Clothing with Trichlorotrifluoroethane - John R. Kominsky and Eugene T. McIlvaine	4-1
17.	Available PCDF Decontamination Technology and Its Ability to Meet Standards - John Woodyard	4-13
18.	Preventative Measures for PCB Risk Reduction in Buildings - Brian W. West, Warren G. Hansen and Weston A. Fenner	4-18
19.	Fires Involving PCBs: Effectiveness of Cleaning Procedures and Quality Control Requirements - Robert Westin	4-23
20.	Fires in Electrical Equipment Containing PCBs: Recommendations for the Prevention of Contamination by PCDFs - Jean M. Carbonneau	4-31
21.	Correlation of Transformer/Capacitor PCB Content with Soot Contaminants Generated in a Fire Incident - Paul E. des Rosiers	4-46
22.	Decontaminating Service Equipment Exposed to PCB Electrical Fires or PCB Liquids - K. C. Ashley	4-48
PART 5:	RISK ASSESSMENT - VICTOR NIEMEYER - MODERATOR	
23.	The Binghamton State Office Building - Nancy K. Kim and George Eadon	5-1
24.	PCB Exposure Assessment and Spill Clean-up - Stuart M. Brown and Scott H. Boutwell	5-6

MONS 018508

Section		Page
25.	Utilization of Quantiative Risk Assessment Techniques in the Development of Decontamination Standards (A Case Study - San Francisco, California) - Richard L. Wade	5-16
26.	The Use of Analytic Models in Regulatory Risk Management Analysis of PCB Equipment - E. Victor Niemeyer	5-24
27.	Comparative Transformer Fire Risk Assessment - Raymond F. Boykin and Mardyros Kazarians	5-28

APPENDIX
List of Participants

MONS 018509

PART 1:

BACKGROUND

EPRI'S PCB INTERDIVISIONAL TASK FORCE

NARAIN HINGORANI

EPRI

Paper not available at time of publication.

MONS 018511

REGULATION DEVELOPMENT PROCESS AS IT APPLIES TO PCB

DENISE KEEHNER

USEPA

Paper not available at time of publication.

MONS 018512

COST-EFFECTIVENESS ANALYSIS OF THE PROPOSED RULE FOR INDOOR PCB TRANSFORMERS

Amy Moll

USEPA - Office of Toxic Substances
Regulatory Impacts Branch

EPA's Office of Toxic Substances prepared a cost-effectiveness analysis for the proposed rule regulating the use of indoor PCB transformers. The analysis estimated the cost-effectiveness of a number of regulatory alternatives to reduce the risks associated with indoor PCB transformers.

The following alternatives were analyzed:

- 15 year, 10 year, and 5 year phase-out of indoor PCB askarel transformers
- Retrofill of indoor PCB askarel transformers within one year to less than 500 ppm PCBs
- Physical isolation of each indoor PCB askarel transformer by 1987 and by 1989 (Isolation is defined as the physical enclosure of a transformer in a sealed vault or smoke-proof barrier)
- Inspection of indoor PCB askarel transformers for incipient failure on a quarterly basis
- Installation of increased electrical protection on each indoor PCB askarel transformer
- Installation of external electrical switches at each indoor PCB askarel transformer location
- Labeling each indoor PCB askarel transformer location for indentification by fire or emergency response personnel
- Registration of each indoor PCB askarel transformer with the local fire department.

The estimated costs include direct labor and capital costs as well as changes in transformer operating costs. Benefits include: 1) a reduction in the number of catastrophic events resulting from PCB transformer fires or failures, 2) clean-up costs associated with PCB transformer fires or failures, and 3) a reduction in PCBs released to the environment. The only benefits measure which we attached a dollar value to was avoided clean-up costs. Costs and benefits were estimated on an incremental basis using a base case of an indefinite use authorization of PCB transformers with quarterly inspections.

The cost-effectiveness measure used to summarize cost and benefits calculations was:

$$\text{Cost-effectiveness} = \frac{\text{Net Cost}}{\text{Avoided Catastrophic Events}}$$

MONS 018513

where: Net Cost = Cost of Regulation - Clean-up Costs Avoided

In addition, the reduction in PCBs released to the environment was calculated for each alternative where sufficient data was available.

There were many data gaps and uncertainties in the data used to estimate the effectiveness of risk reduction alternatives. We did not attempt to estimate the effectiveness of the following regulatory alternatives because of a lack of data: 1) a requirement to install increased electrical protection, 2) a requirement to install external cut-off switches, and 3) labeling and registration of indoor PCB transformers.

Following is a summary of the results of the cost-effectiveness analysis: (See attached table)

- Total regulatory costs range from $5.2 million for registration of indoor PCB transformers with local fire departments to $1.5 billion for retrofill of all indoor PCB transformers.

- When avoided clean-up costs are considered, net regulatory costs are reduced from 4 percent (for the inspection alternative) to 56 percent (for the 3 year isolation program).

- For all indoor PCB transformers the cost-effectiveness of regulation ranges from $5.48 million per avoided catastrophic event for an isolation program implemented in 5 years to $166 million per avoided event for quarterly inspection.

- The estimated cost of the proposed alternative is $612 million. The proposed alternative includes the following provisions:

  - immediate registration of all (indoor and outdoor) PCB askarel transformers with fire departments,

  - marking of all (indoor and outdoor) PCB askarel transformers with labels on the exterior with labels on the exterior of the vault, grate, door, etc.,

  - immediate registration of PCB askarel transformers in or near buildings with building owners,

  - installation of additional protective devices on PCB askarel transformers with higher secondary voltages, and

  - isolation of all PCB askarel transformers in or near buildings over a three-year period, including preparation and retention.

Following are the major assumptions used to make these estimates:

- The total annual failure rate (including catastrophic and noncatastrophic failures) is .2 percent per year. The catastrophic failure rate is .003 percent per year.

- 47.7 percent of noncatastrophic failures result in a spill of PCB fluid.

- 25 percent of contained volume is lost in a spill.

- The clean-up cost for a catastrophic failure is $20,000,000.

- The total number of indoor PCB transformers at the end of 1984 is 104,284.

- 50 percent of the indoor PCB askarel transformers operate at a higher secondary voltage (480/227 volts).

- Preparation and retention of a plan for isolating each transformer was estimated to cost $280 per isolation.

MONS 018515

Table 8-9

COST-EFFECTIVENESS ANALYSIS OF
ALTERNATIVE REGULATIONS FOR SMALL CAPACITY TRANSFORMERS

YEAR FOR ALL TRANSFORMERS

Alternative	Cost Measure: Total Real Resource Cost (Millions of Dollars)	Benefit Measure: Total Clean-Up Cost Avoided (Millions of Dollars)	Benefit Measure: Total Catastrophic Events Avoided (Number of Events)	Benefit Measure: Total PCB Release Avoided (Pounds)	Cost-Effectiveness: Net Cost (Millions of Dollars)	Cost-Effectiveness: Net Cost per Catastrophic Event Avoided (Millions of Dollars/Event)
Phase-Out by 1990	260.66	46.83	15.81	214,992	201.82	12.77
Phase-Out by 1994	518.98	116.59	26.43	359,534	502.39	19.01
Phase-Out by 1989	1,373.47	358.58	39.86	542,152	1,113.96	27.95
Immediate Retrofill to Nonflammify	1,693.94	365.69	47.68	647,366	1,128.26	23.66
Isolate by 1990	427.16	236.33	34.88	10,194	190.84	5.48
Isolate by 1987	488.79	270.55	37.29	14,255	218.25	5.64
Quarterly Inspection for Incipient Failure	829.01	36.75	4.77	0	792.26	166.18
Increased Electrical Protection	308.57	NA	NA	NA	NA	NA
External Cut-Off Switch	72.24	NA	NA	NA	NA	NA
Labeling 5.49	NA	NA	NA	NA	NA	
Registration	5.31	NA	NA	NA	NA	NA

Reference Case: Indefinite use authorization with quarterly inspection; rebuilding precluded.

Parameters: Catastrophic Failure Rate = 0.001 percent of in-service transformers per year.
Clean-up Cost of Catastrophic Failure = $30,000,000 per event.
Total Number of Transformers = 104,284, end of year 1984.

NA: Not Available.

SOURCE: Putnam, Hayes & Bartlett, Inc., July 1984. All dollar amounts reflect 1983 present value calculated using a 10 percent real discount rate.

MONS 018516

PART 2:

ANALYSIS

JACQUES GUERTIN - MODERATOR

MONS 018517

FACTORS AFFECTING THE RELIABILITY OF QUANTITATIVE ANALYSES FOR CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS IN PCB-CONTAINING TRANSFORMER FLUIDS AND THEIR PRODUCTS OF COMBUSTION

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The sequence of analytical operations which is usually applied in characterizing and quantitating polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in PCB-containing samples is as described in the following.

SPIKING OF SAMPLES

Reliable quantitative analyses to determine trace levels of PCDDs and PCDFs in any sample require the utilization of internal standards which are added to the samples prior to analysis in known quantities. Ideally, isotopically-labelled PCDDs and PCDFs are used for this purpose, since they are expected to closely mimic the native PCDDs/PCDFs already present in the sample in terms of their chemical behavior and the efficiency with which they are extracted from the samples and ultimately recovered through the various clean-up procedures applied to the samples. At the same time, these labelled PCDDs/PCDFs give mass spectral responses at different ion masses than those monitored as indicators of the corresponding native compounds. By using the observed signal responses for the native compounds relative to those observed for the labelled compounds as the basis for quantitation, much more accurate quantitative results are thus obtained. While ideally, it would be desirable to utilize a labelled PCDD and PCDF internal standard for each chlorinated class to be determined, this is not practically possible at present because of the limited availability of such standards. A set of labelled standards which is presently recommended for use includes $^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-2,3,7,8-TCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, $^{13}C_{12}$-OCDD and $^{13}C_{12}$-OCDF. With this approach, the labelled TCDD and TCDF are used as the representative standards for mono-, di-,

MONS 018518

tri- and tetra-CDDs and CDFs, the labelled HxCDD and HxCDF are used as the representative standards for penta- and hexa-CDDs and CDFs, and the labelled OCDD and OCDF are used as the representative standards for hepta- and octa-CDDs and CDFS. In general, the fewer the number of internal standards utilized, the less reliable are the quantitative results obtained in such analyses.

EXTRACTION OF PCDDs AND PCDFs FROM THE SAMPLE MATRIX

Solid samples (soils, combustion particulates, surface wipes) are generally extracted in a Soxhlet apparatus with toluene (or benzene). Tests of the efficiency of extraction of spiked samples have shown that the most efficient extraction is achieved with this solvent and an extraction period of 12-16 hours.

PRELIMINARY FRACTIONATION OF THE SAMPLE EXTRACT AND ELIMINATION OF PRELIMINARY MATRIX CONSTITUENTS AND OTHER CHLORINATED RESIDUES

Table 1 shows a series of fractionation and liquid chromatographic column procedures which are efficacious for the concentration of PCDDs/PCDFs in the sample extract, while concurrently removing other major constituents of the matrix (oil, PCBs and other chlorinated compounds). In order to demonstrate that such procedures yield good recoveries for PCDDs and PCDFs, and that quantitative analyses using these methods are accurate, it is necessary to process typical sample extracts which have been spiked with a representative set of these compounds through these procedures. Data obtained in such experiments is also shown in Table 1, and indicatas that with proper selections, good recovery of PCDDs/PCDFs representative of the entire chlorinated spectrum can be achieved.

GC-MS ANALYSIS OF SAMPLE EXTRACTS

GC-MS analyses of sample extracts to measure quantitetively the levels of PCDDs/PCDFs are based on the premise that complete gas chromatographic separation of each chlorinated class of these compounds can be achieved, so that a unique set of mass spectral indicator ions can be monitored for each of the appropriate GC retention time windows. If the objective of the analysis is to obtain data on the concentrations of PCDDs/PCDFs by total chlorinated class (that is, total tetra-, penta- and so on), then complete separation of the individual isomers of each class is not required. For such analyses, a 60-meter fused silica DB-5 capillary column has been shown to be a particularly good choice as the GC column, because when properly temperature-programmed, this column yields resolution of each of

the chlorinated groups of PCDDs/PCDFs from the other chlorinated groups and permits analyses of the entire tetra- through octa- groups from a single extract injection in about 75 minutes. The sequences of GC and MS operating parameters required for such analyses are shown in Table 2.

CALIBRATION STANDARDS

Rigorous quantitative analyses of PCDDs/PCDFs requires that GC-MS response factors be determined for an appropriate set of PCDD and PCDF isomers using pure standards of known concentration. An appropriate set of such standards should include representative isomers from each chlorinated group of PCDDs/PCDFs which is to be determined in the analysis. Use of an appropriate group of isomers for this purpose permits one to also simultaneously define the GC retention time windows for each chlorinated class of PCDDs/PCDFs.

CRITERIA APPLIED TO GC-MS DATA TO ENSURE RELIABILITY

In order to identify specific PCDD/PCDF in samples analyzed, the GC-MS data obtained must satisfy the following criteria:

a. Mass spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of each chlorinated class of PCDD/PCDF identified (see Table 2) and intensities of these ions must maximize essentially simultaneously (within ± 1 second). In addition, the chromatographic retention times observed for each PCDD/PCDF signal must be correct relative to the appropriate stable-isotopically labelled internal standard and must be consistent with the retention time windows established for the chlorinated group to which the particular PCDD/PCDF is assigned.

b. The ratio of the intensity of the molecular ion $(M)^+$ signal to that of the $(M+2)^+$ signal must be within ± 20% of the theoretically expected ratio (for example, 0.77 in the case of TCDD; therefore the acceptable range for this ratio is 0.62 to 0.92).

c. The intensities of the ion signals are considered to be detectable if each exceeds the baseline noise by a factor of at least 3:1. The ion intensities are considered to be quantitatively measurable if each ion intensity exceeds the baseline noise by a factor of at least 5:1.

d. For reliable detection and quantitation of PCDF it is also desirable to monitor signals arising from chlorinated diphenyl ethers which, if present could give rise to fragment ions yielding ion masses identical to those monitored as indicators of the PCDF. Accordingly, in Table 2, appropriate chlorinated diphenyl ether masses are specified which must be monitored simultaneously with

the PCDF ion-masses. Only when the response for the diphenyl ether ion mass is not detected at the same time as the PCDF ion mass can the signal obtained for an apparent PCDF be considered unique.

e. Measurements of the concentration of the congeners in a chlorinated class using the methods described herein is based on the assumption that all of the congeners are identical to the calibration standards employed in terms of their respective chemical and separation properties and in terms of their respective gas chromatographic and mass spectrometric responses. Using these assumptions, for example, the $^{13}C_{12}$-2,3,7,8-TCDD internal standard is utilized as the internal calibration standard for all of the 22 TCDD isomers or congeners. Furthermore, the concentration of the total TCDD present in a sample extract is determined by calculating, on the basis of the standard procedure outlined above, the concentration of each TCDD isomer peak (or peaks for multiple TCDD isomers, where these coelute) and these individual concentrations are subsequently summed to obtain the concentration of "total" TCDD.

f. Frequently, during the analysis of actual sample extracts, extraneous compounds which are present in the extract (those organic compounds not completely removed during the clean-up phase of the analysis) can cause changes in the liquid and gas chromatographic elution characteristics of the PCDD/PCDF (typically retention times for the PCDD/PCDF are prolonged). Such extraneous organic compounds, when introduced into the mass spectrometer source may also result in a decrease in the sensitivity of the MS because of suppression of ionization, and other effects such as charge transfer phenomena. The shifts in chromatographic retention times are usually general shifts, that is, the relative retention times for the PCDD/PCDF are not changed, although the entire elution time scale is prolonged. The analyst's intervention in the GC-MS operating sequence can correct for the lengthened GC retention times which are sometimes observed due to the presence of extraneous organics in the sample extract. For example, using the program outlined in Table 2, if the retention time observed for 2,3,7,8-TCDD (which normally is 19.5 minutes) is lengthened by 30 seconds or more, appropriate adjustments in the programming sequence outlined in Table 2 can be made, that is, each selected ion-monitoring program is delayed by a length of time proportionate to the lengthening of the retention time for the 2,3,7,8-TCDD isomer. In the case of ionization suppression, this phenomenon is inherently counteracted by the internal standard approach. However, if loss of sensitivity due to ionization suppression is severe, additional clean-up of the sample extract may be required in order to achieve the desired detection limits.

QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

Quality assurance and quality control in these analyses are ensured by the following provisions:

a. Each sample analyzed is spiked with stable isotopically labelled internal standards, prior to extraction and analysis. Recoveries obtained for each of these standards should typically be in the

MONS 018521

range from 60-90%. Since these compounds are used as true internal standards however, lower recoveries do not necessarily invalidate the analytical results for native PCDD/PCDF, but may result in higher detection limits than are desired.

b. Processing and analysis of at least one method blank sample is accomplished for each set of samples (a set being defined as 20 samples or less).

c. It is desirable to analyze at least one sample spiked with representative native PCDD/PCDF for each set of 20 or fewer samples. The result of this analysis provides an indication of the efficacy of the entire analytical procedure. The results of this analysis will be considered acceptable if the detected concentration of each of the native PCDD/PCDF is within ± 50% of the known added concentration.

d. At least one of the samples analyzed out of each set (of 20 samples or less) is analyzed in duplicate and the results of the duplicate analysis are included in the report of data.

MONS 018522

Table 1

RECOVERY OF PCDD/PCDF SPIKES FROM CONTAMINATED SOIL MATRIX CONTAINING PCNs, PCBs, CHLORINATED PARAFFINS, AND HYDROCARBON OILS FOLLOWING APPLICATION OF VARIOUS CLEAN-UP PROCEDURES TO SAMPLE EXTRACT

PCDD/PCDF SPIKED	% OF SPIKED RECOVERED				
	Base and Acid Prewashes[a]	Acid, Base, Neutral Silica Column[b]	Alumina Column[c]	PX-21 Carbon Column[d]	Carbopack C Carbon Column[e]
2,4-DiCDF	67	108	83	83	0
2,7-DiCDD	46	101	85	80	0
1,2,4-TriCDD	84	99	96	90	0
2,3,7,8-TetraCDF	95	98	99	98	70
2,3,6,8-TetraCDF	98	99	101	96	32
1,2,4,8-TetraCDF	92	97	93	92	39
1,2,3,4-TetraCDD	92	94	99	99	62
2,3,6,8-TetraCDD	95	100	94	95	86
1,2,4,7,8-PentaCDF	99	101	96	98	97
1,2,3,7,8-PentaCDD	99	100	96	103	98
1,2,4,6,7,9-HexaCDF	96	98	91	97	98
1,2,3,4,7,8-HexaCDD	99	101	93	100	85
1,2,3,4,6,8,9-HeptaCDF	96	98	88	94	66
OCDF	98	98	91	89	0
OCDD	98	109	94	83	0

a. Hexane extract in contact with 40% KOH for 1 hour, followed by contact with concentrated H_2SO_4 for 1 hour.

b. Column containing 1g Bio-Sil-A (100/200 mesh) 2g Bio-Sil-A containing 30% (W/W) H_2SO_4, 2g Bio-Sil-A containing 40% (W/W) KOH, and 1g Bio-Sil-A eluted with total of 90 mL of hexane; Bio-Sil-A is activated at 180°C after series of solvent rinses.

c. Bio-Rad AG-4 Acid Alumina, Activated at 190°C, eluted with 65 mL hexane, 20 mL 20% methylene chloride-in-hexane, and 15 mL methylene chloride, collecting only last fraction.

d. 18% Amoco Px-21 activated carbon on Celite 545, eluted with 1 mL hexane, 1 mL methylene chloride: Cyclohexane (1:1), and 2 mL, 20% benzene in ethylacetate, then reverse eluted with 4 mL toluene.

e. Carbopack C mixed with Celite 545, activated at 130°C, eluted with 2 mL hexane, 1 mL cyclohexane, methylene chloride (1:1), 1 mL of methylene chloride: methanol: benzene (75:20:5) and 2 mL toluene, collecting last fraction.

MONS 018523

Table 2

SEQUENCE OF OPERATIONS IN GC-MS-DS QUANTITATION OF CDDs/CDFs IN EXTRACTS OF ENVIRONMENTAL SAMPLES

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+$:$[M+2]^+$
0.00	Injection, splitless	190					
1.00	Turn on split valve	190					
1.00	Begin temp. program to 220°C	190	5				
6.00	Open column flow to mass spectrometer	215	5				
7.00	Column temperature hold	220					
14.00	Start Tetra Program; sweep = 360 ppm; time/mass = 0.08 sec.			240.930	$[M-COCl]^+$	TCDF	
				258.930	$[M-COCl]^+$	TCDD	
				303.902	$[M]^+$	TCDF	0.77
				305.899	$[M+2]^+$	TCDF	
				315.942	$[M]^+$	$^{13}C_{12}$-TCDF	
				319.897	$[M]^+$	TCDD	0.77
				321.894	$[M+2]^+$	TCDD	
				327.885	$[M]^+$	$^{37}Cl_4$-TCDD	
				331.937	$[M]^+$	$^{13}C_{12}$-TCDD	
				373.840	$[M]^+$	HxDPE[4]	
22.00	Stop Tetra Program	220					
22.50	Start Penta Program; sweep = 360 ppm; time/mass = 0.12 sec.			274.899	$[M-COCl]^+$	PeCDF	
				290.894	$[M-COCl]^+$	PeCDD	
				337.863	$[M]^+$	PeCDF	0.61
23.00	Begin temp. program to 235°	220	5	339.860	$[M+2]^+$	PeCDF	
26.00	Column temperature hold	236		353.858	$[M]^+$	PeCDD	0.61
				355.855	$[M+2]^+$	PeCDD	
				407.801	$[M]^+$	HpDPE[4]	
32.00	Stop Penta Program						
32.50	Start Hexa Program; sweep = 360 ppm; time/mass = 0.20 sec.	235		310.867	$[M-COCl]^+$	HxCDF	
				326.862	$[M-COCl]^+$	HxCDD	
				373.821	$[M]^+$	HxCDF	1.23
				375.821	$[M+2]^+$	HxCDF	
				385.861	$[M]^+$	$^{13}C_{12}$-HxCDF	
				389.816	$[M]^+$	HxCDD	1.23
				391.813	$[M+2]^+$	HxCDD	
				411.866	$[M]^+$	$^{13}C_{12}$-HxCDD	
				443.759	$[M]^+$	ODPE[4]	

MONS 018524

Table 2 (Continued)

SEQUENCE OF OPERATIONS IN GC-MS-DS QUANTITATION OF CDDs/CDFs IN EXTRACTS OF ENVIRONMENTAL SAMPLES

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+:[M+2]^+$
33.00	Begin temp. program to 250°C	235	5				
36.00	Column temperature hold	250					
40.50	Stop Mass Program						
41.00	Start Hepta Program; sweep = 360 ppm; time/mass = 0.30 sec.	250		344.818	$[M-COCl]^+$	HpCDF	
				360.813	$[M-COCl]^+$	HpCDD	
				407.782	$[M]^+$	HpCDF	1.03
				409.779	$[M+2]^+$	HpCDF	
				423.777	$[M]^+$	HpCDD	1.03
				425.774	$[M+2]^+$	HpCDD	
				477.720	$[M^+]$	HDPE[a]	
53.00	Stop Hepta Program	250					
53.50	Start Octa Program; sweep = 360 ppm; time/mass = 0.30 sec.	250		378.768	$[M-COCl]^+$	OCDF	
				394.774	$[M-COCl]^+$	OCDD	
				441.732	$[M]^+$	OCDF	0.88
54.00	Begin temp. program to 270°	250	5	443.740	$[M+2]^+$	OCDF	
58.00	Column temperature hold	270		453.772	$[M]^+$	$^{13}C_{12}$-OCDF	
				457.738	$[M]^+$	OCDD	0.88
				459.735	$[M+2]^+$	OCDD	
				469.779	$[M]^+$	$^{13}C_{12}$-OCDD	
				471.776	$[M+2]^+$	$^{13}C_{12}$-OCDD	
				511.681	$[M]^+$	ODPE[a]	
66.00	Stop Octa Program						
66.00	Begin temp. program to 300°	270	5				
71.00	Column temperature hold	300					
75.00	Cool Column to 190°						

[a]HxDPE, HpDPE, ODPE, NDPE, DDPE are abbreviations which designate (respectively) hexachloro-, heptachloro-, octachloro-, nonachloro-, and decachlorodiphenyl ethers.

*The parameters given here are applicable for a 60-meter fused silica capillary GC column coated with DB-5.

MONS 018525

MATHEMATICAL MODELING OF THE PHYSICAL PROPERTIES USED IN ANALYSIS OF PCDFs

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INTRODUCTION

The analysis of polychlorinated dibenzofurans (PCDFs) has always been difficult due to the many possible arrangements of chlorines about the two aromatic rings which can yield 135 possible congeners. This analytical difficulty arises from the need to identify a particular congener which may be present in a given matrix. The physical property most widely used to identify a given PCDF congener is its gas chromatographic retention behavior. A variety of parameters have been used to characterize this behavior. These include relative retention to 2,3,7,8-tetrachlorodibenzofuran (1,2), relative retention to lindane (3) and relative retention to various esters of 1,3,5-benzene tricarboxylic acid (4). When analyzing for series of compounds with a wide elution range, such as the PCDFs, the use of a single reference compound is not as desirable as using a series of indexing compounds which elute quite closely to the PCDF being indexed. The Kovats retention index system (5,6) is based on a series of straight chain hydrocarbons and can be adapted to temperature-programmed conditions (7) which were used in this work to assign retention indices to all the PCDFs that had been prepared.

Once indices were assigned to the PCDFs, a mathematical model was devised based on molecular structure to explain their elution behavior. Regression techniques were used to derive quantitative relationships between these structural parameters and the retention indices. The model could then be used to look for PCDFs that were outliers, or did not agree with the predicted retention index derived from other PCDFs. Furthermore, the model could also be used to predict the retention indices for PCDFs that had not been synthesized.

EXPERIMENTAL

The PCDFs were prepared by the carefully controlled oxidative degration of individual polychlorinated biphenyl (PCB) congeners (8). In certain instances a selected PCDF was isolated using normal and/or reverse phase HPLC. The isolated PCDF could then be either chlorinated using antimony pentachloride or dechlorinated using UV photolysis (9) to form additional PCDF congeners.

Retention indices were determined on a 30 meter J&W DB-5 capillary column. A Hewlett Packard 5985B GC/MS system was used to detect both the eluting PCDFs and normal hydrocarbons. The column was programmed in a fashion such that the hydrocarbons were eluting linearly in the range of monochloro through octachlorodibenzofuran.

MODEL DEVELOPMENT

The development of a mathematical model began by dividing the PCDF through biphenyl and ether linkage to form two symmetrical halves. The retention index would then be a sum of the derived index for each half. A similar approach has been used for modeling PCBs (10). To assist in this model develop-

MONS 018526

ment, the PCDFs were renumbered replacing the conventional 6, 7, 8 and 9 with 4', 3', 2' and 1', respectively (11). This scheme emphasizes the symmetry of the molecule and greatly simplified the model development.

Through repeated data analyses, a series of variables were established representative of various structural properties of the PCDFs. These variables included the number and position of the chlorines about the aromatic rings and the relationship of these chlorines to each other (i.e., ortho, meta and para). In the final model development it was necessary to include two variables involving the 1 and 1' as well as the 4 and 4' positions to describe the interaction of the two rings with each other. This type of interaction was not accounted for in the simple model of two independent halves being combined to form a whole.

These variables were then assigned values dependent on the number of times that variable occurred in a given PCDF. The regression of these variables against the retention indices was carried out and the derived regression coefficients serve as a quantitative measure of the retentive effect of the molecular structural component represented by that variable.

RESULTS

Using the described variables and regression techniques an R^2 value of 0.9995 and a standard deviation of 6.78 was obtained for the observed versus predicted retention index for 110 PCDFs which have been synthesized to date. This standard deviation is quite acceptable in view of the fact that the error in the measurement of the retention index of a PCDF is ±4 index units. The model has proven useful in detecting errors in the structural assignment given to PCDFs (12). Furthermore, it has allowed retention indices to be assigned to PCDFs which we have not yet synthesized.

At the present time the minimum number of PCDFs that would be necessary to accurately determine the regression coefficients is being established. This is important in that, as the analytical conditions are changed (e.g., different chromatography columns or different analytical systems such as HPLC), it would only be necessary to run the subset of PCDFs to allow the retention characteristics for all other PCDFs to be determined.

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FORMATION OF PCDD AND PCDF IN ASKAREL AND CONTAMINATED MINERAL OIL EQUIPMENT

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ABSTRACT

The Electric Power Research Institute (EPRI) is conducting a program to determine if polychlorinated dibenzofurans (PCDF) and/or polychlorinated dibenzo-p-dioxins (PCDD) are present, or if they can be formed, in dielectric fluids used by the electric utility industry. The program includes the following tasks.

- Literature Review
- Round Robin Analytical Method Evaluation Study
- Survey of In-Service Dielectric Fluids
- Arcing/Corona Tests
- Pyrolysis/Combustion Tests
- Development of a Rapid MS/MS Analytical Technique

DISCUSSION

The Literature Review, prepared by SCS Engineers of Long Beach, California, summarizes much of the background literature on PCDD/PCDF. It describes accidents that generated PCDD/PCDF, degradation of PCDD/PCDF, toxicology, and future research needs. This review is available from EPRI as publication number EPRI CS-3308.

The Round Robin Analytical Method Evaluation Study was designed to validate current methodologies and to determine the accuracy with which specific PCDD/PCDF isomers can be quantified. Four sample preparation methodologies and three mass spectrometry techniques are currently being compared. The study includes the synthesis of native and isotopically labelled standards and the analyses of spiked sample matrices. Radian Corporation synthesized the standards, and prepared the spiked

MONS 018529

matrix samples, which will be analyzed by Battelle, the Illinois Institute of Technology Research Institute (IITRI), Radian, and the University of Umea (Sweden). The isotopically labelled standards will be used to show true recoveries and to provide accurate quantification within congener classes. Presently 1,2,3,7,8-pentachlorodibenzofuran-$^{13}C_{12}$ has been prepared and purified. A labelled hexachlorodibenzofuran is also being synthesized. The native standards were used for spiking and to generate standard curves and response factors. The native isomers that were synthesized include 1,2,3,7,8-pentachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzofuran, and 1,2,3,4,6,7,8-heptachlorodibenzofuran.

The Round Robin Analytical Method Evaluation Study is presently in progress and a comparison of data from the various laboratories will soon be completed to show reliability, accuracy, and ruggedness of the various analytical methods.

The In-Service Dielectric Fluid Survey consists of developing a selection criteria document, obtaining samples of dielectric fluids, and determining the levels of PCDD/PCDF in selected fluids. General Electric (GE) completed the selection criteria document, while Battelle, IITRI, Radian, and the University of Umea are presently carrying out the analyses. This study will show the absence or presence of PCDD/PCDF in currently used dielectric liquids. Hopefully the study will evaluate a broad range of liquids and operating conditions that mirror the dielectric liquid usage of various utilities throughout the United States.

The Arcing/Corona Tests were designed to determine if arcing and corona discharges could produce PCDD/PCDF isomers in dielectric fluids. The tests, which were carried out by GE, consisted of loading various mixtures into a test vessel and producing a short duration arc with an energy of between 5-10 kjoules. Aroclor 1254 at concentrations of 50-10000 ppm (w/w) in mineral oil, and a trichlorobenzene reference liquid containing 50% (w/w) of Aroclor 1254 were arced. The unarced mineral oil, as well as the trichlorobenzene/Aroclor 1254 mixture, were also analyzed as positive controls. The preliminary results from these analyses, summarized in Tables 1 and 2, show little difference in PCDD/PCDF levels between the arced and unarced fluids. This indicates that arcing appears to have minimal effect on either the PCDD or the PCDF levels in dielectric liquids. These data show the type of information that can be gained from this study.

The Pyrolysis/Combustion Tests were designed to characterize the production of PCDD/PCDF isomers during pyrolysis. These tests are being carried out by the New York State Department of Health, and are presently in progress.

The goal of the Rapid MS/MS Technique Study is to develop an analytical method that minimizes the need for extensive sample workup prior to analysis. The advantages of this approach would be a rapid and lower cost analysis as compared to conventional gas chromatography/mass spectrometry (GC/MS). Ideally this technique will provide the same sensitivity and selectivity as conventional GC/MS.

SUMMARY

This research program is designed to evaluate the potential presence of PCDF and PCDD in utility dielectric liquids currently in use in the United States. The study is based on development of well characterized methods to detect PCDF/PCDD in order to generate high quality data for the diverse class of compounds that are expected only at trace concentrations. The in-service fluid characterization will show the relative magnitude of PCDF/PCDD background levels in fluids from various utility operations. The arcing and pyrolysis experiments are designed

to show potential for production of PCDF/PCDD in unusual situations or upset situations.

The overall program is a comprehensive attempt to characterize the potential presence of PCDF/PCDD in operating utility dielectric fluids and to investigate the potential for their production in unusual situations such as catastrophic failure, or overheating.

Table 1

PCDD DATA FOR ARC STUDY SAMPLES
(limit of detection), ppb (w/w)

Samples	Tetra-CDD	Penta-CDD	Hexa-CDD	Hepta-CDD	Octa-CDD
Arced Aroclor 1254	(0.06)	(0.36)	(0.38)	(1.4)	(1.7)
Arced Aroclor 1254	0.20	(0.14)	(0.09)	(1.6)	(2.6)
Arced Aroclor 1254	(0.06)	(0.13)	(0.12)	(1.8)	(1.4)
Arced 50/50 TCB/1254	23.9	12.1	1.7	(1.0)	(1.4)
Unarced Oil	(0.09)	0.11	0.05	1.04	1.00
Unarced 50/50 TCB/1254	21.2	(0.78)	(0.21)	(5.9)	(6.8)
Method Blank	(0.10)	(0.09)	(0.07)	(0.65)	(0.52)

Table 2

PCDF DATA FOR ARC STUDY SAMPLES
(limit of detection), ppb (w/w)

Samples	Tetra-CDF	Penta-CDF	Hexa-CDF	Hepta-CDF	Octa-CDF
Arced Aroclor 1254	0.69	4.2	1.6	(1.7)	(1.6)
Arced Aroclor 1254	(0.07)	(0.19)	(0.10)	(2.2)	(1.7)
Arced Aroclor 1254	(0.07)	(0.12)	(0.08)	(2.6)	(1.2)
Arced 50/50 TCB/1254	173	1740	1180	1360	171
Unarced Oil	(0.06)	(0.03)	(0.01)	(0.6)	(0.71)
Unarced 50/50 TCB/1254	367	1850	1790	2960	217
Method Blank	(0.08)	(0.08)	(0.04)	(0.35)	(0.48)

MONS 018532

Chlorodibenzofuran Analysis Using Two-Dimensional

Gas Chromatography-Mass Spectrometry

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We have developed a two-stage gas chromatography system for sample cleanup prior to mass spectrometry. Schematics of this system in its three modes of operation are shown in Figs. 1,2,3.

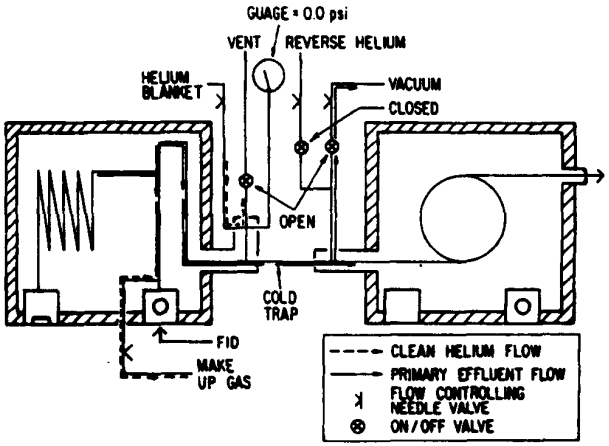

Figure 1. Schematic of the GC-GC system in the "SAVE" mode of operation.

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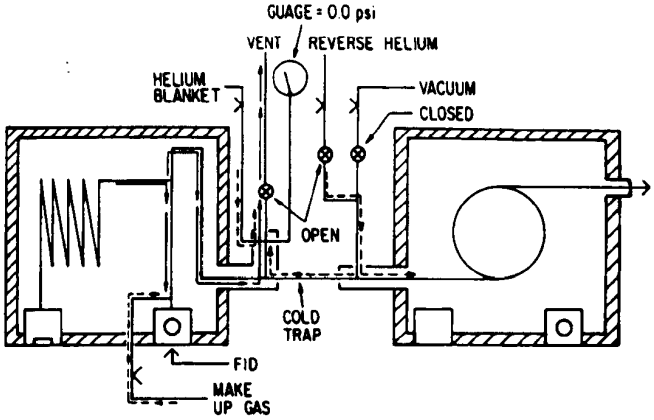

Figure 2. Schematic of the GC-GC system in the "DIVERT" mode of operation.

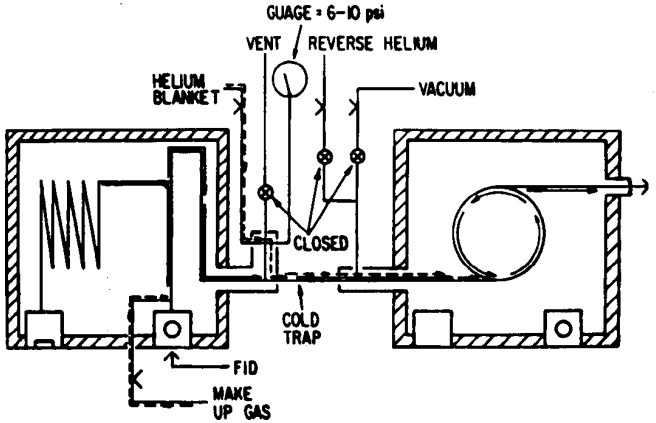

Figure 3. Schematic of the GC-GC system in the "SECONARY SEPARATION" mode of operation.

MONS 018534

The system consists of two coupled gas chromatographs. The first chromatograph uses a high capacity low resolution packed GC column (10 ft x 2 mm , 3% Silar 10C). This column provides a preliminary separation. In the case of the chlordibenzofurans, it serves to limit the number of isomers which must be resolved in the secondary separation and it prevents the great majority of the matrix components from reaching the high resolution secondary column. This column is essentially expendible and serves to collect involatile residues before they reach the secondary column. The condition of the primary column should be monitored regularly because both absolute and relative retention times can change as residues are deposited.

When the system is operated in the "save" mode selected portions of the primary chromatogram are stored in a cold trap. See Fig. 1. When the system is operated in the "divert" mode unwanted components eluting from the primary chromatograph are vented from the instrument. See Figure 2. Changes in operating mode are accomplished by opening and closing valves--none of which is in a heated region.

After the primary separation is complete the system is switched to the "secondary separation" mode and the cold trap is heated to transfer its contents into the secondary chromatograph. See Fig. 3. The secondary chromatograph can contain any high resolution capillary which is compatible with mass spectrometer operation. For the case of 2,3,7,8-TCDF analysis, this chromatograph is fitted with a capillary system which has been described previously. (J. Chromatogr., 294 (1984) 87). This capillary combination was arrived at using the method of Krupcik et al (J. Chromatogr., 213 (1981) 189. The computer model of the separation is shown in Fig. 4. This capillary combination provides baseline resolution of 2,3,7,8-TCDF from all isomers which co-elute from the secondary column. Using this system full baseline separation of 23478 and 123789 from their isomers has also been obtained using various secondary capillaries.

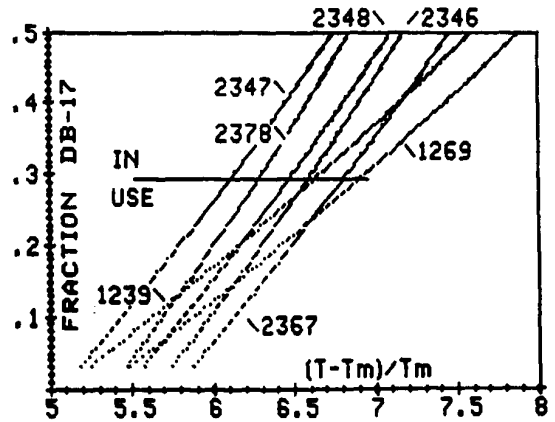

Figure 4. Predicted separations for 7 TCDF isomers using the (DB-17)-(SP2330) capillary system as determined by computer modeling employing the Krupcik equations.

A typical quantitative analysis for a chlorodibenzofuran starts with addition of a labeled internal standard to the sample. At GE standards have been prepared which are 99 atom-% ^{13}C (R. A Bell and A. Gara). Full mass spectra of the standards have been recorded in order to compare them with analogous spectra of the un-labeled materials. It was found that the %-total ionization for the molecular ion and its isotopomers was the same for the labeled and unlabeled materials. Therefore no correction is applied for enrichment errors or isotopic effects on fragmentation.

After addition of appropriate standards, samples are either analyzed by direct injection into the primary chromatograph or are subjected to a modified Stalling clean-up procedure. Arochlors up to 1242 can be analyzed directly by injection of about 2 mg of Arochlor. Flyash extracts and IOC oil have also been analyzed successfully in this way. Larger Arochlors, fish, sediment, etc. require the Stalling procedure.

The sample is co-injected with a retention index marker which elutes from the primary chromatograph just ahead of the component of interest. Collection of the component of interest is accomplished relative to this marker. After the primary chromatogram is complete the system is switched to the secondary separation mode and the cold trap is heated. The components eluting from the secondary chromatograph are carried directly into the electron beam of the mass spectrometer ion source using a section of fused silica capillary.

The mass spectrometer operating conditions are as follows:

Mass Spectrometer: Vg Zab
Ionization: Electron Impact
Resolution (10% Valley): 3000
Acquisition by Selected Ion Monitoring:
e.g. for 2,3,7,8-TCDF ions at 304,306,308,316,318, 320 and 328 are monitored using voltage switching. Mass 328 is generated as a lock mass signal using 4,4'diaminooctafluorobiphenyl added at a very low level from a heated inlet. The lock mass signal is monitored in full profile mode.
Great care is taken to ensure that ion source focusing does not change with voltage switching. Very minor source contamination can cause this effect in the Vg Zab.
Great care is taken to ensure that interfering materials do not co-elute with the lock mass thereby shifting its centroid and causing systematic errors in mass selection.
No data is accepted which does not show the theoretical distribution of intensities for the isotopomers of the respective molecular ions.

MONS 018536

PCDF ISOMERS AND ISOMER LEVELS FOUND IN PCBs

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EXPERIMENTAL

We have developed a new clean-up technique for the determination of PCDFs in PCBs.

1. Dissolve PCB in CH_2Cl_2/c-hexane.
2. Add surrogate.
3. Column Carbon PX 21 on fibers.
4. Reverse elution by toluene.
5. Evaporate toluene, 35°C, 20 mm Hg.
6. Dissolve in n-hexane.
7. Fluorosil column.
8. Reverse elution CH_2Cl_2.
9. Evaporate, add known amount final solvent.
10. Inject 1-2 µl in HRGC/MS using a 60 m fused silica SP 2330 column. The temperature program allows isomer specific analyses. The MS instrument is operating with EI or NCI (methane), SIM.
11. Quantification of 2,3,7,8-substituted isomers as well as total levels of PCDFs.
12. Calculation of recovery of surrogates.

RESULTS

We have analyzed a series of commercial PCB products and the results are given in Table 1.

MONS 018537

DISCUSSION

We have found contamination by PCDFs in all PCB products analyzed. The total level of PCDFs varied from a few ug/g up to 40 ug/g. The chlorination pattern of the PCDFs was found to vary with the chlorination level of the PCBs.

Discussing individual isomers, the toxic 2,3,7,8-substituted Cl_4-, Cl_5- and Cl_6 PCDFs were always middle or major constituents within each group of congeners.

The 2,3,7,8- and 2,3,4,8-tetra-CDFs are eluting very close together. The toxic effect of these two isomers is very different. The ratio of these two isomers was found to vary from 10:1 to 1:10. For a risk evaluation it is essential to have an analytical method where it is possible to separate between these two isomers (see Figure 1).

MONS 018538

Table 1. PCDFs in commercial PCBs.

PCB-typ	TRI- Tot	TETRA- 2378	Tot	PENTA- 12348 12378	23478	Tot	HEXA- 123479 123478	123678	123789	234678	Tot	HEPTA- Tot	Rec 2378 TCDD-%
Pyralene	700	53	630	10	T	35	ND	ND	ND	ND	ND	ND	79
A1254	63	19	1400	690	490	4000	2500	2100	190	130	10000	960	78
A1260	10	13	110	48	56	260	500	120	190	27	1500	1300	88
A30	500	35	573	14	28	160	50	59	ND	ND	220	T	79
A40	1300	180	2600	96	8	1700	79	68	ND	T	310	ND	79
A50	7400	3300	20000	760	1100	8000	700	360	18	98	3100	75	95
A60	770	840	6900	1100	990	8100	1600	330	170	330	6800	2000	95
T64	47	23	360	97	122	840	520	390	58	41	2600	220	72
Clophen C	710	54	1200	34	30	270	ND	T	ND	ND	T	ND	79
Blank	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	90
Blank	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	87

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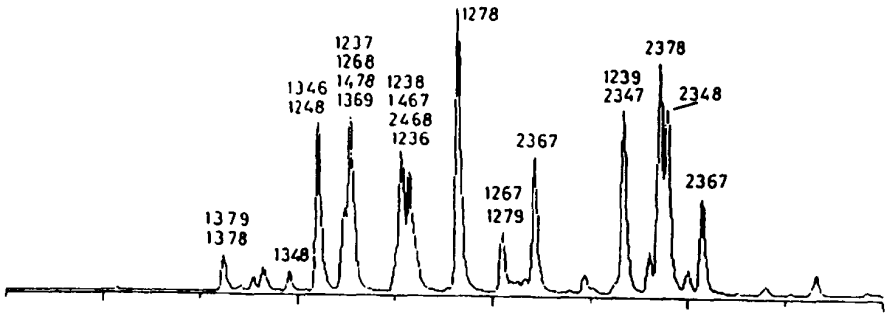
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MONS 018540

PART 3:

PYROLYSIS AND COMBUSTION

MARCUS COOKE - MODERATOR

MONS 018541

FORMATION OF POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS FROM BURNING OF SILICONE DIELECTRIC FLUID SPIKED WITH POLYCHLORINATED BIPHENYLS

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Wright State University

INTRODUCTION

Since 1982 Dow Corning Corporation has had a program of retrofilling PCB containing transformers, using its silicone fluid RetroSil™ process. The concerns over the combustion of PCB's has lead to the desire to better understand the by-products formed during the burning of silicone fluids containing small amounts of PCB's which may remain after the RetroSil™ process. Thus a contract to study this matter was initiated with the Brahm Laboratory of Wright State University under the direction of Dr. Thomas O. Tiernan.

The study had 2 objectives. One was to determine amounts and species of polychlorinated dibenzodioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) formed, when a silicone fluid spiked with various levels of PCB was pyrolyzed. In addition, the effect of pyrolysis temperature on this same system was to be evaluated. This paper discusses the results of these studies.

METHODOLOGY

All spiked samples were prepared at Dow Corning. Burning studies were conducted at the Brahm Laboratory, at Wright State University under the direction of Dr. Thomas Tiernan. Samples of 50 centistoke polydimethylsiloxane (DOW CORNING® 561 Fluid) were spiked with 5, 50, 500 and 11,300 ppm of PCB from Arochlor 1260. The 11,300 ppm sample was initially studied at 4 different temperatures to determine which temperature produced the maximum amount of PCDD's and PCDF's. This was determined to be 600°C. Then the samples spiked with various amounts of PCB were burned in air at this temperature and the by-products analyzed.

MONS 018542

The burning apparatus is shown in Figure I. It consisted of a high temperature tube furnace containing a quartz tube reactor, a cooled sample injection system and a series of three traps to collect the volatile combustion products. Five ml. of sample were used for each test with an average residence time in the burning zone of two seconds. Table I summarizes the weights of the combustion products based upon the 5 ml (4.7 g.) sample injected. The combustion products include any water produced in the burning reaction. Thus the total weight of the combustion products could, and indeed did, at times exceed the amount of sample injected.

Preparation of the pyrolysis products for analysis consisted of soxhlet extraction in toluene for 16 hours and a series of washing steps using KOH, H_2SO_4 and anhydrous sodium sulfate, concluding with a hexane elution through a column packed with silica, and then concentrated by evaporation of the hexane. This was then transferred to a laboratory prepared liquid chromatography column packed with Woelm basic alumina which was previously activated at 600°C. After conducting a series of methylene chloride/hexane elutions, the samples were evaporated to dryness and stored in a freezer until analysis. These samples were then reconstituted by adding tridecane before injection of the appropriate aliquot into the analytical test instrument.

Analyses of the extract were done using a Perkin Elmer Sigma III Gas Chromatograph coupled through a custom fabricated interface including a single-stage glass jet separator to a Kratos MS-25 Mass Spectrometer equipped with a DS-50SM Data System.

RESULTS OF ANALYSES

The results of the analyses of the combustion products from the burning tests for chlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs) are summarized in Tables II and III. Also shown are the results of analyses of a method blank, of a sample of polydimethylsiloxane containing 11,300 ppm of PCBs (which was not pyrolyzed), and a sample of the polydimethylsiloxane containing 130 ppm PCB which had been previously subjected to electrical arcing.

As can be seen from the data presented in Table II, the initial series of tests, in which samples of polydimethylsiloxane fluid containing 11,300 ppm of PCBs were burned at temperatures of 400°C, 600°C, 800°C and 1000°C respectively, revealed that chlorinated dibenzofuran was formed in the 400° and 600° tests. In particular, the tetra-, penta- and hexa-CDFs were produced at these temperatures. All data is presented in the concentration of total CDD & CDFs in nanograms/gram of total combustion products or Parts Per Billion. Minimum Detectable Concentrations are given in parentheses. While the presence of several isomers of each of these chlorinated classes can be discerned from the mass chromatograms obtained in the analyses, it is noteworthy that the tetra-CDFs appear to include 2, 3, 7, 8-TCDF (or at least a TCDF isomer which coelutes with the 2, 3, 7, 8-TCDF). No CDDs other than OCDD were detected in the combustion products from any of these initial tests. There were essentially no detectable CDFs in the products from the 800°C and 1000°C burning tests.

It was clear from the initial series of tests that the quantities of CDFs produced from burning of the PCB-contaminated silicone fluid were greater when the temperature was 600°C. After these results had been reported to Dow Corning and reviewed, the Brahm Laboratory was requested to conduct several additional tests in which each of three samples of the silicone fluid containing 500 ppm, 50 ppm and 5 ppm, respectively, of PCBs, were to be burned at a temperature of 600°C. The results of analyzing the combustion products from these tests for CDDs/CDFs are shown in Table III. As these data indicate, tetra-, penta- and hexa-CDFs were detected in all of these combustion products, although the quantities of these CDFs were clearly directly related to the concentration of PCBs in the fluid pyrolyzed. That is, the greater the concentration of PCBs in the field, the greater the concentrations of CDFs in the pyrolysis products. This trend is, of course, as expected if the PCBs are the precursors of the CDFs which are formed in the combustion process. Table III also shows that the second series of tests found no CDDs (except some OCDD, which may be questionable) when the silicone fluids containing 500, 50 and 5 ppm of PCBs were pyrolyzed.

The analytical results obtained for the polydimethylsiloxane fluid containing 11,300 ppm PCBs which was not pyrolyzed, as well as for the fluid sample containing PCBs which had been previously subjected to electrical arcing, indicate

MONS 018544

that these samples contain essentially no detectable CDDs/CDFs. It will be noted that the detection limits reported for these samples are for the fluid samples themselves (and not for combustion products), since these samples were not pyrolyzed.

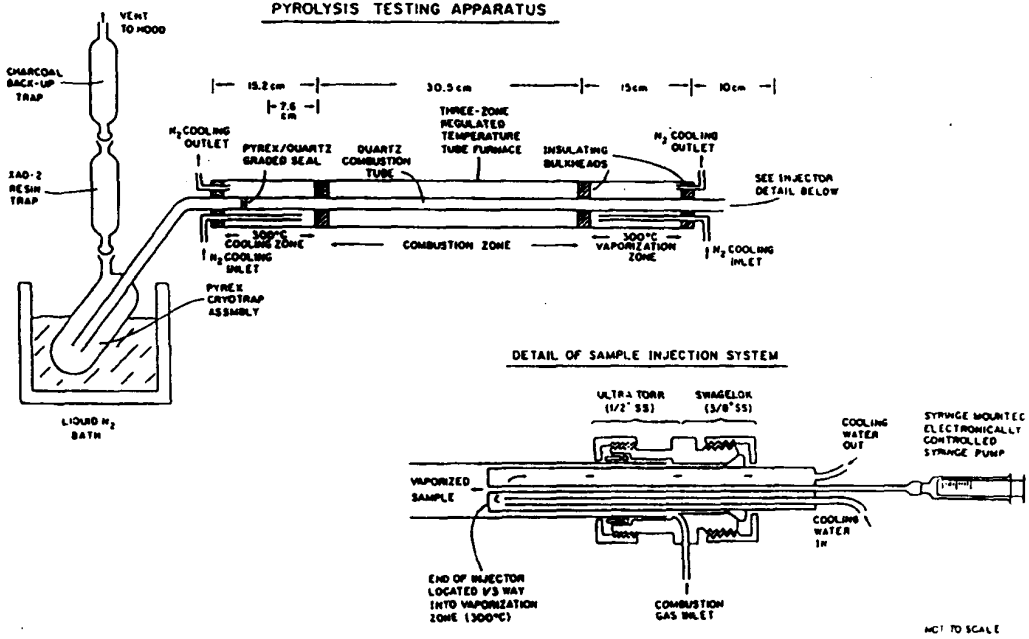
CONCLUSION

Burning studies of polydimethylsiloxane spiked with various levels of PCB show that no polychlorinated dibenzo-p-dioxins are detected but that tetra, penta and hexa species of chlorinated dibenzofurans are detected.

A sample of PCB spiked polydimethylsiloxane fluid which had been subject to electrical arcing showed no detectable PCDD's or PCDF's formed.

Maximum formation of PCDF's appeared to occur at 600°C.

MONS 018545



APPARATUS FOR TESTING PYROLYSES OF SELECTED CHEMICALS FOR PRODUCTION OF CDDs/CDFs

Figure 1.

MONS 018546

TABLE I

WEIGHTS OF COMBUSTION PRODUCTS FORMED FROM PYROLYSIS OF POLY DIMETHYLSILOXANE FLUIDS CONTAINING POLYCHLORINATED BIPHENYLS[a]

PCB Level (ppm)	Burning Temperature	Total Weight of Combustion Products (grams)
11,300	400°C	4.6
11,300	600°C	5.3
11,300	800°C	4.6
11,300	1000°C	5.1
500	600°C	4.6
50	600°C	4.6
5	600°C	4.5

a. In each experiment, 5.0 mL of the silicone fluid were burned. Since the density of the fluid is 0.9428 g/mL, 4.7 g. of fluid were pyrolyzed in each case. The combustion products include any water produced in the pyrolysis reaction, as well as incompletely pyrolyzed fluid in cases where combustion was not complete (lower temperatures).

MONS 018547

TABLE II

THE EFFECT OF TEMPERATURE ON THE PYROLYSIS PRODUCTS OF PDMS SPIKED WITH 11,300 ppm PCB
(Data in parts per billion)

Burning Internal Temp.	TCDFs	TCDDs	Recovery of $^{37}Cl_4$-2,3,7,8-TCDD Internal Standard	PCDFs	PCDDs	HxCDFs	HxCDDs	HpCDFs	HpCDDs	Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8- HpCDD Internal Standard	OCDF	OCDD	Recovery $^{13}C_{12}$-OCDD Standard
Method Blank	N.D. (0.10)	N.D. (0.05)	54%	N.D. (0.20)	N.D. (0.20)	N.D. (0.40)	N.D. (0.30)	N.D. (0.20)	N.D. (0.20)	41%	N.D. (0.40)	N.D. (0.10)	56%
Not Pyrolyzed	N.D. (0.10)	N.D. (0.45)	61%	N.D. (2.0)	N.D. (2.0)	N.D. (2.5)	N.D. (2.5)	N.D. (2.5)	N.D. (2.5)	62%	N.D. (2.5)	N.D. (14)	48%
400°C	3,670	N.D. (2.5)	78%	1,260	N.D. (17)	1,600	N.D. (10)	N.D. (7.5)	N.D. (7.5)	51%	N.D. (44)	10	41%
600°C	46,235	N.D. (24)	68%	11,500	N.D. (20)	3,600	N.D. (10)	N.D. (10)	N.D. (10)	82%	N.D. (30)	8.0	81%
800°C	N.D. (4.0)	N.D. (4.0)	50%	N.D. (5.0)	N.D. (10)	N.D. (25)	N.D. (15)	N.D. (5.0)	N.D. (5.0)	84%	N.D. (42)	N.D. (10)	81%
1000°C	N.D. (2.0)	N.D. (2.0)	73%	N.D. (10)	N.D. (10)	N.D. (20)	N.D. (20)	N.D. (10)	N.D. (5.0)	59%	N.D. (44)	12	45%

MONS 018548

TABLE III

PYROLYSIS PRODUCTS OF PDMS SPIKED WITH VARIOUS CONCENTRATIONS OF PCB
(Data in parts per billion)

PCB Level (ppm)	Burning Temp.	TCDFs	TCDDs	Recovery of $^{37}Cl_4$-2,3,7,8-TCDD Internal Standard	PCDFs	PCDDs	HxCDFs	HxCDDs	HpCDFs	HpCDDs	Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8- HpCDD Internal Standard
11,300	600°C	46,235	N.D. (24)	68%	11,500	N.D. (20)	3600	N.D. (10)	N.D. (10)	N.D. (10)	82%
500	600°C	2,778	N.D. (7.0)	60%	450	N.D. (15)	142	N.D. (15)	N.D. (10)	N.D. (10)	100%
50	600°C	138	N.D. (4.0)	59%	12	N.D. (4.0)	N.D. (30)	N.D. (30)	N.D. (10)	N.D. (10)	86%
5	600°C	12	N.D. (5.0)	63%	2.0	N.D. (4.0)	N.D. (10)	N.D. (10)	N.D. (10)	N.D. (10)	71%
Arced	Not Pyro-lysed	N.D. (12)	N.D. (20)	53%	N.D. (4.0)	N.D. (10)	N.D. (25)	N.D. (25)	N.D. (12)	N.D. (12)	17%

MDNS 018549

SIMULATED BUILDING FIRE STUDY
USING RETROFILLED TRANSFORMER DIELECTRIC COOLANT

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ABSTRACT

In this program a model combustion system was built in the Battelle pilot plant facility. The unit was a 40,000 Btu per hour vertically fired tube furnace with a combustion zone 4.3 ft (131 cm) in length with a 5.5 in. internal diameter (14 cm). A schematic diagram of the combustion system used in this study is shown in Figure 1. The combustion experiments were designed to produce conditions favorable for production of polychlorinated dibenzofuran (PCDF) and polychlorinated dibenzo-p-dioxin (PCDD).

MONS 018550

PROJECT SUMMARY

The tests were conducted using kerosine with 1% (w/w) silicone coolant added to generate condensation nuclei for catalytic production of PCDF/PCDD. The kerosine-silicone mix was injected through the primary injection port. The test dielectric liquids were atomized and sprayed into the near flame region of the combustor where contact temperatures of 700-900 C were obtained at the point of injection. The dielectric fluid was injected through the secondary injection port, resulting in an opposed flame condition. The primary-secondary injection ratio was approximately 2 to 1 for all tests. Test conditions were maintained to produce a combustion gas oxygen concentration of 3 to 5 volume percent.

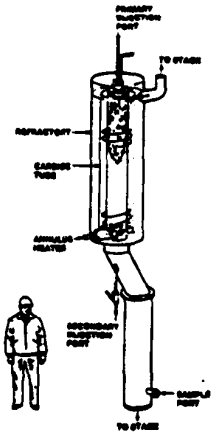

FIGURE 1

SCHEMATIC DRAWING OF THE COMBUSTION TEST APPARATUS

Prior to injecting the dielectric fluid, the combustion gas oxygen concentration was approximately 8 to 9 percent. Hence the dielectric fluid was injected into a high temperature, oxygen deficient environment similar to that expected in an uncontrolled fire. Samples were collected by EPA Modified Method 5 train sampling (MM5).

MONS 018551

The test liquids were simulated retrofill dielectric fluids with 50 ppm (w/w) Aroclor, and residual tri/tetrachlorobenzene (TCB/TTCB) diluents, in a liquid silicone solution. Three Aroclors 1260, Aroclor 1254, Aroclor 1242, TCB/TTCB bland,and a blank with silicone only were combusted.

Samples were extracted by Battelle (BCL), and submitted to three participating laboratories; the University of Umea (Umea), Oneida Research Services (ORS), and BCL, for blind analysis of PCDF/PCDD. Each laboratory used their standard preparation and analysis procedures. Battelle and Oneida used high resolution mass spectrometry(HRMS), while the University of Umea used a quadrupole mass spectrometer (QMS), for analyte detection. All three laboratories used high resolution capillary gas chromatography(HRGCC). The three laboratories split the same samples while preforming blind analyses. This independently verified results and showed the variability in reported data. An illustrative chromatogram of a total ion mass spectrum (TIMS) from the Aroclor 1254 burn is given in Figure 2.

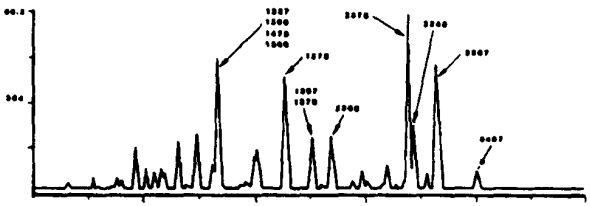

FIGURE 2

AROCLOR 1254 PRODUCT TIMS CHROMATOGRAM (COURTESY OF C. RAPPE)

Umea and ORS analyzed all furan and dioxin congener classes for four to eight chlorine substitution (tetra through octa isomers), and both laboratories reported the 2,3,7,8-tetrachlorodibenzo isomer concentretions for both the furan (2,3,7,8-TCDF) and dioxin (2,3,7,8-TCDD) classes. BCL analyzed and reported the tetra furan/dioxin congener concentrations, 2,3,7,8-TCDF, and 2,3,7,8-TCDD concentrations in the MM5 combustion samples. In addition Umea analyzed and reported the individual isomer concentrations of all tetra and penta isomers, of both furans and dioxins found in these samples.

MONS 018552

The three laboratories showed good agreement in overall results and found no detectable dioxin isomers in any congener class for the four tests reported; a system blank, the Aroclor 1260 test, the Aroclor 1254 test, the Aroclor 1242 test. The averages for the three laboratories reporting the four test burns are given below (PnCDF represents pentachlorodibenzoburans):

QUANTITIES PRODUCED
[ppb (w/w) dielectric consumed basis]

TEST	DOPANT	TCDF	2,3,7,8-TCDF	PnCDF
Blank	None	0.003	<0.002	ND
1	1260	0.43	<0.15	0.31
2	1254	0.38	<0.08	0.14
3	1242	0.08	<0.01	0.04

From these data the polychlorinated biphenyl (PCB) conversion rates were calculated. Conversion of Aroclor 1260 to TCDF ranged from 0.9 to 17 parts per million (ppm) on a weight basis. Conversions of Aroclor 1254 [4 - 11 ppm (w/w)] and Aroclor 1242 [2.4-2.6 ppm (w/w)] to TCDF gave similar values, and were consistent with pyrolysis conversion rates reported in the literature (1). Tri and tetrachlorobenzenes at concentrations up to 1.5% (w/w) in the silicone burned, were found to produce no measureable PCDD or PCDF.

In this study the measured furan concentrations produced by combustion of retrofill dielectric liquids tended to decrease as the degree of chlorination of the spiked PCB decreased. Aroclor 1260 spiked into silicone resulted in higher levels of PCDF than found in the experiment with Aroclor 1242. In all cases, the PCDF levels were extremely low (ppb) on a dielectric fluid consumed basis.

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MONS 018553

FORMATION OF PCOFs UNDER "OPTIMIZED" COMBUSTION CONDITIONS FROM LOW-LEVEL PCB DIELECTRIC FLUIDS

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The Environmental Protection Agency (EPA) issued a final rule on August 25, 1982, authorizing indefinite use of certain electrical transformers containing polychlorinated biphenyls (PCBs). This rule is known as the PCB Electrical Use Rule. At that time, information available to the EPA indicated that fires involving electrical transformers were rare, isolated incidents. However, several recent transformer fires in buildings have brought into question EPA's earlier assumption. The Agency has therefore issued an Advance Notice of Proposed Rulemaking (ANPR) (USEPA 1984a) and proposed rule (USEPA 1984b) to gather data on the specific risks posed by fires involving electrical transformers that contain PCBs and also on mechanisms for mitigating or eliminating these risks. Depending upon the results of EPA's analysis of these data, the Agency may propose further control measures on the use of this equipment.

This abstract describes the methods and results of a study, conducted in support of EPA's data gathering activities under the ANPR, of the potential for formation of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) from uncontrolled fires involving PCB-containing dielectric fluids.

At high temperatures, such as those in transformer fires, polychlorinated biphenyls (PCBs) react to form polychlorinated dibenzofurans (PCDFs) and other toxic by-products. The purpose of this study was to optimize conditions for PCDF formation in order to examine the potential for formation of PCDFs and polychlorinated dibenzodioxins (PCDDs) from combustion of selected PCB-containing dielectric fluids.

The study was conducted in three phases. In Phase 1, a bench-scale thermal destruction system, developed by MRI, was refitted with specific components installed to accommodate this study as shown in Figure 1. Then, a few test runs

MONS 018554

were made under preliminary temperature and oxygen conditions to ensure an acceptable system blank. The concentrations of CO, CO_2, and O_2 in the effluent were monitored continuously. The entire effluent from the thermal destruction system was passed through an XAD-2 trap to collect PCDFs and other semivolatile organics. The XAD-2 trap and a rinse of connective tubing were Soxhlet-extracted and cleaned using column chromatography to isolate the PCDFs and PCDDs. All samples were analyzed for PCDFs (and PCDDs in Phase 3), using high resolution (capillary) gas chromatography/electron impact mass spectrometry (HRGC/EIMS) in the selected ion monitoring (SIM) mode. No PCBs or PCDFs were detected in the Phase 1 samples.

The Phase 2 experiments were conducted to determine the optimum temperature, oxygen, and residence time conditions for PCDF formation. The feed into the system was mineral oil spiked with three individual PCB congeners which form PCDFs by the four known reaction mechanisms. A statistical analysis of the results for 33 runs indicates that both temperature and oxygen have significant effects on the PCDF yield and that the interaction between temperature and oxygen is synergistic. The results indicate that the optimum values are a temperature of 675°C and an excess oxygen concentration of 8%. The residence time did not significantly affect the yield in the range of 0.3 to 1.5 s, although lower times appeared to yield less PCDFs. Since residence time does not appear to significantly affect the PCDF formation, 0.8 s was chosen as convenient for the Phase 3 runs.

In Phase 3, duplicate test runs were conducted with mineral oil and silicone oil dielectric fluids containing PCBs (Aroclor 1254) at concentrations of 0, 5, 50 and 500 ppm. A PCB askarel containing 70% Aroclor 1260 and a non-PCB askarel, containing mostly trichlorobenzene with some tetrachlorobenzene, were also tested in duplicate. PCDFs were found in all samples, except blanks, as shown in Figure 2. PCDDs were found in the samples from the trichlorobenzene runs and occasionally at low levels in some of the other samples. Up to 5,700 ng total PCDFs/mL of spiked feed oil or 4% conversion efficiency (PCBs to PCDFs) was observed for the mineral oil and silicone oil runs. The PCB destruction efficiencies calculated for the 5, 50, and 500 ppm runs ranged from 79 to > 99%. Up to 19,000,000 ng total PCDFs/mL feed oil (19 mg/mL) or 3% conversion efficiency was observed for the askarel fluid. Statistical analysis showed a linear relationship for PCDFs formed versus the amount of PCBs (Figure 3). Although not statistically different, about twice the quantity of PCDFs was formed from PCBs in silicone oil than from the corresponding mineral oil samples. All eight PCDF homologs were detected in the askarel runs with a maximum at the pentaCDF (Figure 4). With a few exceptions, only tri- through hexaCDFs were observed in the lower level runs, with a maximum generally at the triCDF homolog.

PCDFs and, to a lesser extent, PCDDs are formed from the trichlorobenzene dielectric fluid under the optimum PCB-to-PCDF conversion conditions. Up to > 110,000 ng total PCDFs/mL feed oil (> 0.004% yield) and 1,900 ng total PCDD/mL feed oil (0.0001% yield) were observed for the trichlorobenzene runs. The homolog distribution of PCDFs is similar to that found from feeding PCBs. The amount of PCDFs formed is one to two orders of magnitude lower than for the askarel, but substantially higher than that for dielectric fluid containing 500 ppm or less PCBs.

The results of this work indicate that the optimum conditions for PCDF formation from PCBs are near 675°C for 0.8 s or longer, with 8% excess oxygen. Under these

MONS 018555

conditions, PCDFs are formed from mineral oil or silicone oil contaminated with PCBs at 5 ppm or greater. PCDFs are also formed from a trichlorobenzene dielectric fluid which contained no detectable PCBs.

Further work is focusing on identification and quantitation of other products from combustion of these samples, and on running samples of other dielectric fluids, including paraffinic hydrocarbons, ester hydrocarbons, and tetrachloroethylene.

The work was supported by the U.S. Environmental Protection Agency under Contract No. 68-02-3938. A more detailed report was published as EPA Report No. 560/5-84-009.

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USEPA. 1984b. Polychlorinated biphenyls (PCBs); manufacture, processing, distribution in commerce and use prohibitions; use in electrical transformers. Proposed rule. (49 FR 39966-39989).

THERMAL COMBUSTION SYSTEM TO MODEL PCB FIRE CONDITIONS

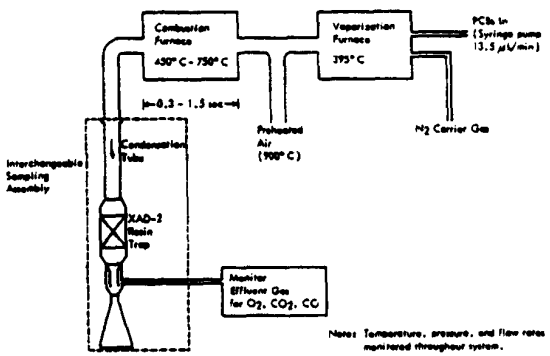

Figure 1

MONS 018556

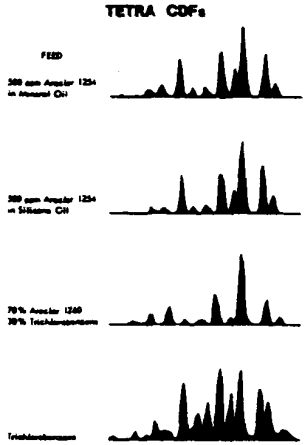

Figure 2. Tetrachlorodibenzofurans formed from various matrices. Note similar isomer distribution for the TCDFs formed from PCBs. Consistent patterns were noted for the other homologs.

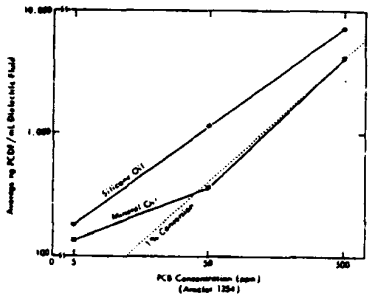

Figure 3

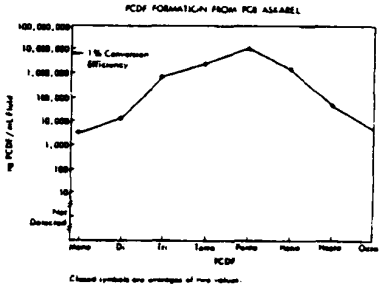

Figure 4

MDNS 018557

LABORATORY INVESTIGATION OF THE HIGH TEMPERATURE FORMATION AND DESTRUCTION OF PCDFs

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The formation of polychlorinated dibenzofurans (PCDFs) as a result of the thermal degradation of polychlorinated biphenyls (PCBs) has become an area of intense interest due to the reported toxicity of these partial oxidation products. Reports of their formation as a result of fires in PCB containing transformers, has caused the United States Environmental Protection Agency (US-EPA) to consider expanded regulations to reduce the risk of accidental combustion of PCB containing material.

Most previous studies of the formation of PCDFs have been concerned with the optimization of conditions for their formation from PCBs. In this study, we have investigated the effect of temperature and oxygen concentration on the rate of formation and destruction of PCDFs as well as the thermal stability of the parent PCB. Additional objectives were to identify other degradation products and provide some information to elucidate the mechanism of PCB destruction and PCDF formation in a flow reactor system.

The thermal degradation of a single PCB isomer was conducted under four reaction atmospheres at a constant gas phase residence time of 2.0 seconds. The isomer selected for study was 2,3',4,4',5-pentachlorobiphenyl (2,3',4,4',5-PCB). The oxygen availability in the reaction atmosphere is described using the equivalence ratio, phi. Phi is defined as the ratio of fuel to oxygen actually in the reactor divided by the ratio of fuel to oxygen required for complete combustion. The values of phi used in this study were 3.0, 1.0, 0.2, and 0.05 which range from oxygen starved to very oxygen rich conditions as the values of phi become progressively smaller. A phi of 1.0 means there is exactly enough oxygen available for complete combustion; thus, the percent excess air is zero. Thermal degradation experiments were conducted at various temperatures ranging from 500-1000C.

The thermal decomposition profiles and reaction products were determined using the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) system and the Thermal Decomposition Analytical System (TDAS). Both pieces of laboratory instrumentation are closed continuous systems that contain a narrow-bore quartz tubular reactor which is capable of subjecting gaseous species to controlled thermal exposures with precise control of residence time and other reaction variables. Mixtures of oxygen and nitrogen were used to obtain the various reaction atmospheres tested in this study. A 40ug sample of 2,3',4,4',5-PCB was used in all experiments.

Following thermal exposure, the remaining parent material and the various thermal reaction products were cryogenically trapped. The numerous trapped samples were subjected to in-line chromatographic analysis using a capillary column, 15 m length by 0.25 mm ID and possessing a 0.25 micron DB-5 film thickness. On the TDU-GC, a hydrogen flame ionization detector was used for detection of the various solutes, and the data were processed and displayed using a Varian CDS 401 chromatographic terminal. The identities of the thermal reaction products from the decomposition of the PCB were tentatively determined from their electron impact ionization mass spectra obtained on the TDAS which incorporates an LKB 2091 GC/MS. The reaction products examined were generated from the degradation of the PCB at 800C and phi = 0.2. Sample handling and chromatographic conditions were the same as those used for the TDU-GC testing.

Table 1 lists the major thermal reaction products tentatively identified for the thermal degradation of 2,3',4,4',5-PCB. A variety of pyrolysis and partial oxidation products have been formed, with PCDF congeners representing the majority of the oxidative products. Significant quantities of partially dechlorinated biphenyl congeners are formed along with dichlorobenzenes and trichlorobenzenes. Tetrachlorobiphenylene isomers were also observed. These are of particular interest due to their suspected toxicity. The formation of tetrachloronapthalene is important because of its apparent thermal stability. At 1000C for phi = 1.0, the reaction product tentatively identified as tetrachloronapthalene exceeded the concentration of the parent PCB. As one might expect, the yield of pyrolysis products decreased with increasing oxygen levels. However, the increase in PCDF concentration with increase in oxygen concentration was far more striking.

Table 2 presents the yields of observed PCDFs at various equivalence ratios. As the oxygen concentration increased by a factor of 60, the yield of total PCDFs increased by a factor of 10. The percentage of total PCDFs identified as tetra isomers ranged from 62-72%. Thermal formation/destruction profiles for observed PCDFs for phi=1.0 are depicted in Figure 1.

MONS 018559

TABLE 1

MAJOR THERMAL REACTION PRODUCTS TENTATIVELY IDENTIFIED FROM THE THERMAL DEGRADATION OF 2,3',4,4',5-PENTACHLOROBIPHENYL

Product Class	Number of Major Peaks
Tetrachlorodibenzofurans	2
Trichlorodibenzofurans	2
Pentachlorodibenzofurans	1
Tetrachlorobiphenyls	5
Trichlorobiphenyl	1
Trichlorobenzene	1
Dichlorobenzene	1
Trichloronaphthalene	1
Tetrachloronaphthalene	1
Trichlorophenylethyne	2
Dichlorophenylethyne	1
Tetrachlorobiphenylenes	2
C_9H_8OCl	1
$C_{10}H_3Cl_3$	1

TABLE 2

MAXIMUM WEIGHT % YIELD OF PCDFs AS A FUNCTION OF REACTION ATMOSPHERE

ϕ	TEMPERATURE OF MAXIMUM YIELD (C)	WEIGHT % YIELD			
		TRI-CDFS	TETRA-CDFS	PENTA-CDFS	TOTAL-PCDFS
0.05	750	0.66	4.3	2.0	6.9
0.2	800	0.34	1.7	0.56	2.6
1.0	900	0.13	1.3	0.25	1.7
3.0	850	0.068	0.71	0.21	0.99

The relative yields predicted for PCDF isomer production may be estimated by examination of the reaction enthalpies for the global reactions. Calculations reveal that an overall reaction involving elimination of a hydrogen atom and a chlorine atom from ortho positions to form either 2,3,7,8-TCDF or 2,3,6,7-TCDF and HCl, has a reaction enthalpy of -29.7 kcal/mole. Elimination of ortho hydrogens to form either 1,3,4,6,7-PCDF or 1,3,4,7,8-PCDF and H_2 has a reaction enthalpy of -14.2 kcal/mole. Using these values as a "zeroth" order approach to the reaction kinetics of PCDF formation, one would predict that the two tetra isomers would be the predominant reaction products. Two major TCDF peaks were, in fact, observed that accounted for 60-70% of the total PCDF formation. Further isomer specific identification work is strongly indicated.

MONS 018560

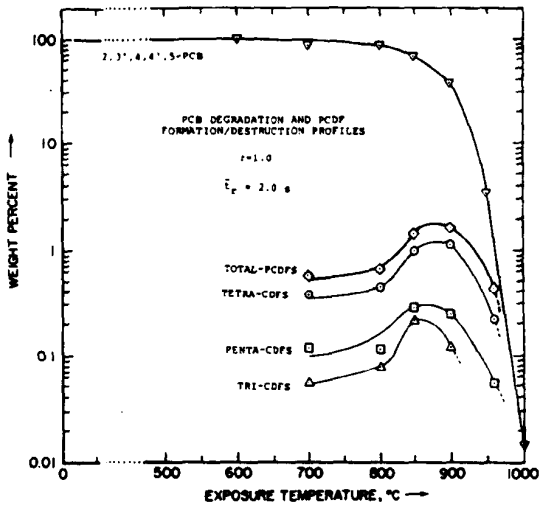

Figure 1. PCDF Formation/Destruction Profiles

In summary, the results of this study show that the yields of PCDFs formed from the thermal degradation of 2,3',4,4',5-PCB are on the order of a few percent; and these yields increase as the oxygen concentration increases (ϕ=3.0→ϕ=0.05). The predominant mechanism for their formation is HCl elimination. For equivalent combustion conditions, it appears that PCDFs <u>can</u> be destroyed at temperatures that are sufficient to destroy the parent PCB. However, there is evidence for formation of pyrolysis products such as tetrachlorobiphenylenes and chlorinated polynuclear aromatics that are major reaction products at very high temperatures.

This work was performed under partial sponsorship by the US-EPA under Cooperative Agreement CR-810783 and has not been subjected to the Agency's peer review process.

MONS 018561

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RP-2028-11

PRODUCTS OF INCOMPLETE COMBUSTION OF DIELECTRIC FLUIDS

BY

DR. C. CLAIR CLAIBORNE

INTRODUCTION

Increasing publicity concerning transformer related fires and the resulting public concern over the hazards associated with these fires has prompted governmental action. The Environmental Protection Agency (EPA) consequently issued a request for information as a first step in promulgating a rule concerning transformer fires (1).

Although this rule is primarily directed at transformers which may contain some PCB's, there have been instances such as the BART tunnel fire in San Francisco and the underground fire in New York City in which partial combustion products of mineral oil were suspected of harmful interactions. The growing public concern over combustion products from plastic seat cushions, plumbing materials and other commonly encountered items will likely expand to include electrical insulating materials.

In the advance notice of proposed rulemaking mentioned above, the EPA requested information on the partial and complete combustion products of several transformer insulating materials. The fluids identified were chlorinated hydrocarbons, fluorocarbons, high temperature hydrocarbons, non-PCB askarels, mineral oil, and silicones. Although some information is available on the products of complete combustion, i.e., with an excess of oxygen present, data is lacking on the products of partial combustion. In many fires, partial or incomplete combustion may be the predominant mode of combustion.

When fires occur in confined areas such as a building, tunnel, or vault, the flow of air may be limited or restricted while the rate of burning may be so rapid that the oxygen is consumed faster than it can be replaced. This may result in the formation of many toxic substances such as carbon monoxide, hydrogen cyanide, hydrogen chloride, halogens, or carcinogenic organic compounds.

The objective of the project described in this report was to examine the products formed from either complete or partial combustion of fluids commonly used as dielectric materials, particularly in transformer applications.

MONS 018562

EXPERIMENTAL

Five liquids were selected for evaluation in this program: Tetrachloroethylene (C_2Cl_4), trifluorotrichloroethane ($C_2Cl_3F_3$), polydimethylsiloxane, a mineral oil, and a high temperature hydrocarbon. The particular tradenames of these materials are, respectively: WECOSOL*, Freon 113, Dow Corning 561 Silicone Transformer Liquid, Wemco C, and RTEmp.

In order to characterize the reacting materials in the mixed compounds, mineral oil and the high temperature hydrocarbon, high performance liquid chromatography was carried out on a Dupont 850 liquid chromatograph. The best separations were achieved for Wemco C utilizing gradient elution with methanol and water; for RTEmp, with tetrahydrofuran (THF) and methanol in the gradient elution mode.

To establish boundary levels of likely products of partial combustion to be found in analytical investigations, thermodynamic equilibrium concentrations were calculated from 300 to 1500 K (27° to 1227°C) at 100° intervals for each of the fluids mixed with 20% and 80% air by volume. For C_2Cl_4, calculations with 1% H_2O were also made to approximate atmospheric conditions and evaluate the potential for formation of HCl. These calculations were performed on a main frame computer and the major species of interest were displayed in semilog plots.

Two experimental arrangements were selected to evaluate the combustion process and the resulting products. In the Materials and Manufacturing Technology facilities, the combustion was carried out in Dupont thermogravimetric analysis (TGA) equipment. The material to be investigated was placed in a platinum boat and dry air was admitted to the combustion chamber at a controlled rate in order to achieve the desired levels of 30% and 70% of the air that would be required for theoretical total combustion. The instrument was then programmed to heat the combustion chamber from room temperature to 1000°C at 30°/min. A trap containing ice water was located at the exit of the chamber, in order to contain the reacting material in the combustion chamber. The combustion products were collected in cold traps placed in two separate Dewar flasks, containing a mixture of dry-ice and isopropanol (-90°C), on the one hand, and methyl butane and liquid nitrogen (-160°C), on the other hand. The materials collected in each of these traps were analyzed by gas chromatography.

The other experimental arrangement was located at the Research and Development

MONS 018563

Laboratories of Westinghouse. This apparatus consisted of a stainless steel tube which was heated to 1000°C. The reactant was then admitted to the tube. The amount of material injected into the preheated tube was varied in order to achieve the desired levels of 30% and 70% of the air required for theoretical total combustion. The combustion products were then withdrawn with a microliter syringe and injected into a Hewelett Packard 5935 GC-MS (gas chromatography-mass spectrometry) system for analysis. (* Westinghouse trademark)

RESULTS:

The decomposition of C_2Cl_4 at 1000°C in varying levels of air generated substantial quantities of Cl_2 and CO_2. Phosgene was not detectable either by gas chromatography or mass spectrometry. These results are consistent with the thermodynamic predictions. In the Materials and Manufacturing Technology Department apparatus, a small amount of HCl was found. The HCl was likely produced from sorbed water on the interior surfaces of the combustion apparatus, because this system is heated from ambient temperatures.

The silicone fluid generated copious amounts of SiO_2 which tended to plug the tubing leading to the traps, thereby influencing the capture of the product gases. Aside from CO_2, the products of the decomposition were methane, carbon monoxide, and water, on the order of 1% by volume, with amounts of ethylene, acetylene, and ethane between 0.01 and 0.1% by volume.

Tentative results from partial combustion of $C_2Cl_3F_3$, indicated six compounds separable by gas chromatography, besides CO_2. The thermodynamic calculations indicated that likely products of the decomposition of $C_2Cl_3F_3$ would be CF_4, Cl_2, COF_2, CO, $CClF_3$, and phosgene. However, the identification of these compounds will necessitate confirmation by mass spectrometry, as some of these materials are not readily available as standards.

The determination of the combustion products of the mineral oils is currently underway, and will be reported at a later date.

REFERENCES:

1. Federal Register, March 23, 1984, Page 11070.

MONS 018564

PYROLYSIS AND COMBUSTION OF MINERAL OIL, TETRACHLOROETHYLENE AND SILICONE OIL MIXTURES CONTAINING AROCLOR 1254

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This laboratory has initiated, with Electric Power Research Institute support, a major study of the tendency of various fluids, either neat or contaminated with Aroclor 1254, to form polychlorinated dibenzofurens (PCDFs) and polychlorinated dibenzodioxins (PCDDs) when subjected to high temperatures. Although a broad range of fluids of potential or current use as dielectrics will eventually be studied, this report presents preliminary data obtained from studies of mineral oil, tetrachloroethylene, and silicone oil during pyrolysis and combustion.

For purposes of this work, two distinct heating regimens were studied. Samples were either pyrolyzed (heated in the absence of a flame) or combusted (either injected into a flame or heated under conditions resulting in self-ignition). Pyrolyses were conducted using a simple thermostatically controlled apparatus, capable of accommodating glass or quartz tubes of diameters up to 6 cm within its 9 cm-long heated region. In order to minimize hazards and disposal problems, yet permit sufficient product formation to facilitate detection of PCDDs and PCDFs, pyrolyses were performed on 100 ul samples. In an attempt to differentiate this work from other earlier and ongoing investigations, as well as to simulate more accurately certain catastrophic incidents, pyrolyses were conducted at atmospheric pressure. The necessity of containing the starting materials and non-gaseous pyrolysis products in an open system led to the use of 8 mm ID x 0.5 M glass tubes, sealed at one end, and mounted vertically. The material to be pyrolyzed was deposited at the sealed end, then inserted into a tight-fitting preheated metal block in the heating apparatus. Typically, the liquid refluxed up the inner walls of the tube; the length of the tube and its comparatively large unheated volume kept the reflux level well below the open end in all experiments. To assure containment, the topmost 5 cm of the tube were chilled in dry ice and the end of the tube was connected to a charcoal trap. No visible material was trapped in the chilled region and excellent mass balances were generally observed.

MONS 018565

The design of the combustion apparatus was constrained by the necessity of assuring that all discharged gases pass through a trapping system capable of efficient removal of PCBs and any potentially toxic products. The combustion chamber consists of a 1 M quartz tube with a 22 mm i.d. One end of the chamber accommodates a modified blast burner and inlet tube through which the end of a 1/16" x 24" syringe needle is introduced via airtight connections. The inlet tube and needle are mounted to allow sample introduction into the flame of the blast burner. Sample addition is accomplished using a 10 ml syringe mounted in a worm syringe drive. The combustion chamber is mounted in a pyrolysis furnace capable of maintaining temperatures of 100 - 1100°C in three independently controlled zones. The effluent of the combustion chamber is passed through a water filled impinger, then an XAD-2 packed adsorbent tube which in turn is attached through an orifice to a vacuum line. XAD-2 has been shown here and elsewhere to be an efficient trapping agent for dibenzofurans and dibenzodioxins.

Preliminary experiments to refine experimental apparatus, to develop necessary techniques and to optimize reaction conditions were conducted using single biphenyl congeners. This approach minimized exposure of laboratory personnel to potentially dangerous materials and simplified analytical procedures. It was anticipated that capillary GC/FID or GC/EC would permit quantitation of the one or a few PCDF congeners produced in such reactions. This expectation was realized with one exception; pyrolysis of mineral oil, even in the absence of biphenyls, produces a very complex mixture. Despite elaborate sample cleanup, reliable data could not be produced without resort to GC/MS techniques.

Before discussing results and interpretations it should be emphasized that these studies are on-going and substantial data remains to be gathered. Further, data interpretation is complicated by the nature of the atmospheric pressure pyrolysis experiment. Thus, actual temperatures inside the pyrolysis apparatus in the heated zone are not well defined, since the reflux process may provide an efficient heat-transfer mechanism. Further, the fraction of a particular biphenyl congener in the heated zone versus the fraction in the cooler reflux region will be a complex function of that congener's physical properties, and those of the other constituents of the bulk liquid.

Aroclor 1254 has been pyrolyzed neat, and as 5,000 and 50 ppm mineral oil solutions at 500°, 550°, and 600°C, and the extracts analyzed for tetra and penta CDFs using high resolution GC/MS. Pyrolysis of the 50 ppm mixture gave concentrations

MONS 018566

of 2,3,7,8-TCDF, total TCDF and total penta-CDF below detection limits (0.4, 1 and 1 ng/g, respectively) at all three temperatures. Concentrations of PCDFs produced on pyrolysis of neat Aroclor and 5,000 ppm solutions were moderately sensitive to nominal pyrolysis temperature, with maximum formation at 550°C. All data are consistent with the proposition that tetra and penta CDF yields are roughly proportional to PCB concentrations in the starting mixture. However, the detection limit for the 50 ppm mixtures was about an order of magnitude higher than the concentrations expected based on this assumption. Lower detection limits will be sought for these samples.

An interesting feature of the mineral oil-Aroclor 1254 data is the clear and reproducible differences between the patterns of tetra-CDFs and penta-CDFs formed by pyrolysis of neat Aroclor 1254 versus those formed by pyrolysis of the 5000 ppm mixture. For example, 2,3,7,8-TCDF and co-eluters comprise 16-21% of the tetra CDF mixture formed from neat Aroclor, but 45-55% of the mixture from mineral oil/Aroclor. Other differences are apparent when chromatographic traces are compared.

Preliminary experiments to assess the tendency to form PCDFs from the pyrolysis of biphenyl-containing tetrachloroethylene (TCE) have been completed. Thus, 5,000 ppm solutions of biphenyl, 2-chlorobiphenyl, and decachlorobiphenyl were pyrolyzed at various temperatures. No evidence for the formation of the expected dibenzofuran products was obtained with detection limits corresponding to 0.1% conversion for dibenzofuran itself and 0.001% for octachloro dibenzofuran. However, literature data suggests that pyrolysis of TCE generates free Cl_2 as well as chlorine radicals. Thus, the possibility that biphenyl and 2-chlorobiphenyl were instead forming a complex mixture of chlorinated dibenzofurans not readily identified by simple gas chromatography required investigation. Scanning GC/MS showed that if any PCDFs were formed, their concentrations were below detection limit. It confirmed that chlorination of biphenyl did occur, but yields were low (ca. 1%). Instead, three much larger peaks with empirical formula $C_{14}H_9Cl_3$ were observed. A reasonable structure for this compound postulate ortho, mete and para substitution of a C_2Cl_3 group on the biphenyl structure. Efforts are underway to confirm the identity of this compound. However, if this reaction represents a facile reaction pathway for biphenyl destruction, PCDF formation may be minimal in this matrix. Pyrolysis of TCE (neat) and TCE containing 5,000 ppm Aroclor 1254 were conducted in duplicate at 500°, 550°, and 600° and submitted for high resolution GC/MS analysis.

MONS 018567

Pyrolysis of 2-chlorobiphenyl and 2,3,4,5,6-pentachlorobiphenyl as 5000 ppm solutions in silicone oil suggested that the optimal temperature for PCDF formation was ca. 550°C. Scanning GC/MS experiments demonstrated the formation of significant concentrations of fluorene from 2-chlorobiphenyl (corresponding to CH_2 insertion and CL loss) and various congeners of methylated/chlorinated fluorenes from pentachlorobiphenyl. Duplicate samples of Aroclor 1254 (5000 and 50 ppm) in silicone oil have been pyrolysed at 500°, 550°, and 600° and submitted to GC/MS for analysis.

Some interesting general observations have been made on the combustion process. For example, combustion of biphenyl in TCE produced decreasing net dibenzofuran as the residence time was varied from 18 sec to 6 sec and the wall temperature maintained at 450°C. In contrast, at 550°C, there is a net increase in dibenzofuran yield as residence time decreases; this suggests that at the higher temperature, significant dibenzofuran destruction is occurring. There are also large effects on dibenzofuran yield in the presence of different solvents: typically yields obtained on combustion in TCE are much higher than those obtained in silicone or mineral oil. Some sharp differences on the effects of particular variable parameters on dibenzofuran yields have also been noted.

MONS 018568

FORMATION OF PCDFs FROM PCBs

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In 1978 it was found in our group that PCBs can be converted to PCDFs under pyrolytic conditions. The pyrolysis of PCBs in sealed quartz ampoules in the presence of air yielded about 30 major and more than 30 minor PCDFs. The optimal yield of PCDFs was about 10% calculated on the amount of PCB decomposed. Later we studied the pyrolysis of 15 individual synthetic PCB isomers. This study showed that the formation of PCDFs can follow several competing reactions. The reactions involve the loss of ortho-Cl_2 and ortho-HCl with and without a 2,3-chlorine shift or loss of ortho-H_2. In the present report we are discussing identification and quantification of PCDFs in the following samples:

a. used PCBs
b. PCBs after sparking experiments
c. samples from thermal PCB degradation
d. samples from PCB fires

The analytical method used is described earlier.

Results

Used capacitors

We have opened some used and swollen capacitors, collected and analyzed the drained PCB. The levels of PCDFs was approximately 2 ppm, mainly tetra-CDFs, which is similar to the levels we found for the new and unused PCB.

MONS 018569

Examination of the paper layer reveaked dark points, probably caused by electrical arcing. The PCB around these dark spots was extracted and analyzed. The levels were similar to the levels found in the drained PCB or new PCB.

Sparking experiments in PCB

No increase in PCDFs (approx. 2 ppm) could be found after up to 7 sparks (18 kV, 2 µF) in pure PCB. In another experiment 1% of 1-epoxyethyl-3,4--epoxycyclohexane (Union Carbide ERL 42 06) was added before the sparking (4 sparks, 15 kV, 2.5 µF). In this experiment the PCDF levels increased, see isomers the increase was 30 times, for others no increase was found.

Thermal degradation of PCB

We have analyzed samples taken from the thermal degradation of PCB in special incinerators including rotary cement kiln. The critical parameters are minimum temperature
minimum residence time
excess of oxygen

A test-burn was performed in a Swedish rotary cement-kiln (>1500°C, >5 sec) obviously with oxygen deficiency. A series of PCDFs were found in the emissions, Figure 2 illustrates the hexa-CDFs found in these samples, 15 of the 16 isomers could be found.

PCB fires

During the period 1981-1984 a series of accidents have been reported in Scandinavia and the United States that can illustrate this risk. These accidents can be subdivided into three different categories.

a) PCB fires with mineral oil as the external energy source
b) PCB fires with electrical energy as the external energy source
c) Explosions in PCB filled capacitors

These accidents all resulted in the formation of PCDFs, in some cases also polychlorinated dioxins (PCDDs), biphenylenes (PCBPs) and pyrenes (PCPYs).

MONS 018570

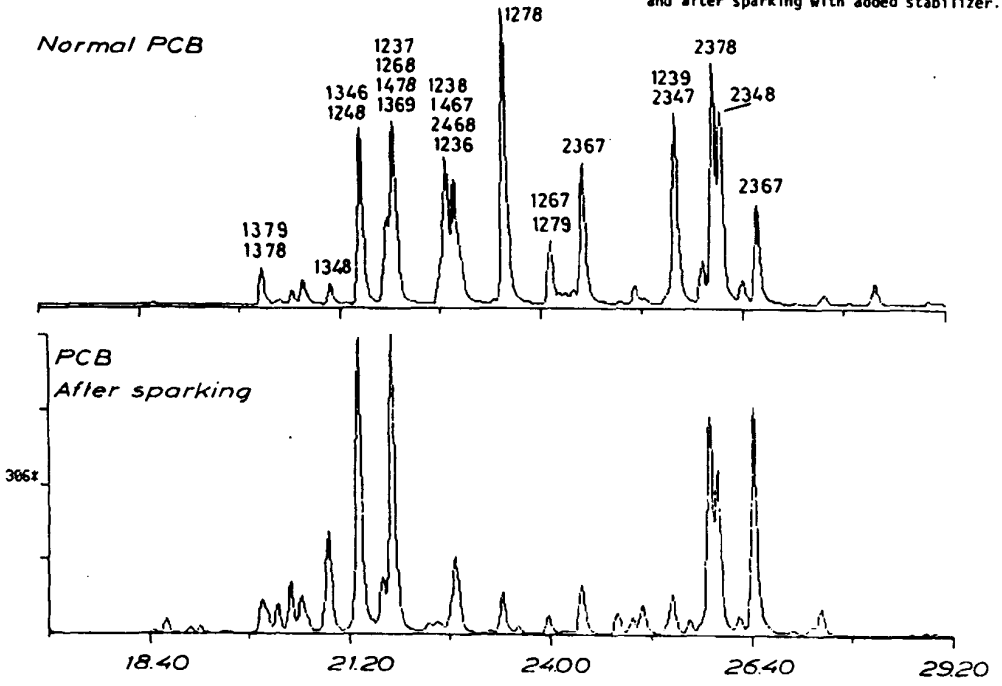
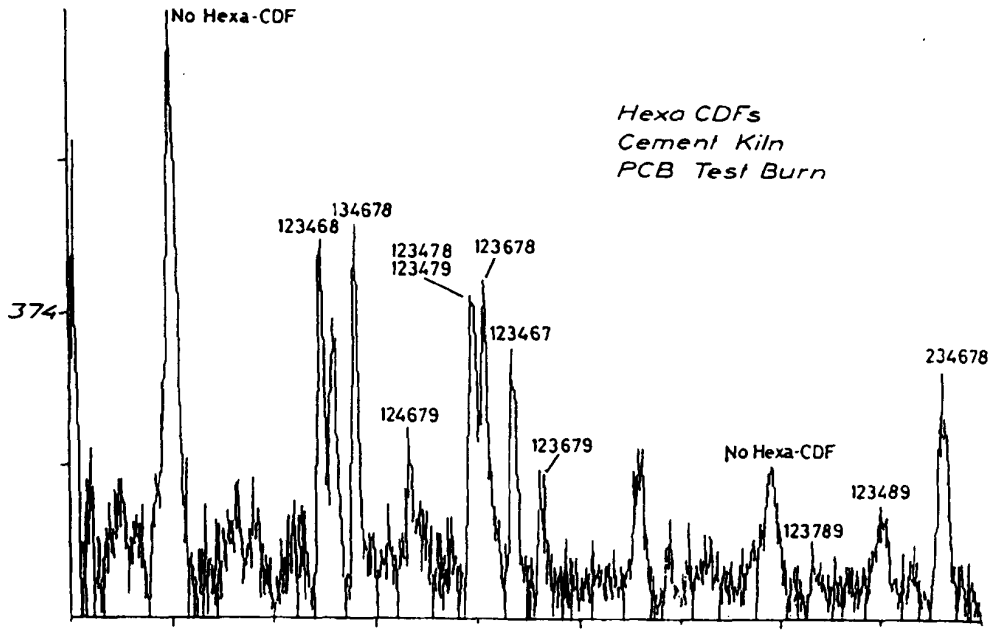


Figure 1. Tetra-CDFs found in a normal PCB and after sparking with added stabilizer.

MONS 018571

Figure 2. Hexa-CDFs from a PCB test burn.



MONS 018572

PART 4:

DOCUMENTATION OF FIRES, SPILLS AND CLEAN-UP

BRIAN WEST - MODERATOR

DECONTAMINATION OF FIRE FIGHTERS' PROTECTIVE CLOTHING WITH TRICHLOROTRIFLUOROETHANE

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ABSTRACT

A limited laboratory study was conducted to evaluate the efficiency of a 1,1,2-trichloro-1,2,2-trifluoroethane-based system to decontaminate Nomex® protective clothing worn by fire fighters during a fire at an electrical transformer oil reclamation facility. Both garments contaminated at the site of the fire and garments that were contaminated in the laboratory with a known concentration of polychlorinated biphenyls (PCBs) were laundered using the 1,1,2-trichloro-1,2,2-trifluoroethane-based system. The removal efficiency of the system was determined by the ratio of the after to before PCB concentrations in terms of micrograms of PCB per gram of fabric. Overall, the PCB removal efficiencies ranged from 66 to 99%. Until permissible fabric concentration levels for PCBs are established, it can not be determined whether this system is adequate to allow the safe reuse of the clothing. Research is urgently needed to define decontamination end-points for reusable protective clothing, i.e., "how clean is clean".

MONS 018574

INTRODUCTION

Uncontrolled fires involving polychlorinated biphenyl (PCB) containing fluids produce a complex and potentially highly toxic mixture of chlorinated products in the soot, including polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins (1-6). In some of the incidents, there also has been the formation of polychlorinated derivatives of biphenylene, chrysene, and pyrene (4,5,7). These incidents have resulted in the contamination of fire fighters' protective clothing and equipment with PCBs (8-10) and most probably the polychlorinated pyrolysis products.

In early 1984, a fire occurred at an electrical transformer oil reclamation facility in Jacksonville, Florida (11). The fire destroyed the building and several storage tanks containing PCB-transformer fluids and various organic solvents. A sample of the soot contained 1460 micrograms PCB (as Aroclor 1260) per gram (ug/g), and samples of liquid that had pooled on the site contained 67 to 5330 ug/g Aroclor 1260 (11). Neither the soot nor the liquid samples contained detectable concentrations of polychlorinated dibenzofurans, or dibenzo-p-dioxins (tetra-through octa-chloro homologs), or the respective 2,3,7,8-tetra isomers (11).

The protective clothing worn by the approximately 40 fire fighters, Nomex® turnout coats in combination with bunker pants, was assumed to be contaminated with PCBs. An attempt by the on-site cleanup contractor to decontaminate the garments with a common method (i.e., detergent-water wash with a water rinse) showed a mean residual PCB

MONS 018575

concentration of 239 ug/g (S.D. ± 411, range 15 to 1060, n=5). These levels of contamination remaining in the protective clothing after the detergent wash prompted a limited laboratory study to evaluate the efficiency of a 1,1,2-trichloro-1,2,2-trifluoroethane based system to remove PCBs from the Nomex® fabric protective clothing. This paper describes the results of the laboratory evaluation.

METHODS AND MATERIALS

Decontamination Process Description

A RADKLEEN® Model 1550 Clothing Decontamination System* was used to remove the PCB contamination from the protective clothing (12). The RADKLEEN® System is a 1,1,2-trichloro-1,2,2-trifluoroethane (Freon® 113)-based dry cleaning machine (Figure 1). The contaminated clothing is placed in the cleaning chamber which consists of a sealed, rotating drum that will cause the garments to tumble through the solvent. Solvent is pumped from the solvent reservoir through the filter adsorber set and then flows through the cleaning chamber. The contaminated solvent then returns to the solvent reservoir. Freon® 113 vapor and vapor pressure buildup within the sealed system are controlled by vapor recirculation across a condenser coil, with condensate returning to the solvent

*Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

MONS 018576

reservoir. Periodically, the solvent is regenerated and purified by a built-in distillation process. Contaminants are removed from the system as still bottoms and materials trapped on replaceable filter-adsorber cartridges.

Fabric Sampling Protocol

The test protocol consisted of decontaminating both site-contaminated and laboratory-contaminated garments. The site-contaminated garments are those that were presumably contaminated during the fire. The laboratory-contaminated garments are those that were site-contaminated, but also were contaminated in the laboratory with a known concentration of PCB as Aroclor 1242. The PCB test concentrations of 2.4, 9.0, 33% (volume-to-volume in dielectric grade mineral oil) and 100% were applied via a brush to selected areas on the garments to the point of saturation. The volume of PCB applied was approximately 20 milliliters.

The fabric sampling technique consisted of marking an area five inches square (12.7 cm) and within that area marking off five one-inch squares (2.54 cm). Four of these five one-inch squares were located at the four corners of the larger square, with the fifth located at the center. To determine the pre-decontamination concentration, each of the five one-inch squares were cut from the larger square to form a composite sample. To determine the post-decontamination concentration within the same area, the remaining fabric within the marked off section was removed. This checkerboard technique was used to average out or minimize

MONS 018577

concentration variations within the sample area. To eliminate variations based on cutting errors and unequal areas being removed, all results were normalized by reporting the contaminant concentration in terms of micrograms of PCB per gram of fabric (ug/g). The authors assured that bulk density variations in the fabric and substrate were minor. For comparison consistency, fabric sections were removed from the same approximate location on each turnout coat and bunker pant sampled.

The removal efficiency of the system was determined by the ratio of the after to before PCB concentrations in terms of ug PCB/g fabric. The pre-and post-decontamination changes in PCB concentration were compared using a paired t-test.

The Nomex® fabric samples were extracted with toluene and analyzed by gas chromatography with electron capture detection. The presence of Aroclors 1242 and 1260 was determined by comparison with standard samples of same obtained from U.S. Environmental Protection Agency. Quantitation was performed by summing the heights of the five major peaks of the standards, and comparing that to the sum of the same peaks in the sample. The instrumental limit of detection was 0.5 ug/g for both Aroclors. Since no recovery studies were performed on the Nomex® fabric, the results are considered to be the minimum amount of Aroclor present.

RESULTS AND DISCUSSION

Table 1 presents the pre-and post-decontamination concentrations of PCBs and percent removal for the site-contaminated garments. The PCB concentrations prior to laundering ranged from 5.3 to 480 ug/g (mean 85, S.D. ± 130). By comparison, the post-decontamination concentrations ranged from 1.1 to 25 ug/g (mean 7.8, S.D. ± 6.4). The percent of PCBs removed ranged from 66 to 99%, with a mean of 88% and a 95% lower confidence limit of 82% removed.

Table 2 presents the pre-and post-decontamination concentrations of PCBs and percent removal for the laboratory-contaminated garments. Although the PCB concentrations applied to the garments ranged from 2.4×10^4 to 1.0×10^6 ug/g (2.4 to 100%, volume-to-volume), the actual concentration in the fabrics ranged from 1.6×10^4 to 9.9×10^5 ug/g (1.6 to 99%, weight-to-weight). The post-laundered concentrations ranged from 5.4 to 230 ug/g (mean 63.5, S.D. ± 64.2). The reduction in PCB concentration exceeded 99% for all of the garments tested.

Post-laundering inspection of the garments revealed that the tumble-wash action of the machine did not appear to cause any physical damage to the garments such as cuts, abrasions, or alteration of the retro-reflective trim. Tests are currently being conducted by an independent laboratory to determine if solvent-washed garments still meet key performance criteria specified in the National Fire Protection Association (NFPA) 1971 Standard on Protective Clothing for Structural Fire Fighting (13).

MONS 018579

CONCLUSIONS

This limited study indicates that a relatively high percentage of fire-borne and liquid PCB contamination can be removed from fire fighters' protective clothing using a trichlorotrifluoroethane-based system. The toxicological significance of the PCB contamination levels remaining in the garments is uncertain. However, until permissible fabric concentration levels of PCBs are established, it cannot be determined whether this technique is adequate. The discarding and replacement of fire fighters' protective clothing and equipment can be very costly (10,11). The incident described in this paper resulted in the replacement of approximately 40 sets of bunker gear (including turnout coats, pants, and boots) with a replacement cost of approximately $20,000. Research is urgently needed to define decontamination end-points for reusable protective clothing, i.e., "how clean is clean".

MONS 018580

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MONS 018581

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MONS 018582

Table 1

PCBs Removed from Site-Contaminated Garments

ug PCB/g fabric		
Pre-Decon	Post-Decon	% Removal
480	25	95
240	13.3	95
200	1.8	99
68	1.3	98
60	5.4	91
56	3.5	94
37	5.1	86
35	4.2	88
35	2.4	93
15	1.1	93
14	2.9	79
10	1.2	88
7.8	1.3	83
6.7	2.2	67
5.3	1.8	66

$p<0.05$, $t=2.49$

MONS 018583

Table 2

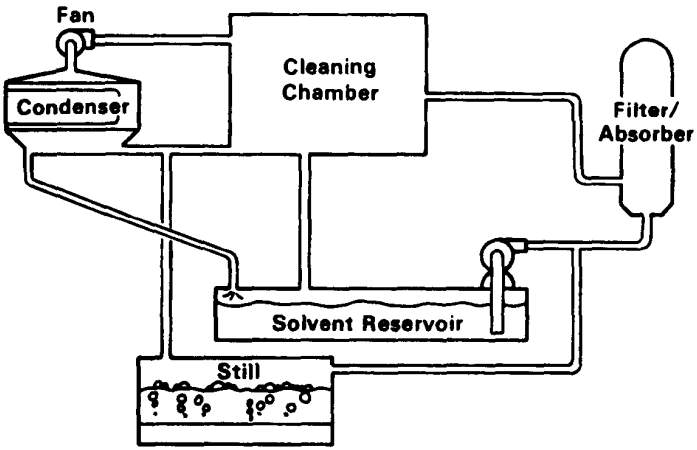
PCBs Removed from Lab-Contaminated Garments

ug PCB/g fabric		
Pre-Decon	Post-Decon	% Removal
9.9×10^5	24	99
9.4×10^5	100	99
6.3×10^5	60	99
6.3×10^5	53	99
5.4×10^5	230	99
2.5×10^5	110	99
1.8×10^5	97	99
1.8×10^5	62	99
7.2×10^4	13	99
6.1×10^4	8.2	99
5.8×10^4	63.1	99
5.7×10^4	63.5	99
2.0×10^4	1f.4	99
1.8×10^4	5.4	99
1.7×10^4	18	99
1.6×10^4	11.9	99

$p<0.05$, $t=3.34$

Figure 1

Basic Freon® 113 Decontamination Process



MONS 018585

AVAILABLE PCDF DECONTAMINATION TECHNOLOGY AND ITS ABILITY TO MEET STANDARDS

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EXTENDED ABSTRACT

INTRODUCTION

This paper discusses the state of technology in PCB and PCDF decontamination from a PCB fire, with emphasis on the relative importance of approach and technique when attempting to clean to a standard. The approaches discussed represent IT Corporation's general philosophy on building and site decontamination, but other projects' examples are cited as well. In particular, IT is nearing completion on an EPRI case study evaluation of the Binghamton and San Francisco projects focusing on technology applications, the preliminary results of which are reflected here.

BASIC APPROACH TO DECONTAMINATION

Proper decontamination of a site involves five steps, as follows:

- Perimeter definition and control
- Risk assessment/ratio development
- Source removal
- Final decontamination and isolation
- Closure sampling design and execution.

Although the focus of decontamination discussions is typically source removal and final decontamination techniques, the other three steps are <u>at least as important</u> to successful project execution and completion. It is assumed here that the principles and techniques applied to PCB decontamination apply equally well to PCDF removal. Depending on the surface to be cleaned and the choice of cleaning fluid, this is not always true.

MONS 018586

The term "perimeter definition" refers to the initial sampling following the incident. The data are used to define the nature and level of decontamination, its location, and the sources involved. The results are used to assess human health risks and set cleanup levels/standards, locate the decontamination complex, and help select the proper sequence of decontamination techniques. Failure to properly define and control the perimeter results in repeated recontamination before, during, and following cleaning (particularly at high initial PCDF concentrations), and can delay site reopening.

The risk assessment defines, among other things, the level of decontamination required. From a decontamination technique perspective, a key element of the risk assessment is the site-specific PCB/PCDF ratio. The perimeter sampling results define this ratio which, along with the cleanup standards for PCB and total PCDF defines which one is most important. For example, if a PCB/PCDF ratio of 500 is observed, and the PCDF standard is 25 ng/100 cm^2, the guiding of PCB decontamination standard is 12.5 ug/100 cm^2 (25 x 500/1000). A low PCB/PCDF ratio could result in a PCB standard below 1.0 ug/100 cm^2, where decontamination is difficult and economics may favor disposal instead.

Ratios commonly range from 500 to 1200 for PCB fires, so the PCDF standard normally predominates. A lower observed ratio results in a lower PCB standard, and requires more PCDF analysis during cleanup and closure sampling.

Common sense dictates that the decontamination effort be set up to avoid tracking or otherwise transmitting contamination to a clean area. However, when ratios are low, significant recontamination can occur through airborne vapor/particle deposition. Removing major sources of PCB/PCDF is therefore, performed first, usually through a gross cleaning step. Final cleaning is conducted once gross cleaning is complete. Cleaned areas are isolated from remaining sources as the project proceeds.

Closure of the site is often the most difficult step, as success is not so much a function of proper technology application as it is of complete removal from all points of exposure. The closure sampling plan should be separate and distinct from the sampling during cleanup, in order to confirm that recontamination has not occurred, and to methodically sample low-contact and high-contact areas if the standards are different. Approval of the closure sampling plan beforehand by all affected parties is encouraged to avoid disagreements later. Declaring a site safe to reoccupy is much more difficult than declaring it unsafe.

MONS 018587

SURFACE CONTAMINANT REMOVAL

As a general rule, source removal involves disposal of porous items, removal and (possibly) cleaning of non-porous or valuable items, and cleaning of non-porous surfaces.

Numerous attempts to clean ceiling and floor tiles, wallpaper, textiles, and other porous or absorbent materials have failed on different projects; surface wiping does not prevent later diffusion of contaminants from within, even if sealed, and solvent decontamination can either ruin the surface or cost too much.

The exception to the above is concrete. Concrete must be cleaned in many building incidents, so cost-effectiveness is not as critical as efficiency and cleaning effectiveness. Based on the results of core samples, surface treatment and/or surface removal may be desirable. Surface treatments including sandblasting, wet vacuuming, hydroblasting with crushed shells, surfactants or solvent, or any combination of the above can work on concrete, particularly where contamination is fresh and has not penetrated significantly. Older contamination or other causes of surface penetration will require scabbling or other methods of concrete removal. Surface coatings may be used to slow diffusion of deeper contamination, but can put restrictions on the ultimate use of the building. There is little research data on the effectiveness of concrete cleaning techniques, or the absorbent characteristics of concrete for organic compounds.

Electrical and mechanical components can be cleaned with the same solvents and surfactants noted above, taking special care to note the compatibility of cleaning agent and target, and the method of application. Most components are best cleaned by low pressure, high volume washing with Freon, TCA, or other solvents, particularly if the spent solvent can be captured and recycled. There is some data available on solvent compatibility with components (from solvent vendors), but little data on decontamination effectiveness, long-term effects on equipment, and absorbency of component materials. These techniques have nevertheless been accepted and succeeded in most applications.

MONS 018588

AIRBORNE CONTAMINANT REMOVAL

Airborne contaminants at a PCB fire site are routinely removed through the use of a HEPA filter/carbon adsorption system. A negative pressure system is developed, venting air away from the working areas toward the building exit area (in the direction of cleaning sequence). These control systems have been proven effective at removing contaminants from vented air. They are not, however, to be considered a method of site decontamination, but instead a method of preventing recontamination. IT estimated that high volume exhaust as a decontamination technique would require almost 100 years to clean a concrete vault following gross wipedown only. Airborne contamination is, of course, a useful and important measure of personnel safety during the job, and can be controlled through temperature as well as isolation.

CONCLUSIONS

The technology exists for cleaning almost any site contaminated with PCDF from a PCB fire. Higher PCDF yields require more thorough decontamination, in terms of improving isolation of cleaned areas, increasing cleaning passes, and technique.

The key to achieving standards is not only in technology selection, though, but in proper perimeter definition, flexible ratio development, isolation of clean areas, and development of an accepted and thorough closure/sampling plan. Even the best technique cannot alone result in effective decontamination without proper execution of these other steps.

Further research is warranted in the following areas:

- Concrete decontamination through surface wiping with various solvent mixtures.
- Concrete contamination suppression through coating.
- Material compatibility with cleaning fluids, both long and short-term
- Sampling techniques for irregular shapes.
- Standard ratio development and sampling plan protocols.

The author wishes to acknowledge the assistance of EPRI, which is sponsoring the IT case studies of the Binghamton and San Francisco incidents, thereby permitting a closer look at technology effectiveness. The assistance of several IT utility

MONS 018589

clients is also acknowledged, through their permission to discuss project findings at this level of detail.

MONS 018590

PREVENTATIVE MEASURES FOR PCB RISK REDUCTION IN BUILDINGS

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The electric utility industry's goal to continue using askarel filled electric equipment is dependent upon implementation of measures reducing the risk of costly PCB contamination events. Available risk reduction measures include protection, defined as preventing the formation of airborne PCB contaminants, and isolation, defined as restricting contaminant migration.

A preventative engineering program for airborne PCB spill risk reduction can be broken down into three principal steps:

1. define program goals and criteria
2. evaluate spill risk and select preventative approach
3. specify and implement risk reduction measures

RISK EVALUATION

Risk is a function of probability and consequence. Both factors can be quantified in order to make an objective evaluation of airborne PCB risk level. The major parameters affecting spill probability are:

- equipment condition
- electrical system design
- operating environment

The major parameters affecting spill consequence are:

- public safety
- building value
- contaminant migration potential
- cleanup complexity

MONS 018591

PREVENTATIVE APPROACH SELECTION

Preventative engineering, other than replacement, is not applicable to 100% of all utility askarel transformer installations. Preventative measures available to choose from include:

1. replacement
2. relocation
3. isolation
4. protection: electrical, mechanical, fire, alarm, maintenance

Technical, economic, environmental, regulatory, and policy considerations all affect selection of the most applicable risk reduction approach.

Replacement

Replacement is the preferred alternative where building use or value is such that no contamination risk is acceptable, or in the situation where the askarel transformer is old, undersized, or has some other electrical shortcoming. In some cases it is prohibitively expensive, or technically impractical, to provide other types of risk reduction besides replacement. Installations in this category represent about 15-20% of utility indoor transformers.

Replacement is expensive, disruptive, time consuming, and results in rapid generation of PCB waste. If all askarel transformer owners were to commence replacement programs simultaneously severe delays would be caused by undercapacity in the electrical manufacturing, design, installation, and PCB disposal industries.

Relocation

Transformer relocation offers the potential for significant reduction in airborne PCB spill risk without the capital expense and waste disposal disadvantages associated with replacement. Unfortunately, relocation of utility type askarel equipment is of limited technical practicality due to the lack of suitable alternative sites. It appears relocation will be a minor alternative for utility risk reduction programs.

MONS 018592

Isolation

Isolation is the blocking of migratory pathways between the askarel transformer room and other building areas. An isolation design may provide for the containment of released PCBs within the transformer enclosure, or may seek to direct contaminants out of the building. In particular, openings into the building ventilation system are sealed, either permanently, or utilizing smoke actuated dampers.

Compared to other risk reduction measures isolation is inexpensive, non-disruptive, technically uncomplicated, rapid to implement and does not result in the generation of PCB waste. Its principal disadvantages are a lessor degree of risk reduction and the lack of any improvement to the electrical system. As a general rule, if the isolation design project costs more than about 35% of replacement, most owners will prefer to invest in a new installation. For typical utility type indoor askarel transformers this equates to a maximum isolation cost of $20,000 - 25,000.

Protection

Alternatives for transformer failure prevention are broken down into five categories based on the protective approach.

Electrical. Lack of effective means to provide for adequate transformer de-energization upon failure has been implicated as an aggravating factor in several past airborne PCB contamination episodes. In the past, utilities have used a variety of transformer protective devices. The most conservative designs included three phase fault interruption devices on both the primary and secondary sides. Less conservative designs utilized utility-owned fuses for primary protection and rely on the customer's main service disconnect for secondary protection. Most large commercial building electrical services are of the less conservative design.

In order to provide more complete de-energization a primary fuse protective system can be installed. These devices utilize stored energy switches acting to disconnect all three phases upon failure of any one fuse. Retrofit of load interrupting primary and secondary breakers is

MONS 018593

also an option. Installation of a secondary breaker alone will not provide effective arc protection as the primary winding will remain energized. The only technical impediment to retrofitting electrical protective devices to utility askarel transformers is the possible lack of sufficient physical space within the enclosure for installation. Retrofit of electrical protective devices to askarel transformers will cost from $10,000 - 60,000 depending upon the protective system selected, transformer size, and voltage ratings.

Mechanical. Most askarel transformer failure scenarios resulting in formation of airborne PCB contaminants involve heating of the dielectric fluid either by internal sources (e.g. arcing), or external sources (e.g. an adjacent fire). The resultant heating increases the pressure within the transformer tank eventually expelling the contents either as a liquid or gas. Mechanical protective devices are intended to prevent hazardous pressure buildups either by controlled discharge through a pressure relief valve, or by signalling for de-energization. Retrofit of pressure relief valves and pressure sensor relays costs only $200 to $300 and provides effective failure protection.

Fire. External fire threats to indoor askarel transformers can be mitigated through the installation of automatically actuated fire suppression systems. Of commercially available systems, carbon dioxide or halon flooding is the most applicable to electrical equipment protection.

Due to the cost of installing and maintaining an automatic fire system, this approach is applicable only for installations exposed to a higher than usual fire threat. It is estimated less than 15-20% of indoor askarel transformer installations fall into this category.

Alarm. Although the time from transformer failure to airborne PCB generation may be quite brief there often are indications of incipient failure well in advance of the actual spill event. Monitoring of selected parameters such as temperature, pressure, noise, vibration, load, or voltage can potentially provide adequate failure warning to initiate preventive action. Installation of alarm equipment costs from $200 to $600. Carrying the alarm signal to a remote location can coat much more.

MONS 018594

Maintenance. Five of the ten most common causes of transformer failure can be prevented by increased maintenance. Establishment of a cost effective preventative maintenance program includes analysis of manufacturers recommended maintenance procedures to select those providing substantial failure risk reduction. An annual maintenance program to protect against these hazards costs approximately $1,000 per transformer per year.

MONS 018595

FIRES INVOLVING PCBs: EFFECTIVENESS OF CLEANING PROCEDURES AND QUALITY CONTROL REQUIREMENTS

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FIRES INVOLVING PCBs:

The potential costs resulting from any fire involving PCBs are, in decreasing order:

Litigation costs and injury awards;
Business interruption costs;
Cleanup costs;
Sampling and analysis costs.

Since the potential presence of PCDFs and PCDDs essentially causes every incident to turn into a piece of the Agent Orange controversy, the overriding concern of every cleanup action is to end up with an occupied building and a strong defense against claims based on alleged health effects resulting from exposure to toxic chemicals produced by the fire. The primary input for establishing the cleanup strategy should come from legal counsel, so as a chemical engineer I am probably not the right person to be addressing you on this subject. However, I will try to pass along some of the lessons that I have learned through my involvement in the incidents at the Binghamton (NY) State Office Building, One Market Plaza in San Francisco, and similar problems that occurred in Syracuse (NY) and Tulsa Oklahoma.

The basic problem that I, as an engineer, have had to face is a tendency to concentrate on the technical issues to the point that the more important public relations issues are slighted. One must always keep in mind that the goal of a cleanup is not just a clean building, but one that is occupied. For a good insight into the non-technical issues resulting from a fire, I would recommend that you read carefully a recent article that addresses the financial impacts of PCB fire incidents (1). The prescription for obtaining an occupied building consists of a limited number of simple steps:

1) The decision that the building is clean is a question of public health policy, not one of technology. The decision must be made by the responsible government agency. Since the U.S. EPA has not accepted responsibility for addressing the safety of environments inside buildings, the decision as to how clean is clean enough must be made by the local and state health departments on a case by case basis. It may well take the health department longer to decide how clean a building has to be than it will take to clean it. Since the health department must act immediately to decide whether to close the building and what level of protective clothing and medical surveillance will be required for those who were possibly exposed, the initial decisions will probably be based on very conservative criteria.

MONS 018596

2) The building manager has the primary interest and responsibility for communicating with the tenants of the building and for arranging alternate accommodations if the building must be evacuated during the cleanup. Therefore, the building manager should be kept completely informed, and should be both the spokesman for the tenants and their major source of information.

3) The owner of the PCBs will probably end up paying for most of the costs, and so might as well get involved immediately so as to have some control as to what cleanup work is done and who does it.

In short, the major players in a building cleanup are the government health department, the building owner, and the owner of the PCBs. Each of these organizations should be responsible for obtaining its own advice and counsel since their interests are not necessarily identical, but they must work together and have completely open communications to assure that they are all telling the same story to the media. The next point is probably the most important of all in getting the building reoccupied:

4) Make sure that the media has constant easy access to reliable information on the incident. The government officials will have the most credibility, and so should be the major spokesmen. However, efforts should be made so that everyone involved who is likely to be approached by a reporter is fully briefed so that the "no comment" response will not be necessary and there will be no appearance of managing the news.

EFFECTIVENESS OF CLEANING PROCEDURES:

The rest of this discussion is concerned with the details of actually getting a building clean and preparing to defend the adequacy of the cleanup.

The pyrolysis of PCBs can form total PCDFs and PCDDs in amounts up to one part per thousand parts of PCBs. If the toxicity of PCDFs and PCDDs is assumed to be 10,000 times greater than PCBs, about 90% of the toxicity of the resulting mixture will be from the combustion products and not from the PCBs that are present. The smoke from fires involving PCBs is usually a mixture of soot and vapors. In general, the PCDFs and the PCDDs are somewhat less volatile than the PCBs and therefore tend to stay with the soot, but sampling data from Binghamton indicates that both the PCBs and the combustion products can and do slowly evaporate and redeposit on other surfaces, thereby changing the ratio between the PCBs and other chemicals as a function of time, the type of surface that is contaminated, and the distance from the source of the contamination.

The cleanup of PCBs and contaminated soot is pretty straigtforward, and fancy technology is generally not required. Outside the immediate area of the fire, the deposits are the result of the soot or PCB aerosol settling out on the surface of materials, or adsorbtion of the chemicals from the gas phase. The major concern is in removing these deposits without either evaporating the PCBs (which will then

MONS 018597

settle out on an area that has already been cleaned) or helping the contamination soak into the material. A solution of non-ionic detergent in water has been found to be adequate to pick up light surface deposits into the rinse water, which can then be treated with activated carbon to decontaminate it before it is discharged into the sewers. The addition of a mild caustic such as trisodium phosphate will help emulsify any thin grease deposits that were on the surfaces prior to the fire, and will help lift floor waxes and some furniture polishes that will otherwise adsorb PCBs from the air. Commercial formulated cleaning agents such as Caraclean, Seawash, Penetone and similar materials all seem to perform about equally well, and the choice as to which one to use can be based on cost and availability. Solvents such as kerosene or freon have not been found to be useful in removing light deposits of contamination from porous surfaces, and instead seem to help carry the contamination into the pores of the material. Solvent cleaning should only be considered for electrical equipment where the materials are not porous and where contact with water based cleaning materials is not recommended by the manufacturers of the equipment.

The levels of residual PCBs on surfaces in the Binghamton State Office Building, as measured by the hexane wet wipe sampling procedure discussed in the following section, have been found to range from one to ten micrograms per square meter on hard surfaces such as glass and painted metal that were washed with detergent in water. Vinyl floor tile could not be cleaned to below about 100 micrograms PCBs per square meter, even after multiple washings with strong cleaners and solvents. Porous surfaces such as quarry tile and concrete that were exposed to heavy concentrations of soot continued to show levels of PCBs up to 1000 micrograms per square meter, even after aggressive cleaning with solvents.

Recent tests have demonstrated that the levels of 2,3,7,8-tetraclorodibenzofuran on surfaces in the Binghamton State Office Building have been reduced to below thirty nanograms per square meter on all surfaces except concrete stair treads and a few surfaces that were hard to reach and have since been recleaned. Washing has been successful in decontaminating all surfaces in the Binghamton and One Market Plaza buildings except the unsealed concrete and cement blocks immediately adjacent to the fire in the transformer vault or mechanical room and in the main smoke exhaust path. The only successful cleaning method found for the severely contaminated porous surfaces was physical removal with jackhammers and sledge hammers.

The secret of a successful cleanup following a PCB fire is not in the technology, but in the thoroughness of the effort. The actual work of cleaning is hot and uncomfortable because of the necessary protective clothing, and is inherently boring. The most person most responsible for the success of the cleanup is the crew supervisor who is responsible that the workers do a thorough job. In general, elbow grease is far more important than high technology, and this factor comes from experienced supervision, not from a can.

MONS 018598

QUALITY CONTROL REQUIREMENTS

The goal of a cleanup is a reoccupied building, and this will be achieved only if everyone is convinced that it is actually clean. Consensus is achieved by having everyone concerned participate in the decision process and buy into the criteria before the final decision to reoccupy the building is made. In general, the results from any tests performed to demonstrate cleanliness will be accepted only to the extent that everyone agrees before the tests are made as to the locations that will be sampled, the sampling procedures, the chain of custody procedures, the analytical procedures, the standard of cleanliness that is agreed upon as sufficiently clean, and the specific test results that will be sufficient to demonstrate that this level of cleanliness has been met. Reaching a complete consensus on any one of these items is usually timeconsuming, and achieving complete agreement on all of the points can (and usually does) take months. In going through this process in Binghamton and San Francisco, Versar has used the preparation of a test plan as the mechanism for addressing each of these technical issues in a public forum. The final test plan has a signature page for each interested party, and the final tests of cleanliness does not start until everyone indicates their agreement with the procedures and decision criteria by signing the cover of the test plan. Preparation of a major test plan can be done within three months and eight revisions if a lot of work has been done in advance to educate all of the parties. Since we don't start preparing a test plan until there is a general consensus as to what will be acceptable, this estimate of time and effort is probably optimistic. A good definition of quality control is the achievement of results that everyone agrees with.

Each of the technical issues that are addressed in the test plan has its own set of problems. The following paragraphs are a short discussion of the issues that we have addressed in preparing test plans in Binghamton and San Francisco.

Cleanliness Criteria

There is no generally accepted standard as to how clean is clean enough. Setting such a standard is equivalent to setting an acceptable level of human exposure to dioxin as a public health policy, and government officials are reluctant to take this responsibility. The standard must address all of the toxic chemicals that are present, including PCBs and all of the various PCDDs and PCDFs, as well as other chemicals that may have become an issue and which can be identified as being present and (hopefully) quantified. The data developed by the U.S. EPA (2) and NIOSH (3) on levels of PCBs in air in normal buildings is useful in setting standard based on the criteria of "as clean as other buildings". No data has been published on the levels of PCDDs and PCDFs in normal buildings, and I have been epectacularly unsuccessful in finding any building owner who is willing to let me measure the levels of contaminants to which his tenants are being exposed. As a result, the criteria for the PCDDs and PCDFs must be based on a risk assessment that quantifies the risk of exposure to various levels of these chemicals and establishes a safe level of risk as a matter of public policy.

MONS 018599

There appears to be a general consensus that all of the various PCDDs and PCDFs are toxic by the same mechanism, and that the different congeners and isomers differ only in their specific degree of toxicity. The New York State Department of Health proposed an aggregation scheme that converts the measured levels of all of the various PCDDs and PCDFs to an amount of 2,3,7,8-TCDD that would have the same toxicity; the weighting factors for the various isomers are based on their relative acute toxicity in terms of LD-50 or other available information. The algorithm for calculating the total toxicity of a mixture in terms of "2,3,7,8-TCDD equivalents" also includes factors which estimate the fraction of each measured congener which is chlorinated at the 2,3,7, and 8 positions, as chlorination at these locations is a factor that is common to all of the highly toxic isomers. The use of this algorithm allows the limits of allowable exposure to be set based on 2,3,7,8-TCDD, and for the measured levels of all of the PCDDs and PCDFs to be evaluated in terms of this TCDD criteria. The California Department of Health Services developed a somewhat different algorithm for use in calculating the equivalent toxicity of the measured levels of PCDDs and PCDFs in One Market Plaza. Although the details of the algorithm differ from that used in New York, the resulting limits of acceptable exposure are similar. In both New York and California, implicit assumptions were made as to the relationship of measured surface contamination levels to the resulting levels of human exposure that would result from skin contact with those surfaces.

Since the testing must achieve a detection limit below the criteria and must quantify all of the chemicals that are considered to be toxic in determining whether the building is clean enough, it is important that the local or state department of health that has jurisdiction over matters of public health policy establish the criteria before the test plan is written. Until it is established what "clean" means in operational terms, both the cleaning and testing will be performed without a defined goal.

Sampling Locations

In preparing a test plan, the kind of samples, number of samples, and locations of samples must be defined and agreed to a adequate. The risk assessments that establish the criteria of cleanliness address exposure by both inhalation of contaminated air and skin contact with contaminated surfaces. Definition of the air samples must address the number to be collected, the locations, and the building ventilation and temperature conditions during the testing period. Since PCB samples are easier and cheaper to collect and analyse than PCDD/PCDF samples, a larger number of PCB samples can be proposed to demonstrate that the air in the building is homogeneous. This data will support the use of a smaller number of PCDD/PCDF samples as representative of the conditions throughout the building.

Surface samples must define the number and kind of surfaces to be sampled and the locations of the samples. Since it is not feasible to sample every square inch of a building, agreement must be reached that

MONS 018600

the proposed surface samples are both representative and sufficient to provide a reliable measure of the residual contamination levels. As with air samples, a larger number of PCB samples may be used to demonstrate the range of cleanliness of surfaces throughout the building in order to support the use of a smaller number of PCDD/PCDF samples as being representative. However, enough PCDD/PCDF samples must be taken to independently assess the levels of these chemicals on various surfaces. Wipe samples collected in Binghamton have shown that, although the levels of PCBs and PCDDs/PCDFs are correlated, the ratio is by no means constant throughout the building. A regression analysis of log transformed PCB and PCDD/PCDF levels from adjacent areas found a correlation of 0.77; an estimate of the PCDD/PCDF levels based on the PCB levels had a 92% chance of being within a factor of ten of the meaaured PCDD/PCDF levels.

Sampling Procedures

The sampling and analytical procedures should achieve a detection limit substantially below the cleanliness criteria. In Binghamton and San Francisco, PCBs were determined by air samples of 1.3 cubic meters passed through Florisil, and the PCDD/PCDFs by samples of 75 cubic meters of air passed over silica gel. Both the PCB and PCDD/PCDF samplers were developed and validated by the New York State Department of Health. The samplers and the sampling procedures were described in detail in the sampling plans.

The surface samples collected in both Binghamton and San Francisco were collected by using a 3" x 3" Johnson & Johnson cotton gauze steripad that was wetted with 8 milliliters of pesticide grade hexane immediately before use. Each pad was used to wipe an area of 0.25 square meters; the area was wiped twice in a raster pattern, once vertically and once horizontally. The sample pads were held by hand. Previous work was done in Binghamton to compare the results obtained by holding the sampling pad in the hand to the results achieved when the pad was held in a sampling fixture that applied constant pressure. Careful control of the pressure did not achieve any significant reduction in sample to sample variability. PCB levels were measured by analyzing the extract from a single wipe sample. PCDD/PCDF levels were measured by analyzing the extracts combined from four samples, ie. the sample area was one square meter.

The wipe sampling procedure was fully specified in each test plan. This is necessary because there is no generally accepted standard procedure for collecting wipe samples, and the effects of different sample areas, sample media, solvents, and other variables have not been investigated. Therefore, the criteria of cleanliness must specify the method by which wipe samples are to be taken; this level of specificity is achieved by obtaining formal approval of the test plan. The test plan also defined the number of field blanks and duplicate samples that would be collected. In general, about 10% duplicates and 10% field blanks were collected for both air and wipe samples.

MONS 018601

Chain of Custody Procedures

The test plan described in detail the procedures that would be implemented to assure the integrity of the samples. These procedures included guarding the air samplers during the sampling period, and documenting the security of all samples from the time they were collected until they were logged into the analytical laboratory. A formal chain of custody form was defined, and a copy accompanied each sample and was signed by each person who was responsible for the security of the samples.

Analytical Procedures

The analytical procedures were defined in detail in the test plans for both air and wipe samples. The description of the procedures included the amount and kind of internal standards added to both the PCB and the PCDD/PCDF air samplers before they were taken into the field, the extraction procedures, the cleanup procedures, and the analytical equipment and its operating conditions. The procedures that were used to quantify the amount of the various chemicals from the chromatograms and the computer generated peak area measurements were also specified. Included in the description of analytical procedures was a specification of the number of check samples to be run in the laboratory with each run and the performance criteria that defined acceptable laboratory performance.

CONCLUSIONS

The quality control requirements have been set for each test as required to gain the egreement from each interested party that the resulting data would be acceptable and adequate to judge whether the pre-determined decision criteria were achieved. Although the several months of effort required to gain consensus for each test plan seemed arduous at the time, the benefits derived from reaching detailed agreements as to the requirements for demonstrating building cleanliness made the effort worthwhile. In San Francisco, the decision to open One Market Plaza for normal occupancy was made within 24 hours after the final test report was submitted, and there were no challenges to the validity of the data by anyone who was involved in the review and approval of the test plan. In Binghamton, where the outside reviewers include an international panel of experts, representatives of the community and unions, and the Environmental Defense Fund, the process of obtaining approval for a test plan has been even more time consuming. The success of this effort in Binghamton should be known within a few weeks when the analytical results from recent samples collected to demonstrate the cleanliness of the building are made public and compared to the criteria in the teat plan that define the cleanliness required for the resumption of normal HVAC operations and the reconstruction of the building.

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MONS 018603

FIRES IN ELECTRICAL EQUIPMENT CONTAINING PCBs: RECOMMENDATIONS FOR THE PREVENTION OF CONTAMINATION BY PCDFs

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Section 1

INTRODUCTION

This presentation has two purposes: (i) to enhance awareness of fires implicating electrical equipment containing PCBs; and (ii) to recommend a course of action for the prevention of contamination by PCDFs.

This course of action defines the general context from which more refined procedures should arise for each specific workplace or location. The recommendations put forward were prepared by a consultant to Environment Canada and address individual health and safety, equipment and facilities, and environmental concerns. They relate to conditions before a fire (i.e., preventive measures), during the fire (i.e., firefighting measures), and after the fire (i.e., clean-up measures).

MONS 018604

Section

PREVENTIVE MEAS

(1) INDIVIDUAL HEALTH & SAFETY

These measures aim primarily at the benefit of personnel; the also facilitate action by the emergency response crews.

1. Information and Training

Personnel should be informed on the procedures to follow in case of fire. This will prevent exposure to those taking uninformed actions in case of fire, and instill caution.

Practice, rehearsal and training are necessary to ensure that personnel can be evacuated or take appropriate precautions and countermeasures, pending arrival of emergency response crews.

Fire wardens should be familiarized with the additional hazards posed by PCDFs, and with any special countermeasures necessary in the event of a fire implicating electrical equipment and possibly PCDFs.

2. Identification of Equipment

Each piece of electrical equipment containing PCDF precursors should be identified, properly labelled, and its location recorded on a schematic lay-out of the facility. This will prevent exposure to those taking uninformed actions in case of fire, and instill

MONS 018605

caution. In addition, areas to be avoided or restricted to authorized personnel can be more easily defined.

The emergency response crews (fire department, environmental protection departments) should also be informed on the identity and location of such equipment in order to, in the event of an emergency, enable them to use appropriate material and implement adequate countermeasures.

3. Protective Material

Fire alarm systems and fire extinguishers should be clearly labelled and readily accessible. Voice communication systems should be checked periodically. Fire exit doors should be free of any obstacles.

Fire extinguishers and self-contained breathing apparatus (SCBA) should be inspected periodically.

4. Contingency Plan

This plan should contain clear courses of action and various options for dealing with emergency situations. This contingency plan should also be provided to and discussed with emergency response crews. The plan should also consider evacuation needs and actions to be taken prior to arrival of emergency response crews.

MONS 018606

(ii) EQUIPMENT & FACILITIES

These measures aim primarily at protecting equipment and facilities.

1. Programs

(a) Of Operation. Equipment should not be operated above design ratings.

Undersized (overloaded) equipment is more prone to deterioration and failure, thereby increasing the risks for fire.

(b) Of Maintenance and Inspection. Maintain and repair equipment to avoid hazardous conditions. A good inspection program keeps operating equipment in condition and identifies defective equipment.

2. Safety Systems

(a) A properly designed fire-extinguishing system can begin the fire control procedure even before emergency response crews are aware of the fire. Install automatic fire-extinguishing systems and distribute small portable extinguishers at strategic locations.

(b) Shutting the power off reduces both the arcing and the production of PCB/PCBZ degradation products; it also cuts the energy input and reduces the intensity of fires. In addition, firefighting is always delayed pending equipment shut-off. A prompt intervention reduces damage to equipment and limits generation of smoke and fumes. Install alarms, shut-down systems, or both on equipment.

MONS 018607

For transformers, a two-stage gas alarm relay installation should be considered; the first stage will trigger an alarm when the tank pressure reaches a certain level (e.g. 40 kPa) and the second-stage will de-energize the transformer (and possibly shut down Electrical Room ventilation, including dampers) when the tank pressure reaches a higher level (e.g. 55 kPa).

(c) The ventilation system is a major route by which contamination spreads. Smoke, fumes, particulates, and hot gases may be carried throughout an entire building by convective effect, resulting in massive widespread contamination from a relatively localized occurrence. Install auto-close mechanisms on the ventilation network.

3. PCB MANAGEMENT

(a) Do not mix PCB equipment with non-PCB equipment. PCB transformers and capacitors should be physically separated from non-PCB equipment so that in case of a fire in a mineral oil transformer, the fire will not spread to PCB equipment.

A fire starting in PCB equipment may not be self-sustaining when the power is off, whereas a fire in a mineral oil transformer will continue to burn. If PCBs are involved in a self-sustaining fire the difficulty of controlling the contaminant dispersion is compounded; not only must contaminants be contained, but the containment must take place during the control of another emergency of higher priority.

(b) Remove PCBs from equipment and retrofill with non-PCB fluids. Where possible, this course permits the reduction of hazard without incurring the major capital expense of replacing the equipment.

MONS 018608

There are several caveats with this course:

- the flammability with a retrofilled appliance is greater than with a PCB appliance
- draining and retrofilling of equipment may not be practical
- the replacement fluid will become contaminated and may contain more than 50 ppm PCBs.

(iii) ENVIRONMENTAL CONCERNS

These measures aim primarily at minimizing dispersion into the environment.

Containment

(a) Of Equipment Fluids. A containment system, e.g. berms, curbs, dams, capable of holding more than the total volume of fluids contained within the equipment should be provided for each piece of equipment.

Drains in the floor must be outside the containment area.

A drain sealing system must be in place to prevent contaminants from escaping to the sewer system.

(b) Of Contaminants. All surfaces (walls, ceilings and floors) should be painted with materials impermeable to PCBs and PCDFs. This precaution will facilitate clean-up and may also avoid the necessity of removing building materials as part of the decontamination process.

MONS 018609

Section 3

FIREFIGHTING MEASURES

(1) INDIVIDUAL HEALTH & SAFETY

These measures highlight the additional precautions necessary to avert anticipated hazards arising from fires involving PCBs.

1. Awareness of the Presence of PCBs

Warn emergency response crews about the identity and location of PCB equipment. This will lead to the use of proper extinguishing techniques, including personal protective gear.

2. Use of Proper Protective Gear

Hazards are likely to be associated with an electrical fire as well. Therefore, protective gear should guard against heat, asphyxiants, and corrosive atmospheres.

Protection against PCDFs should be based on a limit of 1.5 ng/m^3 (24 hour average)*. This means use of full protective suit and self-contained breathing apparatus.

*Based on (i) PCDFs are about 50 times less toxic than PCDDs.
(ii) the recommended ambient air guideline for 2,3,7,8-TCDD (the most toxic) is 30 pg/m^3 not to be exceeded on the average over a year (Ontario Ministry of the Environment, 1982).

MONS 018610

3. Medical Aid

Due to the extremely toxic effects involved, emergency medical aid should be on call. Where personnel has been exposed to gases from a fire, decontamination of both skin and protective material is required.

Medical testing is also required.

4. Evacuation

All ventilation openings (inlets and outlets) in the building should be closed automatically. Otherwise evacuation of adjacent buildings must be considered whenever contamination could reach other buildings. The hazardous nature of PCDFs justifies a conservative course of action.

(ii) EQUIPMENT & FACILITIES

These measures aim at promoting a quicker control of fire and, in turn, minimizing hazards and damage.

1. Firefighting Strategies

(a) Concerning Power. Ensure that power is off. A power-on situation complicates firefighting considerably, requiring extra precautions to avoid potentially live sources, both for personal safety and fire control.

(b) Concerning Ventilation. If one of the three necessities for fire is absent - in this case the oxidant (O_2, air) - then control and extinguishment may be achieved at much less cost and with much less damage.

Ensure that air inlets/outlets and access to building's ventilation are closed.

If this is not done, what should have been a localized confined contamination can become a major environmental problem, contaminating all areas accessible to the building's ventilation system.

Once a fire has been extinguished in this way CAUTION is required to avoid re-ignition when air is re-admitted, if ignition sources still remain.

2. Firefighting Materials

Carbon dioxide (CO_2) and HALON® act by segregating the oxidant (O_2, air) from the fuel. Although they do not have as significant a cooling effect as water does, they do not have the drawbacks that water has.

(iii) ENVIRONMENTAL CONCERNS

The emphasis on environmental concerns has been placed in the Preventive Measures to warrant the precedence given to firefighting measures during the emergency.

Section 4

CLEAN-UP MEASURES

(1) INDIVIDUAL HEALTH & SAFETY

These measures aim at minimizing exposure to the hazards posed by the contaminants.

1. Information

Training of clean-up crews in recognizing the hazards of the task is a necessary adjunct to the provision of protective gear.

Personnel must be informed of the occupational health concerns of PCBs, PCDDs, PCDFs and the cleaning materials used.

2. Protective Procedures

(a) Area. Monitor contamination of the area to:

(i) indicate the degree of hazard,

(ii) provide boundaries for the clean-up,

(iii) provide information for the use of proper protective gear,

(iv) indicate when clean-up is satisfactory.

MONS 018613

(b) Individual. Although fire-related hazards are not present in the clean-up phase, protection against PCDFs must be maintained at a high level. Generally, protective gear must lend itself to decontamination or discard.

Reduction in air contamination through an air-cleaning vacuum system will reduce the inhalation hazard and skin contamination from airborne particulates, thus permitting less stringent requirements for breathing apparatus.

3. Medical Attention

Prompt medical attention is essential for any case of exposure to the substances produced in a fire involving electrical equipment. Response crew members should undergo medical examination if there has been any possibility of exposure.

Decontamination procedures must ensure that no hazardous material remain on the clean-up crew members, and that clothing and equipment have also been cleaned or disposed of.

(11) EQUIPMENT & FACILITIES

These measures aim at the efficient and thorough removal of contaminants.

1. Soot Removal

The major location of PCDF contamination is expected to be in soot deposited on surfaces. PCDFs are quite strongly adsorbed by soot, thus removing the soot also removes much of the hazard. Removal of loose soot is best accomplished by vacuuming with a high-efficiency vacuum cleaner, with high-efficiency filtration for the exhausted air. Remaining soot adhering too well to be removed by vacuum, is removed by washing with organic solvents. Water and detergent systems, with mechanical scouring, may also be effective.

MONS 018614

particularly as a final cleaning step. Washing should be repeated until the surface contamination is reduced to 10 ng/m^2 PCDFs. All cleaning materials and residues must be contained for treatment or disposal.

The curtain-wall technique is effective in permitting the intensive cleaning of small sections of an area without recontaminating the area with debris or contaminants from uncleaned sections. Although installation and use of curtain-walls is expensive in terms of material and time, it does minimize the need to reclean areas.

2. Inspection

Ventilation inlets of all buildings in the vicinity of the fire should be closely examined. Should any soot be found at these inlets, it must be analyzed immediately and appropriate clean-up procedures must be put into effect with respect to all contaminated areas.

(iii) ENVIRONMENTAL CONCERNS

These measures aim at preventing the spreading of contamination.

1. Decontamination

Prevention of contamination spread is achievable by maintaining the contaminated area under reduced pressure. Exhausting air through a high-efficiency filtration system maximizes the benefits of decontamination.

Decontaminating workers and cleaning up equipment on site keeps contamination localized.

MONS 018615

2. Disposal

Contaminated materials should be stored in labelled and numbered containers. All clean-up materials must be considered contaminated and must be stored until treated or disposed. This requirement includes clothing and tools; once these are decontaminated, the wash liquids must be treated as contaminated and then stored.

Contaminated materials should be disposed in an approved hazardous waste disposal facility.

MONS 018616

Section 5

CONCLUSION

TABLE 5-1 gives the synopsis of the recommendations. These recommendations will not prevent the occurrence of accidental fires. They only highlight the additional precautions that will hopefully reduce the threat to humans and the costs to society from contamination by PCDFs.

MONS 018617

Table 5-1

RECOMMENDATIONS

	PREVENTIVE MEASURES	FIREFIGHTING MEASURES	CLEAN-UP MEASURES
Individual Health and Safety	1. Information and Training 2. Identification of Equipment 3. Protective Material 4. Contingency Plan	1. Awareness of PCBs 2. Use of proper Protective Gear 3. Medical Aid 4. Evacuation	1. Information 2. Protective Procedures . area . individual 3. Medical Attention
Equipment and Facilities	1. Programs . operation . maintenance/inspection 2. Safety Systems 3. PCB Management	1. Firefighting Strategies 2. Firefighting Materials	1. Soot Removal 2. Inspection
Environmental Concerns	Containment of: . equipment fluids . contaminants		1. Decontamination 2. Disposal

MONS 018818

Correlation of Transformer/Capacitor PCB Content with Soot Contaminants Generated in a Fire Incident

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Summary

In the paper that I presented at the last EPRI PCB Seminar in Atlanta in December 1983, I made two rather profound statements:

- that the soot produced as a result of PCB transformer/capacitor fires contains the highest concentrations of PCDFs and PCDDs (the latter only if chlorobenzene diluents are present in the askarel mixture) found in the U. S. today.

- that, on a weight basis, however, municipal combustion devices account for the largest quantities of PCDFs and PCDDs produced currently.

I believe that now is the time to adjust one of those statements: upon re-analysis, it becomes apparent that pentachlorophenol (PCP) contains the largest concentrations of PCDFs/PCDDs produced in the U. S. today, which amount to an estimated 70,000 lbs/yr. What is important to note here, however, is the fact that the PCDF/PCDD contaminants are mostly contained in the PCP product.

One might ask what all this has to do with the matter at hand. In this respect, one must be aware that the Agency currently is conducting, under a national dioxin strategy, investigations to identify sites contaminated by dioxin (specifically, the 2,3,7,8-TCDD isomer). To implement this strategy, the Agency has established seven categories or tiers of investigation and study. Tier 4 covers: combustion sources such as municipal and hazardous waste incinerators, PCB transformer/capacitor fires, reactivation furnaces for spent granular activated carbon, boilers using PCBs and PCP-treated wood, etc.

As a result of discussions within the Agency on methods to deal with Tier 4, a special technical group was charged to draft an "Other Dioxins" Strategy, which would cover other PCDDs and PCDFs associated with thermal stresses or fires involving precursors.

Recently, an interim draft health hazard assessment for PCDDs and PCDFs has been prepared. In addition, a draft working paper on how to deal with environmental samples containing mixtures of PCDDs and PCDFs was written. These documents represent the basis for "delisting criteria" as called for in the RCRA amendments signed into law on November 9, 1984. Furthermore, by May 9, 1985, the Agency must list dioxin waste streams as acutely hazardous. Lastly, a recent Environmental Defense Fund/National

MONS 018619

Wildlife Federation Dioxin Petition has been presented to the Agency that concerns all chlorinated and brominated dioxins and furans.

Therefore, the impact of these new RCRA amendments and the EDF/NWF Dioxin Petition upon the final disposition of PCDDs/PCDFs from thermally stressed PCBs is unclear at this time. However, I wish to share this information with you.

I wish to apologize for not having data available from ongoing studies involving the Binghamton, NY, Chicago, IL, Miami, FL, and Columbus, OH incidents. As I said earlier, these samples are currently being analyzed for chlorobenzene isomer and PCB homologue concentrations and an attempt will be made to correlate these results with the PCDD and PCDF content of the soot and transformer vault wipe samples.

Table 1. EPA Dioxin Related Workgroups and Office Affiliation.

Dioxin Disposal Advisory Group (OSWER)
Chlorinated Dioxins Work Group (OPTS)
Dioxin Management Task Force (OSWER)
Tier 4 Dioxin Work Group (OAQPS)
PCB Transformer Fires Work Group (OTS)
RCRA PCB Regulation Work Group (OSW)
"Other Dioxins" Work Group (OTS/OSW)
EDF/NWF Dioxin Petition Work Group (EPA-wide)
ORD Dioxin Team
FIFRA PCP RPAR Work Group (OPP/OGC)
Wood Preserving Industry Work Group (OSW)

Table 2. Polychlorinated (and Polybrominated ?) Toxic Artifacts.

Acronym	Common Name	Number of Isomers	
PCDDs	dioxins	75	
PCDFs	furans	135	
PCBs	biphenyls	209	
PCBPs	biphenylenes	75	caused only by arcing
PCXs	xanthenes	135	
PCPYs	pyrenes	75?	
PCDPEs	diphenylethers		
PCABs	azobenzenes		
PCAOBs	azoxybenzenes		
PCNs	naphthalenes		
PCCYs	crysenes		

MONS 018620

DECONTAMINATING SERVICE EQUIPMENT EXPOSED TO PCB ELECTRICAL FIRES OR PCB LIQUIDS

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INTRODUCTION

This paper focuses on technology to remove PCB liquids and PCB pyrolysis products from otherwise recoverable service equipment installations. The cost-effective removal of such contaminents would permit returning the equipment to operational service. Recent field experience with decon techniques using liquid Freon® solvents indicate that contaminated electrical and mechanical equipment can be safely cleaned and returned to service.

CONTAMINATION SCENARIO

In the event of a fire involving PCB liquids contained in transformers and capacitors, it has been documented that PCB contaminants, pyrolysis products, and smoke and soot residues tend to settle on and contaminate service equipment otherwise not involved in the source fire. This equipment can include electrical switchgear, bus bars, control cabinets and instrumentation, and a facility's heating and cooling system including heat exchangers, motors and blowers. Such equipment has high installed capital value.

Unlike cleaning PCB contaminated floors and walls which is typically approached (depending on the nature of the surfaces) by using water and a selected detergent, and perhaps followed by a solvent wipe, the use of water-based systems to decontaminate electrical and mechanical equipment raises obvious compatibility issues. These include electrolyte formation, moisture retention, corrosion, electrical shorting, construction materials incompatibility, and overall cleaning effectiveness. The latter is particularly significant in trying to remove organic residues from within recessed areas and crevices.

Significant experience exists in removing contamination from within operating machinery such as air compressors and receiving systems. In these instances, PCB lubricants and additives were used for their superior heat and fire-retardant properties. Initial field attempts to remove such internal PCB contaminants used open cycle steam and kerosene approaches and were abandoned in favor of a closed system using a recirculating solvent.

MONS 018621

TECHNOLOGY DESCRIPTION

The basic technology to remove PCB contaminants from service equipment is to apply a spray and flushing action of liquid Freon® TF to the surfaces to be decontaminated. The cleaning action takes place within an enclosed glove-box chamber in which the contaminated item is placed, and then sprayed with a recycled and continuously purified solvent. Solvent vapors and PCB contaminated liquids are contained completely within the chamber, eliminating environmental or operator exposure. Contaminated solvent returns to a reservoir, from which it is pumped through a series of particulate filters and PCB separators using absorbers or distillation.

The purified solvent is then pressurized up to 2000 psi and sprayed 4 gpm on the object. A mechanical refrigeration system is used to control solvent vapor pressure within the cleaning chamber, to "dry" the item after cleaning and also to cool the solvent. The volume of PCB disposal wastes is significantly reduced, being concentrated in filters, adsorbants or as a still bottom. This technology is used extensively within the nuclear utility to remove radioactive scale, dusts and residues from otherwise serviceable equipment.

FIELD DOCUMENTATION

* ONE MARKET PLAZA, SAN FRANCISCO

The removal of PCB smoke and pyrolysis product residues included decontamination of the electrical switchgear located near the transformer vault and also the large (10' high x 15' long) HVAC heating and cooling coils, which ingested the fire's smoke. These were decontaminated in-place. Each object was enclosed within a temporary decon tent and sprayed with Freon® TF. The tent's edges, top and bottom were sealed to control solvent losses; a sump pump returned contaminated solvent from the tent's bottom to the solvent processing equipment. It was found that set-up time took longer than actual decontamination, which each HVAC coil requiring one to three hours to

MONS 018622

clean. While contamination concentration varied with location on the HVAC coils, before and after surface samples showed reductions from over 700 $\mu g/100cm^2$ to less than 10 $\mu g/100cm^2$ and in some instances, to 1 $\mu g/100cm^2$.

- PCB CAPACITOR CASE DECONTAMINATION

As an alternative to shredding and incineration, the metal cases from PCB capacitors are conveniently sectioned and the surfaces exposed to a high velocity spray of Freon® TF. Initial surface concentration is essentially that of the PCB dielectric fluid; after decontamination, the PCB concentration on unpainted steel was reduced to below 9 $\mu g/100cm^2$. The sealed cleaning chamber and solvent processing steps used were very similar to that previously described.

Additional applications include "tenting" whole sections of control room panels containing instruments and annunciators, with decontamination proceeding as described for the electrical switchgear. Virtually all of the interior surfaces of the control room were variously contaminated with PCB soot and pyrolysis products.

SUMMARY

In situations involving high value service equipment which becomes contaminated as a result of a PCB fire, spill or prior PCB use, an effective technique has been developed to remove such contamination to acceptable levels without consequential degradation or potential damage to such equipment. Further, the waste volumes generated using a solvent based system are a fraction of that generated by water and detergent approach. There are applications, however, such as contaminated masonry and concrete, where solvent use is unadvisable due to adsorptive losses.

MONS 018623

PART 5:

RISK ASSESSMENT

VICTOR NIEMEYER - MODERATOR

The Binghamton State Office Building

Nancy K. Kim, Ph.D. and George Eadon, Ph.D.

The tallest building and most prominent landmark in Binghamton, a city of some 60,000 people in southeastern New York, is the 18-story State Office Building. On February 5th, 1981, an intense fire occurred in the electrical switching equipment in the basement mechanical room of the building. The switching equipment was located adjacent to two electrical transformers filled with a non-flammable insulating compound. Sixty-five percent of this material consisted of polychlorinated biphenyls (PCB-1254) and 35 percent was chlorinated benzenes.

The heat from the fire cracked a ceramic bushing on one of the transformers and about 180 gallons of the insulating oil sprayed onto the floor and into the hot switchgear. The fire produced a fine soot that spread up the open vertical chase that carried exhaust from the men's room on every floor and thence throughout every floor of the building.

Immediately following the fire and before the extent and nature of the toxic contamination became known, more than 300 people reentered the building to help with the cleanup or to retrieve documents and personal effects. A cleanup effort was begun involving State workers and employees of a private firm. Three weeks after the fire, on February 26, the extent of the toxic contamination was discovered.

Analysis of soot samples recovered from the building revealed high concentrations of PCBs and the presence of polychlorinated dibenzofurans, dibenzo-p-dioxins and biphenylenes at lower concentrations. These chemicals were apparently formed by the pyrolysis of the PCBs and chlorinated benzenes that leaked from the transformer. The highly toxic compounds 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) were present; duplicate analyses gave concentrations of 2.9, 2.8 and 273, 124 ppm, respectively (1). The building was closed and secured; the decision was made to engage the services of a firm with specialized knowledge in the field of toxic removal and cleanup.

On April 1, 1981, the State Office of General Services hired Versar, Inc., of Springfield, Virginia, to oversee the planning, preparation and conduct of the cleanup operations. A 14-member panel of scientific experts who are not associated in any way with New York State government and who are knowledgable in the area of epidemiology, medicine, and toxicology, was convened and held its first meeting in April, less than two months after the fire.

After careful study, including extensive sampling and analysis of various components, materials and surfaces to assess levels and patterns of contamination, a plan was generated and implemented to decontaminate the building. A systematic combination of removal/disposal and cleaning has been conducted under a stringent health and safety program. The goal is to achieve levels of cleanliness prescribed by the panel of expert scientific advisors. The panel has reviewed and approved the State standards for ventilating the building, for working and protective devices, and for reoccupancy. They also approved the plan of medical surveillance of persons exposed to the soot.

MONS 018625

To give you an idea of the extent of the cleanup effort, through February of this year solid waste disposal from the site reached a total of 4,676 cubic yards of material. This material filled 1,464 barrels which were buried in an approved secure landfill site. All of the furniture in the building was removed, destroyed and buried, and will have to be replaced.

Contamination of the air around the building has been prevented during the cleanup by routing all exhaust air from the building through air pollution control units that were installed on the roof. These units have special filters that trap PCBs and other toxic chemicals. No untreated air will be released from the building until the air is so clean that people cleaning and restoring the building can work safely without using respirators.

The target date for reopening the building is next summer by which time the cost of the cleaning operation is estimated at close to $22 million, which exceeds the building's original cost of $20 million. Estimates of the cost of tearing down the building, safely disposing of the contaminated materials, and building a replacement building reached as nigh as $100 million.

Reoccupancy is based on an exposure assessment carried out by the Bureau of Toxic Substance Assessment of the New York State Department of Health. The clean-up workers will no longer need to use respirators when it can be demonstrated that the level of contaminants in the air of the building results in a toxicity less than that which would result from the presence of 14 pg/m^3 2,3,7,8-TCDD equivalents. This corresponds to the expert advisory panel recommendation that the building not be reoccupied until exposure by all routes to the toxic chemicals be limited to a level no greater than that which would result from ingestion of 2 picrograms of 2,3,7,8-TCDD equivalents per kilogram of body weight per day.

For 2,3,7,8-TCDD, a no-observed-effect level of 1 nanogram/kg-day (1 x 10^{-9} g/kg-day) in rats has been reported in both a three generation reproduction study (2) and a two year oncogenic study (3). The uncertainty factor of 500 between this NOEL and the recommended 2 pg/kg-day daily intake for humans was considered appropriate by the expert advisors.

We have developed and adopted a concept of "2,3,7,8-TCDD equivalents" as a measure of the effective toxicity of all chemicals present in the Binghamton State Office Building. This parameter is utilized as the determinant for assessing exposure and risk. The algorithm for calculating this equivalent incorporates factors for the relative toxicity of individual compounds.

The 2,3,7,8-TCDD equivalents concept was developed because the only PCDD and PCDF compound studied extensively for its toxic effects is the 2,3,7,8-TCDD isomer; hence, risk assessment is only feasible for that compound. The equivalents concept can be used to estimate risks from exposure to mixtures, if synergism or antagonism are not major factors. An additional assumption is that data from short-term toxicity studies can be used to extrapolate to long-term toxic effects.

The toxicity of the soot of the building, expressed in terms of 2,3,7,8-TCDD equivalents, was measured by scientists associated with the Wadsworth Center for Laboratories and Research of the State Health Department. The oral LD50s of the soot, its benzene extract, and 2,3,7,8-TCDD, each administered to female guinea pigs in aqueous methyl cellulose, were found to be 610 mg of soot/kg, 327 mg of soot equivalent/kg and 19 ug of 2,3,7,8-TCDD, respectively. If the soot had contained only 58 ug of 2,3,7,8-TCDD/g of soot, its extract would be predicted to exhibit an LD50 of 327 mg soot equivalents/kg b.w. Therefore, the "2,3,7,8-TCDD equivalent" contamination of the soot is 58 ug/g (4).

MONS 018626

The chemical analysis of the soot can also be used to "predict" the "2,3,7,8-TCDD equivalent" concentration of the soot, based on the known toxicities of the components. This is a complicated task since no data are available on the LD50s of dibenzofurans in guinea pigs other than 2,3,7,8-tetra CDF and since very limited data are available on the PCDDs (5). The following assumptions are made about the LD50s of these compounds: (1) The ratio of the LD50s of a particular PCDF congener and 2,3,7,8-tetra CDF will be the same as the ratio of the LD50s of the correspondingly substituted PCDD congener and 2,3,7,8-TCDD. There is no direct experimental data to support this assumption. (2) The LD50s of PCDFs and PCDDs lacking chlorines on all four lateral positions will be sufficiently high that their influence can be ignored in this calculation. This assumption is based on the LD50s in guinea pigs of 2,8-diCDD, 2,3,7-triCDD, and 1,2,4,7,8-penta-CDD. All have LD50s more than 450 times higher than that of 2,3,7,8-Tetra CDD itself. (3) Introduction of a single additional chlorine substituent on a 2,3,7,8-substituted congener has essentially no effect on the congener's guinea pig LD50. This assumption is based on comparison of the LD50s of 2,3,7,8-TCDD and 1,2,3,7,8-tetra-CDD. (4) Introduction of two additional chlorine substituents on a 2,3,7,8-chlorinated congener raises its LD50 by a factor of at least 29. The assumption is based on comparison of the LD50s of 1,2,3,4,7,8-, 1,2,3,6,7,8-, and 1,2,3,7,8,9-hexa CDD and 2,3,7,8-tetra CDD. (5) The LD50s of compound with more than 6 chlorines will be sufficiently large that their influence can be ignored in this calculation. This assumption is based on comparison of the LD50s of 1,2,3,4,6,7,8-hepta CDD and 2,3,7,8-tetra CDD.

These assumptions require that attention be focussed only on the tetra, penta, and hexasubstituted PCDDs and PCDFs. The concentration of 2,3,7,8-TCDF in the sample used in animal experiments was measured at 48 ppm; since the LD50 of 2,3,7,8-tetra CDF is about three times that of 2,3,7,8-TCDD, this is equivalent in terms of acute toxicity to a 2,3,7,8-TCDD concentration of ca. 16 ug/g. Based on assumption (2), other tetra CDFs can be neglected in this calculation. The penta CDFs were measured at 120 ug/g. If 1,2,3,7,8- and 2,3,4,7,8-penta CDF together constitute 50% of the penta CDFs and if their LD50s are equal to that of 2,3,7,8-TCDF, this is equivalent in terms of acute toxicity to a 2,3,7,8-TCDD concentration of ca. 20 ug/g. Based on assumption (2), other penta CDFs can be neglected in this calculation. The hexa CDFs have been measured at 70 ug/g. The isomers believed to have the lowest LD50s (1,2,3,4,7,8-, 1,2,3,6,7,8-, and 2,3,4,6,7,8-hexa CDF) are expected to comprise 50% of the total hexa CDF mixture. Since, based on assumption (4), their LD50s are 29 times higher than that of 2,3,7,8-TCDF, this is equivalent to a 2,3,7,8-TCDD concentration of 0.4 ug/g. Thus, the PCDFs are calculated to constitute a "2,3,7,8-TCDD equivalent" concentration of 36 ug/g.

The concentration of 2,3,7,8-TCDD itself has been measured at 1.2 ppm in this sample. Other tetrachlorinated dibenzodioxins are predicted to have much higher LD50s and can be ignored. The concentration of other PCDDs in this sample are unknown, but are likely to be comparable to the TCDDs. Thus, the dioxins as a whole probably have a negligible influence on the soot's "2,3,7,8-TCDD equivalent" concentration.

Stalling (6) has reported on the presence of polychlorinated biphenylenes in a soot sample from BSOB; he cites unpublished results by Dr. Alan Poland that suggests that the toxicity of the 2,3,6,7 congener is comparable to that of 2,3,7,8-tetra CDD. If Stalling's ratio of biphenylene to dibenzofuran is (.067) is assumed to hold for all of these compounds and if it is assumed that the biphenylenes have acute oral toxicities three times that of the corresponding dibenzofurans, it can be calculated that the biphenylenes will contribute about 0.2 times as much "2,3,7,8-TCDD equivalent" activity as the dibenzofurans. Thus,

MONS 018627

to a very crude approximation, the polychlorinated biphenylenes account for a "2,3,7,8-TCDD equivalent" concentration of 7 ppm.

In summary, using the known concentration of chlorinated dioxins, furans and biphenylenes in the soot and making certain assumptions about their toxicity as compared to 2,3,7,8-TCDD, the toxicity of the soot was calculated to be approximately 44 ppm of 2,3,7,8-TCDD equivalents. This value closely correlates with the observed value of 58 ppm.

In September we began the first of three rounds of air sampling to determine whether the cleanup, which is now substantially complete for floors 2 through 18 of the building, has reduced the level of toxic contaminants sufficiently to allow workers to remove their respirators and to allow untreated air to be vented from the building. The air samples will be analyzed by two different laboratories. When these results are available, the 2,3,7,8-TCDD equivalents will be calculated and compared to the re-entry criteria.

MONS 018628

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MONS 018629

PCB EXPOSURE ASSESSMENT AND SPILL CLEAN-UP

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INTRODUCTION

Continued arguments for and against the accelerated removal of PCB's from use in utility electrical equipment have generated a number of issues:

1. Which equipment locations are likely to produce significant exposures should a spill occur?
2. How effective are different spill clean-up and containment alternatives in reducing potential exposure levels?
3. What are the potential health hazards associated with available retrofill and replacement alternatives?
4. What are the health hazards associated with PCB residues remaining at substations, storage areas and old spill sites?

The PCB Spill Exposure Assessment Methodology was developed to help the electric utility industry address these issues.

PCB SPILL EXPOSURE ASSESSMENT METHODOLOGY

The PCB Spill Exposure Assessment Methodology is a quantitative framework for estimating general public exposure levels associated with spills (1). The methodology consists of four basic steps: 1) characterization of the spill in terms of the quantity of fluid released, its composition and the areal extent of contamination; 2) simulation of PCB transport and fate to obtain on-site and off-site environmental concentrations; 3) characterization of potential receptors in terms of their location and number; and 4) combination of environmental concentrations with receptor characteristics to obtain exposure levels.

MONS 018630

The core of the methodology is the PCB On-Site Spill Model, POSSM. POSSM simulates daily changes in on-site environmental concentrations and losses from a spill site via volatilization, leaching and runoff/erosion. Key hydrologic and physical/chemical processes (see Figure 1) are simulated for spills on both soils and impervious surfaces (i.e., asphalt and concrete). POSSM is a modified version of the Pesticide Root Zone Model, PRZM (2), a numerical (finite difference), chemical transport model developed by the EPA for use in evaluating pesticide transport and fate in soils.

Off-site PCB concentrations in air, surface water or ground water are simulated with three relatively simple, analytical models:
PTDIS - A Gaussian plume dispersion model capable of estimating airborne concentrations at any distance downwind from a source (3).
RIVLAK - A contaminant transport model that can estimate concentrations in a river or along the near-shore region of a large lake (4).
GROUND - A contaminant transport model that can estimate concentrations in a saturated ground-water system or loadings of chemical to a near-by river (4).
As Figure 2 illustrates, volatilization, runoff/erosion and leaching losses predicted by POSSM are input to PTDIS, RIVLAK, and GROUND, respectively. Chemical loadings to a river predicted by GROUND are input to RIVLAK. POSSM and the three off-site models represent a flexible capability for evaluating a broad range of spill conditions.

EXPOSE, a computer program that combines predicted environmental concentrations with receptor characteristics, is also incorporated into the methodology to facilitate exposure calculations (1). The program is applicable to a number of potential exposure routes, including inhalation, ingestion (water, soil and foodstuffs), and dermal contact (water and soil).

CAPACITOR SPILL EXPOSURE ANALYSIS

Exposure levels associated with different strategies for the clean-up of a hypothetical capacitor spill were estimated with the PCB Spill Exposure Assessment Methodology. The spill conditions analyzed were for the complete rupture of a pole-mounted capacitor containing 1.5 gal of Aroclor 1242. Fluid sprayed from the capacitor was assumed to contaminate an area of 250 sq. ft. Two different types of residential spill sites were examined: 1) a site composed of 50 percent grass and 50 percent asphalt and 2) a site composed of 50 percent grass and 50 percent vegetable garden; these sites will be referred to as Residential Areas 1 and 2, respectively. The soil at the spill site is a silt-loam and the depth to ground water is 5 ft.;

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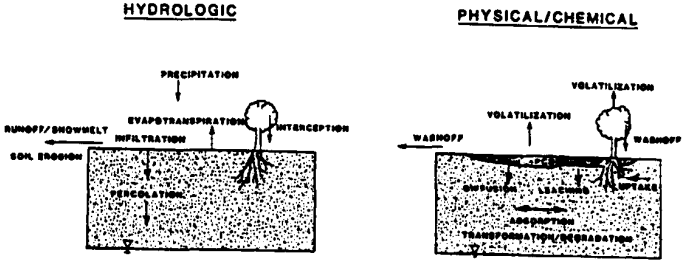
SOIL SURFACES



IMPERVIOUS SURFACES

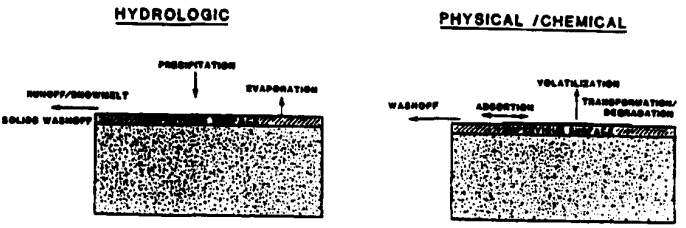


Figure 1. Key hydrologic and physical/chemical processes simulated by POSSM.

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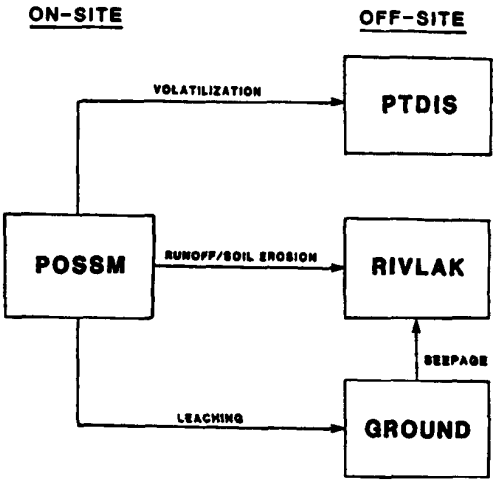

Figure 2. Interfaces Between POSSM and the Off-Site Models

MONS 018633

there is no surface water in the vicinity of the spill site. Climatic conditions representative of those for Chicago, Illinois were used.

Different clean-up strategies were also examined. They included a one time clean-up either 1 day or 14 days after the spill. A clean-up strategy involving a succession of three clean-up efforts which incrementally reduce PCB levels was also examined. This strategy was meant to represent a practice used by some utilities wherein the visible signs of the spill are removed followed by sampling and analysis. Subsequent clean-up/sampling efforts are conducted until PCB concentrations are below a prescribed limit. Reclamation of both spill sites was assumed to occur through the placement of a clean soil and sod cover 30 days after clean-up. Table 1 summarizes clean-up levels and the timing of clean-up for each strategy.

Table 1
CLEAN-UP LEVELS AND TIMING OF CLEAN-UP

	Clean-Up Level		
	Soil	Asphalt	Timing
Strategy	(ppm)	(ug/100 sq cm)	(days)
1	1	10	1
2	1	10	14
3	50	100	1
4	50	100	14
5	500	-	1
	100	-	9
	50	100	19

Predicted PCB losses for Residential Area 2 are summarized in Table 2. These results are totals for the four year period following the spill. Of the possible loss mechanisms, volatilization is the most significant. Runoff/erosion losses are negligible, and no leaching to ground water occurred. Predicted volatilization losses for Residential Area 1 were slightly greater mainly because a portion of the capacitor fluid was spilled on asphalt. Asphalt will produce higher volatilization losses because it is generally warmer than soil or grass.

MONS 018634

Table 2

PREDICTED PCB LOSSES FROM RESIDENTIAL AREA 2

(Losses as a fraction of total amount spilled)

Strategy	Volatilization	Runoff/Erosion	Leaching	Clean-Up	Remaining
No Clean-Up	0.823	0.001	-	-	0.176
1	0.024	0.000001	-	0.976	0.0001
2	0.188	0.00001	-	0.812	0.0003
3	0.028	0.00004	-	0.966	0.006
4	0.192	0.00004	-	0.802	0.006
5	0.042	0.00006	-	0.952	0.006

The other major loss of PCB was spill clean-up. The clean-up strategies evaluated accounted for 80.2 to 97.6 percent of the total amount spilled on Residential Area 2. Similar clean-up losses were found for Residential Area 1. As Table 2 shows, the quantity of PCB remaining at the end of the four year period was less than 1 percent of the amount spilled for all of the clean-up strategies.

Cumulative exposure levels were calculated for the inhalation, dermal contact and ingestion pathways. Two different receptors were assumed to reside near the spill site. The first was a child that plays on the spill site 6 hours per day, 150 days per year. The second was an adult who works in the garden 6 hours per day, 75 days per year. Exposure resulting from dermal contact with contaminated soil was estimated for both receptors; exposure due to the ingestion of contaminated soil was estimated for the child only. Inhalation exposures were estimated for both receptors assuming their residence was located different distances up to 100 m downwind from the site.

Figure 3 shows calculated inhalation exposure levels as a function of distance for an adult residing near Residential Area 2. These results show that exposure levels decrease by an order of magnitude as the adult moves from the spill site to a distance of 100 m. They also show that exposure levels do not decrease linearly with clean-up level. That is, a 50-fold decrease in clean-up level (from 50 ppm to 1 ppm) does not produce an equivalent decrease in exposure.

Decreasing the clean-up response time from 14 days to 1 day reduces inhalation exposure levels by almost an order of magnitude. This reduction is much greater than that associated with reducing the clean-up level.

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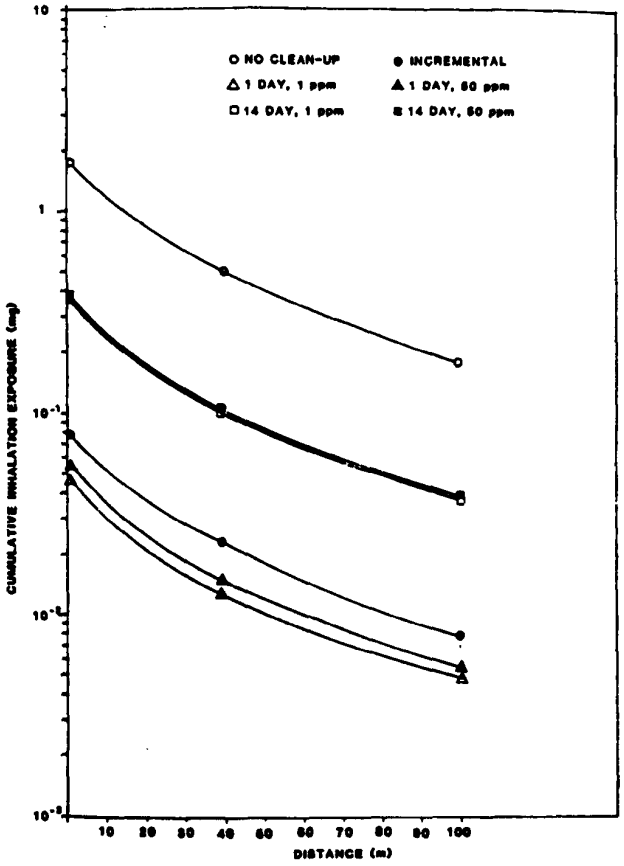

Figure 3. Cumulative Inhalation Exposure Levels as a Function of Distance for Residential Area 2

MONS 018636

The variation in cumulative inhalation exposure with time is shown in Figure 4 for an adult receptor located 100 m downwind from Residential Area 2. Cumulative exposure levels for all five clean-up strategies level off after the first month indicating that most of the exposure occurs just after the spill. Also shown on this figure are cumulative exposure levels assuming no clean-up and for continuous exposure to current, measured PCB air concentrations in urban areas (5). The latter shows that exposure to background exceeds that for each of the clean-up alternatives within a few months following spill clean-up.

The degree of access to a spill site can also affect exposure level. Table 3 lists calculated dermal contact exposure levels for the child assuming three different types of access: 1) complete access before and after spill clean-up (total access); 2) access after spill clean-up but before site restoration (limited access); and 3) access only after spill clean-up and site restoration (no access). These results show that exposure levels can be reduced by one to three orders of magnitude when access to the site is controlled or prevented.

Table 3

CUMULATIVE DERMAL EXPOSURE FOR THE CHILD ON RESIDENTIAL AREA 1

(Exposure in milligrams)

	Level of Access		
Strategy	Total	Limited	None
No Clean-Up	400.0	-	-
1	0.44	0.015	0.0072
2	9.4	0.018	0.0080
3	1.1	0.70	0.28
4	10.0	0.64	0.26
5	2.8	1.1	0.28

Based on the results of the exposure analysis, several observations can be made:

1. Most of the PCB was lost from the spill sites through volatilization over the four years that were simulated; no PCB leached to ground water and losses via runoff and soil erosion were insignificant.
2. Reducing spill clean-up levels from 50 ppm to 1 ppm does not produce an equivalent reduction in exposure levels.
3. The immediate clean-up of a spill can lead to reduced exposure levels.
4. Limiting receptor access to the spill site until reclamation has been

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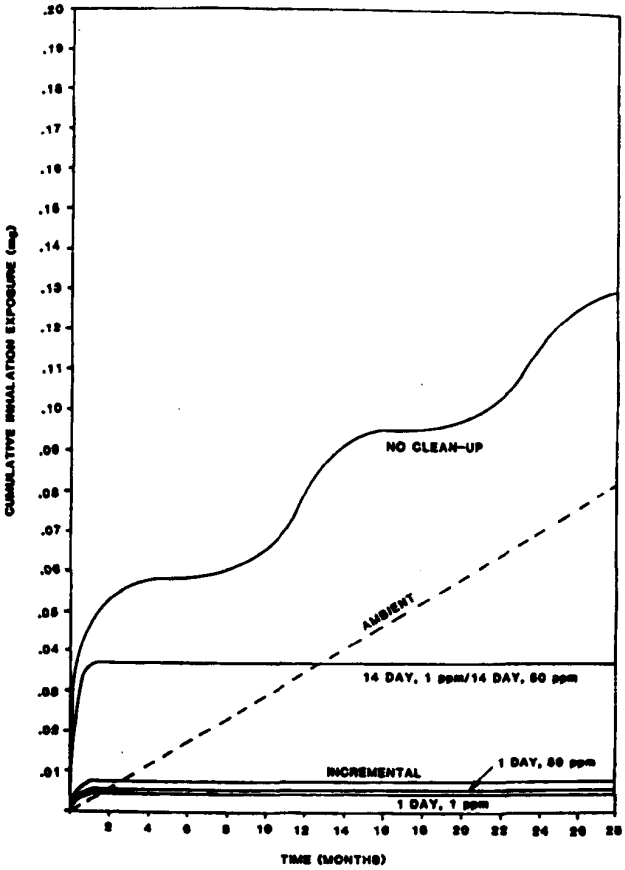

Figure 4. Variation in Cumulative Inhalation Exposure with Time at 100 m for Residential Area 2

MONS 018638

completed can reduce exposure levels by one to three orders of magnitude.

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MONS 018639

UTILIZATION OF QUANTITATIVE RISK ASSESSMENT
Techniques in the Development of Decontamination Standards
(A Case Study - San Francisco, California)

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Determination of what constitutes safe levels of exposure to a "hazardous" material is difficult, often due to the lack of scientific consensus as to what constitutes a non-effect level for both acutely toxic materials and materials with chronic health effects. This is true for both materials for which there are established permissible exposure levels (PEL's) and even for those with regulatory defined standards. For materials with well defined acute toxicities, questions as to what is safe center around actual and potential exposure levels. These questions can be resolved with the use of environmental sampling and analysis. Controversies then surface as to the use of which standards - occupational exposure standards vs environmental standards.

For "hazardous" materials with the potential for human chronic health effects such as irreversible hepatoxicity and neurotoxicity, teratagenicity, reproductive effects, genotoxicity and carcinogenicity, there is less scientific consensus as to the potential and/or potency of a given material to produce one or all these effects. Considerable uncertainty exists as to the effects of a number of materials since they haven't been subjected to any form of chronic study bioassays. For many materials only one conger or isomer of the material has been tested, thus leaving open to speculation the effects of sterochemistry on toxicity. Uncertainty almost always exists as to the slope of dose/response relationships as higher doses are extrapolated to lower doses.

These factors are especially relevant when addressing questions of risk and decontamination standards for PCBs, (polychlorinated biphenyls), PCDFs (Polychlorinated dibenzofurans) and PCDD (Polychlorinated dibenzodioxins).

On May 15, 1983, a fire occurred within an Electric Utility vault in downtown San Francisco. This fire went unchecked for approximately three (3) hours. The fire and resulting explosions generated considerable quantities of black smoke which contained PCBs and PCDFs. These materials contaminated both the exterior of the building as well as some areas inside the building. The building was closed by the building owners on advise from state and local health authorities, with entry

MONS 018640

defined the areas contaminated and areas that would need to be decontaminated prior to employee reentry.

Major questions to be addressed centered around when decontamination efforts could be terminated and employees allowed to reenter the building without their experiencing any significant increased risk as a result of exposure to residual PCBs and PCDFs.

The San Francisco Health Department in coordination with the State of California Department of Health Services undertook the task of establishing these reentry guidelines. What follows is an outline of the process of logic used in this Risk Assessment and Risk Management exercise.

The first task was to define in quantitative terms the toxicity of the PCBs and TCDFs. The second major task was to evaluate real and potential exposure levels for people reentering the building. Risks could then be calculated from the above information. Risks are a function of toxicity (X) exposure.

Conversely, once acceptable levels of risk are defined and opportunities for exposure are quantified (i.e.) forty (40) years work in building, inhalation rates, dermal penetration rates, areas of dermal contact, etc., then calculations as to permissible exposure levels and resulting doses could be derived.

The first step was to evaluate the toxicity data on PCBs and PCDFs. Table (1) shows this information. At this point, numerous assumptions had to be made, such as: since there has been no long term bioassays on TCDFs, its chronic toxicity had to be evaluated relative to its potency of acute effects in relationship to TCDD[1]. Another assumption was made regarding the similar biological activities given structural similarity of the two compounds[2] [3].

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MONS 018641

Given the relative toxicity of PCDFs and PCBs, the driving force in all these risk assessments were the PCDFs.

Table (2) - shows the NOEL (non-observed effect levels) in animal studies for TCDDs/TCDFs; using $1X10^{6}$ excess acceptable risk of cancer as a guideline[4]. Since the bioassays indicated carcinogenicity as the greatest biological potency of TCDDs and TCDFs, total daily allowable intake would be 2 pg/kg/day.

Thus, one would expect no more than one excess case of cancer if you were to allow $1X10^{6}$ people in this building for 250 days/year for forty (40) years if everyone got 2 pg/kg/day TCDD or TCDF.

Once these upper limits are defined, assessments can be made as to permissible environmental levels that would result in exposures and doses not to exceed 2 pg/kg/day TCDD or TCDF.

In making the transition from environmental exposure to accumulated dose, additional assumptions were made:

1. All TCDFs and PCBs that are respired are retained and are available for absorption.
2. The average employee at One Market Plaza weighs 50 KG_2 for worst case estimates, and a 65 KG_2 for most plausible case estimates.
3. The maximum possible exposure period is for forty (40) years at 8 hrs/day for 250 days/yr (Case A) (worst case) and 20 years at 8 hrs/day 24 hrs/yr for Case B (most plausible).
4. The building will maintain constant air levels of TCDFs throughout its useful lifetime for Case A and purge itself with a half life of five (5) years as a first order exponential decay for Case B.
5. Average adult inhales approximately 20 m^3 of air per day (24 hours).
6. Limited access areas are defined as places where access does not occur any more than 2 hrs/month average.

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[4] California Department of Health Services (DHS) cancer identification policy: A Statement of Science as a Basis of Policy. Section 1 - considerations used in evaluation of qualitative evidence for carcinogenicity; methods for identifying carcinogens; Berkeley, CA 1982.

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Based on an acceptable risk factor of $1X10^{6}$ of an additional case of cancer above background (each of us has a .25 chance of getting cancer) the following environmental exposure levels were estimated:

1. Office environments:

A.	Total CDDs/CDFs in air	10 pg/m^3
B.	Total CDDs/CDFs on surfaces	3 ng/m^2
C.	PCBs in air	1.0 $\mu g/m^3$
D.	PCBs on surfaces	100 $\mu g/m^2$

2. In areas of limited access:

A.	Total CDDs/CDFs in air	80 pg/m^3
B.	Total CDDs/CDFs on surfaces	24 ng/m^2
C.	PCBs in air	1 $\mu g/m^3$
D.	PCBs on surfaces	1000 $\mu g/m^2$

A summary of the logic that went into determination of these numbers is as follows:

Using a $R=1X10^{-6}$ assumption non-effect daily permissible level of exposure, calculations were done for inhalation, dermal and ingestion. 2.0 pg/kg/day (PCDF) was used as an upper limit, both worst case and most plausible exposure opportunities where calculated as follows:

Air-Inhalation:

Employee inhales approximately 7 m^3 air/8 hr shift.

50 kg person, 2.0 pg/kg/day upper exposure limit = 100 pg/day.

Approximately 10-14 pg/m^3 maximum intake.

If hours worked in area environment - 2 hrs/month.

$$\frac{7\ m^3}{8\ Hrs} \times 2\ Hrs = 1.75\ m^3$$

MONS 018643

If 50 Kg person $\frac{100\ pg/day}{} = 57\ pg/m^3 = 1.75$

For 70 kg/male wkrs. $57/pg/m^3 \times \frac{70\ Kg}{50\ Kg} = 80\ pg/m^3$

For dermal absorption the logic was as follows:

50 Kg woman = 154 cm average height

Average surface area (S) = $1.46m^2$

Dermal exposure:

Arms = approximately 20% of Total Body Surface = $.292\ m^2$

If 50% of exposed arm surface contacts contaminated surfaces (desks, walls, etc.) = $.146m^2$ of arm wipes the contaminated surface.

If 10% of contaminant material is absorbed through skin; skin equivalent = $.0146\ m^2$.

Using the same total, not to exceed, non-effect maximum of 2.0 pg/kg/day, a determination of 3 ng/m^2 was made for the office 8 hr/day exposure areas and 24 ng/m^2 for areas of exposure 2 hrs/month.

For these risk assessments, regulatory agencies usually make the most conservative (Public Health) protective assumptions. It should be recognized that a number of assumptions are made in these analyses and that these assumptions significantly effect the outcome. These guidelines should be considered as just that and not a firm number. Given the levels of uncertainty involved, the results can be off by factors of 10 to 100.

MONS 018644

Table I

Comparison of the Biological Activities of
2,3,7,8 -TCDD and 2,3,7,8 -TCDF

Species/Effect	Response[1] TCDD	TCDF	Remarks
Laboratory animals			
Lethability			
Acute Oral LD_{50}			
Guinea Pig	0.006 µmol/kg (2 µg/kg)	0.016-0.032 µmol/kg (5.2-10 µg/kg)	Guinea Pig is the most sensitive species
Mouse	0.88µmol/kg (0.28 mg/kg)	19.6 µmol/kg 6.3 mg/kg)	LD_{50} of TCDF is 2-4 fold higher than that of TCDD in Guinea Pig
Lymphoid atrophy Thymus, spleen	+	+	
Progressive body weight increase	+	+	
Acne/alopecia	+[2]	+[2]	
Porphyria	+[3]	+[3]	

MONS 018645

Enzyme induction AHH[4]	+	+	Potency TCDD = 100 TCDF = 67
Cytosolic binding	+	+	Affinity TCDD = 100 TCDF = 37
Hepatoxicity	+	+	
Embryotoxicity	+	ND	
Teratagenicity	+	ND	
Reproductive effects	+	ND	
Genotoxicity	+/-	-(limited)	
Carcinogenicity	+	ND	
Human			
Acne/alopecia	+	+	
Hepatoxocity	+	ND	
Porphyria	-	-	
Neurological/ psychiatric	+	ND	
Chloracne	+	PCDF[5]	

(1) + = positive, - = negative, ND = no data.

(2) Positive in monkey; negative in rat, mouse, guinea pig, chicken.

(3) Positive in rat, mouse, chicken; negative in guinea pig, monkey.

(4) AHH=aryl hydrocarbon hydroxylase. The presence or inducibility of of AHH is associated with the detoxification or activation of polycyclic aromatic hydrocarbon in chemical carcinogenesis. Data suggested thet this enzyme plays a major role in the susceptibility to carcinogenesis induced by 3-methecholanthrene and benzo(a)pyrene.

(5) PCDF = polychlorinated dibenzofurans.

MONS 018646

Table II

Animal No Observed Effect Levels And
Suggested Permissible Levels[1] Of TCDD/TCDF For Humans

Adverse Effect	NOEL (Animal Data)[2]	Permissible Human (50-kg) Exposure Levels
Chronic toxicity	1.0 ng/kg/day	100 pg/day
Embryotoxicity	30 ng/kg/day	3,000 pg/day
Reproductive Effects	1.0 ng/kg/day	100 pg/day
Teratagenicity	100 ng/kg/day	10,000 pg/day
Carcinogenicity	----------	2 pg/day[3] 100 pg/day[4]

MONS 018647

The Use of Analytic Models in Regulatory Risk Managment Analysis of PCB Equipment

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This paper focuses on how formal risk management methodologies, typically implemented as computer programs can aid the process of discussing and ultimately making decisions concerning risks to human health or to the environment.

Many different types of studies and analytical techniques are used to assist decision makers concerned with risks to human health. Toxicology studies quantify the effects of the substance of concern on humans or ecological groups with dose-response functions. Exposure assessment characterizes the pathways and quantities of exposures that the population of concern may experience. Risk assessment combines information on toxicity and potential exposure, typically at their upper bounds, to provide a measure of an issue's merit as a matter of concern. Cost analyses focus on the cost of different measures to reduce exposure which, when combined with the changes in exposure that those measures bring about, gives a means of ranking those measures by their cost effectiveness. These studies and techniques contribute to the decision making process by providing information about different facets of the problem. None, however, addresses the decision as a whole.

Risk management models can contribute to the process of discussing and making decisions concerning risk. They do this by organizing information from diverse sources into a single consistent framework that is oriented toward providing insights about the specific decision alternatives.

In this paper we discuss the contribution of risk management models in the context of an application to risks from fires involving PCB transformers. The specific model, known as the Transformer/Capacitor Risk Management Model (TRIM), consists of an analytic framework for evaluating alternative PCB-controlling decisions that have been implemented in the form of a computer program.

Making decisions concerning risks is a often difficult undertaking for either a utility or a regulatory agency..

- The stakes can be high in terms of human health, ecological effects, cost of control (a priori), and cost of cleaning (ex-post) after failure or accident.
- There are typically many different parties with a stake in the decision and therefore interested in reviewing the analysis.
- There are frequently many alternative courses of action for controlling the risks.
- Information and judgement are needed from diverse scientific disciplines to estimate the costs and benefits of alternatives.
- The uncertainties in the existing information are often very great.
- Implicitly or explicitly, the decision maker must make difficult trade-offs between the level of risk and cost.

MONS 018648

Risk management models can aid the process of reaching decisions about alternatives to control risks in the following ways:

First, risk management models provide a decision context to guide the analysis. Because the ultimate pay-off of risk management analyses is in providing insights for ranking decision alternatives, models that estimate the bottom-line concerns (i.e., risks to health, environmental effects, and costs) help to keep the analysis focused on what really matters. What should be important to the decision maker is not whether exposures are possible or that the material in question can cause health effects. What should be important is whether specific policies change the number of people exposed or reduce the amount of exposure sufficiently for the reduction in expected health effects to warrant the cost of the policy. Risk management models can integrate the available information in a form that is useful for decision making.

Second, risk management models can provide a common framework for discussion among the participants of the decision making process. They provide a mechanism for making the structure of the issues and the quantitative assumptions driving the results explicit and available for scrutiny by all parties. They can also be used to trace the basis for results through the intermediate calculations. If the participants can "show their work" it is easier to focus subsequent discussions on where they differ.

Third, having a risk management model that is implemented as a computer program can result in a better quality of analysis. Because such a model can perform its calculations quickly, it permits the user to conduct sensitivity analyses to help identify critical parameters that deserve more attention in the analysis. The computer's speed also permits explicit consideration of uncertainties with probabilistic analysis. These two aspects permit the user to conduct a more thorough analysis. Having a risk management model in computer code also permits easy correction or revision of assumptions and helps assure computational accuracy.

The Transformer/Capacitor Risk Management Model (TRIM) is model that provides these capabilities for analysis of alternatives for managing risks from PCB-containing electrical equipment. TRIM was developed through the sponsorship of EPRI Research Project No. 2595 by Decision Focus Inc. It was subsequently applied by the Utility Solid Waste Activities Group (USWAG) in response to an EPA rulemaking concerning risks from fires involving PCB transformers in buildings [1,2]. EPA has since acquired the model, as have several utilities interested in performing risk management studies for their service territories.

The model consists of equipment, incident, exposure, ecological effects and health effects submodels integrated into a comprehensive analytical tool to evaluate the costs and benefits of risk management options. The model's structure allows it to represent decisions affecting the replacement of PCB-containing equipment, chances of accidental releases, and amount of human exposure during and after incidents. These decisions influence the 1) number and severity of incidents, 2) number of people and amount of exposure to PCB's and other substances, 3) ecological effects, and 4) number of potential severe health effects resulting from the human exposures.

The equipment use and replacement submodel provides a detailed inventory of the PCB equipment under consideration at any time, given a particular regulatory environment. The model tracks equipment use in various locations and accounts for units being taken out of service and different units being installed. It also calculates the costs of phasing out and replacing equipment, and of any special risk management activities that cut the rate of occurrence of incidents.

MONS 018649

The spill/accident incident submodel specifies the amount of PCB material released during different types of incidents defined by the user; the frequency of occurrence of these incidents; the production of byproducts (such as polychlorinated dibenzofurans - PCDFs and polychlorinated dibenzodioxins - PCDOs) during the incidents, if any, and the residual concentration of the material after cleanup.

The human exposure and deposition submodel calculates both the number of people exposed and the average lifetime deposition for user-specified population groups possibly exposed to PCBs and by-products, for each of the substances of concern, for each of the several types of incidents in various locations. Exposure is calculated both for the short period during the incident and cleanup and for multiyear periods after cleanup is complete.

The ecological impacts submodel calculates the damage to the environment stemming from the accidental releases calculated in the incident submodel.

Finally, the human health effects submodel, calculates the occurrence of potential serious health effects due to exposure to PCBs and any byproducts or contaminants, for each of the previously specified population groups.

TRIM was designed to explicitly represent uncertainties such as those governing the rate of occurrence of spillsand fires, the degree of human exposure and dose-response relationships. The model combines discrete probability distributions with a probability tree structure that expresses the possible outcomes and their probabilities of occurrence.

The initial application of TRIM by USWAG illustrates the model's scope and capabilities. As part of its response to the March 1984 EPA Advanced Notice of Proposed Rulemaking (ANPR) Concerning PCB's, USWAG sponsored an analysis of four policy options to reduce the risk from transformer fires [1].

The USWAG analysis covered one type of equipment (PCB transformers) in three locations (utility substations, low exposure-risk buildings, and high exposure-risk buildings) for three types of incidents (small leaks and spills, large incidents without fires, and fires) and four population groups (office workers, utility workers, emergency workers, and others). Later, a second USWAG analysis was conducted concentrating on fire incidents in high risk locations [2].

For each policy alternative considered, TRIM was used to calculate the total number of potential life-time health effects in the U.S. for each population group stemming from exposure to PCB's, PCDF's, and PCDO's released through PCB transformer incidents. The model was also used to estimate the costs of equipment phase-out and other risk control measures and incident cleanup expenses.

The application of TRIM by USWAG contributed to the analysis of measures to manage risks from fires involving PCB transformers in buildings in several ways.

First, TRIM contributed to the analysis by addressing the bottom line question of what are the specific benefits (in reduced health effects) that could be expected from the policy alternatives. Although it is widely accepted that there is PCB equipment in buildings, that this equipment is subject to possible but very infrequent fires that may result in release of PCBs and PCDFs, that fire fighters, utility workers, and office workers are likely to be exposed to these substances in the event of a release, and that these substances can cause serious health effects (when sufficient quantities enter the body), prior to the application of TRIM there were no explicit analyses of the number of health effects that might be

MONS 018650

expected under the status quo. Nor were there any analyses of how the estimated number of effects might be expected to change with the control measures under consideration. Thus, a major contribution of the TRIM application was to address the right questions.

TRIM contributed to the analysis in other ways as well. Sensitivity analyses were conducted to determine what uncertainties were most important in determining the expected number of health effects for the policy scenarios. These uncertainties were represented directly in a probabilistic analysis that estimated cumulative probability distributions on health effects associated with each alternative. This analysis demonstrated that the major uncertainties did not greatly change the total number of health effects to be expected nor change the ranking of the policy alternatives considered.

The portability of TRIM as a computer program has given EPA the capability to check the USWAG analyses and test the implications of alternative assumptions. Although EPA has obtained the model, the nature and extent of EPA's use of the model is not clear at this point. Comparative analyses with the model have the potential for providing focus and specificity to future discussions if they occur.

In conclusion, risk management models provide a useful complement to toxicology studies, exposure assessment, risk assessment and cost analysis. Risk management models such as TRIM can provide a decision choice context to the analysis, provide a common ground for discussion among the interested parties, and can improve the quality of the analysis.

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MONS 018651

COMPARATIVE TRANSFORMER FIRE RISK ASSESSMENT

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Summary

A risk assessment comparing the use of mineral oil and Askarel dielectric fluids in two typical office building transformer applications has been completed (1). The study was done by the consulting firm of Pickard, Lowe and Garrick, Inc. of Newport Beach, California. The study shows that the average frequency of a fire starting and spreading beyond the office building transformer room is 300 times greater for a mineral oil-filled transformer than for an Askarel-filled transformer. The analyses of both office building transformer applications indicate that there is a significant decrease in the risk of fatalities when a mineral oil transformer is replaced by an Askarel transformer. A typical Askarel consisting of 50% Aroclor® 1254 (PCBs) and 50% 1,2,4 trichlorobenzene was used in the study. The use of trichlorobenzene as a blending fluid reduces the fire resistance of the resulting Askarel mixture when compared to essentially 100% PCB fluid.

Scope

The study was done to evaluate the impact on fire risk of the decision to replace mineral oil by PCBs as the cooling and insulating fluid for electrical equipment. Risk is taken to mean the likelihood of a hazard resulting in the actual delivery of loss, injury or some form of damage (2). By contrast, a hazard is defined as the source of danger (2). In this study, fire risk was defined to include the frequencies of fatalities, injuries and fires spreading beyond the room of origin.

MONS 018652

In the study, mineral oil transformers are compared to Askarel transformers. The term Askarel generally refers to a generic name for a broad class of fire resistant synthetic chlorinated hydrocarbons used as dielectric fluids. For the purpose of the study, the term Askarel refers to a mixture containing 50% PCBs (Aroclor® 1254) and 50% 1,2,4 trichlorobenzene.

Two separate cases are considered in the evaluation of fire risk for the two types of transformer fluid. The first (Case 1) involves the installation of the transformer in a one-hour fire-rated room in a general use basement area of an office building. The other (Case 2) involves a transformer room with a three-hour fire rating in a non-public use basement of an office building. These two cases describe typical transformer installations used for Askarel and mineral oil transformers respectively in building applications, and meet current National Electrical Code standards (3). The fire frequency, injury, and fatality data used in this study were obtained by analysis of several fire incident data bases which are detailed in the final report (1).

Results

The results of this study show a significant decrease in fire risk when a mineral oil transformer is replaced by an Askarel transformer. The likelihood of fire spreading beyond the room of origin is 300 times greater for a mineral oil transformer than for an Askarel transformer in Case 1 and 1000 times greater in Case 2. Table 1 presents the mean fire frequencies for each case.

MONS 018653

Table 1

Transformer Fire Frequencies

(Events per Transformer Year)

	Transformer Fire	Fire Spreads Beyond Transformer Room
Case 1		
Askarel	2.0 x 10-4	4.6 x 10-7
Mineral Oil	2.5 x 10-4	1.5 x 10-4
Case 2		
Askarel	2.0 x 10-4	7.3 x 10-8
Mineral Oil	2.5 x 10-4	7.3 x 10-5

To provide a better understanding of the numbers presented in Table 1, consider the Case 1 Askarel transformer fire frequency. The frequency of an Askarel transformer fire is 2.0 x 10-4. This means one fire every 5000 years or every 5000 transformer years. If the current number of Askarel transformers is 140,000, this equates to 28 Askarel transformer fires per year.

An important factor of the Askarel transformer fire is the presence of trichlorobenzene. If an Askarel transformer did not contain trichlorobenzene, the frequency of fire would be significantly smaller. This is because the trichlorobenzene has a flash point of 99°C and PCB (Aroclor® 1254) does not have a flash point (Cleveland open cup flash point test (4)).

MONS 018654

Using the fire frequencies from Table 1, the fatality frequencies were calculated and are listed in Table 2. These calculations assume that about 1 in 1000 (1.2 x 10-3) of all fires confined to a transformer room would involve one or more fatalities. For fires spreading beyond the transformer room, about 1 in 100 (8.8 x 10-3) were assumed to result in one or more fatalities. The frequency of a fire being confined to the transformer room was computed by subtracting the frequency of a fire spreading beyond the transformer room from the total frequency of transformer fires. Several statistical points of comparison are presented in Table 2 to show the uncertainty in the calculations. For all points of comparison, Askarel-filled transformers have a lower frequency of fatalities than mineral oil-filled transformers.

Table 2

Transformer Fire Fatality Frequencies

(Fatality Events per Transformer Year)

Statistical Point of Comparison	Case 1		Case 2	
	Askarel	Mineral Oil	Askarel	Mineral Oil
Mean	2.4 x 10-7	1.4 x 10-6	2.4 x 10-7	8.5 x 10-7
Percentile				
5th	8.6 x 10-10	1.7 x 10-7	2.0 x 10-9	1.3 x 10-7
95th	5.9 x 10-7	4.3 x 10-6	5.9 x 10-7	2.7 x 10-6

In both of the cases, room fires are the dominant contributors to the risk of Askarel transformers. Fires that spread beyond the room are the dominant contributors to the risk from

mineral oil transformers. This suggests that the risk from mineral oil transformers could be much greater than from Askarel transformers, since a fire that spreads beyond the transformer room is of more concern than a fire that is contained within the room. Historical data (5) suggest that there is a greater likelihood of multiple fatalities when a fire spreads from its room of origin.

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MONS 018658

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MONS 018659

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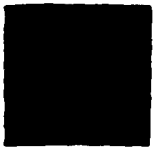

Attenuation of Polychlorinated Biphenyls in Soils: Literature Review

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MONS 018662

TABLES

Table		Page
2-1	Sorption Coefficients of PCBs	2-3
2-2a	Range of Partition Coefficients for PCB Mixtures	2-5
2-2b	Range of Partition Coefficients for Individual Congeners	2-6
2-3	Physical Properties of PCBs	2-10
2-4	Physical Properties of TCDD	2-20
2-5	Half-Lives of TCDD	2-21

MONS 018663

SUMMARY

Polychlorinated biphenyls (PCBs) have found their way into a wide variety of industrial applications, a major one being coolant-insulation in transformers. Perceived toxicity to humans and other organisms in conjunction with environmental persistence has led to a highly regulated climate of PCB use. Due to the ubiquity and persistence of PCBs, the ability to predict their long-term mobility in the soil-water environment is of particular interest to the electric utility industry and regulatory agencies.

This report reviews the current literature on 1) PCB attenuation in soils and subsoils, and 2) conceptual and mathematical models that deal with hydrophobic sorption in soils and subsoils and thus may be applicable to PCB studies. Because recent research has suggested that toxicity attributed to PCBs may be caused or enhanced by other closely associated compounds such as polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs), this report also briefly reviews the available literature on PCDD and PCDF attenuation in soils (PCDF attenuation data were virtually absent in the literature at the time of this review). The report identifies key issues where conflicting information exists; gaps or deficiencies in available data or in an understanding of the sorption/desorption processes; and models and estimation techniques that have not yet been tested quantitatively but may be applicable for describing the role sorption/desorption plays in determining the mobility of PCBs and related hydrophobic compounds such as PCDDs and PCDFs. Based on this review, the following conclusions were reached.

1. For aqueous solvents and soils containing 'typical' organic carbon (OC) concentrations ($0.1\% < OC < 15\%$ by weight), insufficient equilibrium sorption data exist for PCBs to 1) reliably test the applicability of sorption models for sorption of individual PCB isomers or Aroclor mixtures (although a few preliminary tests may be made), and 2) make accurate, scientifically defensible predictions of PCB mobility in soils.

2. Conflicting information and active debate exist regarding the rates and reversibility of the PCB sorption/desorption process for typical OC soils in aqueous solvents. The rates at which equilibrium conditions are achieved and the existence of sorbed PCB fractions, which are desorbed rapidly (hours), desorbed very slowly (months) or not

MONS 018664

desorbed at all, must be understood and quantitatively modeled if we are to predict PCB soil/subsoil mobility.

3. No data or models exist for PCB sorption/desorption/reversibility under equilibrium or nonequilibrium conditions for aqueous-soil systems where the soils contain less than 0.1% OC. These "low" organic carbon levels are typical of subsoils and subsurface ground water aquifer materials. Polychlorinated biphenyls mobility in these materials may differ significantly from that in typical OC soils.

4. Models are currently under development for describing sorption/desorption/reversibility of organic compounds (pesticides) on various sorbents in miscible aqueous-organic or pure organic solvent systems; however, these models have not been used or tested for PCBs. Research in this area along with investigation of the effects of cationic and anionic surfactants on sorption processes would provide a sound basis of understanding and possible improvements for soil washing methodologies.

5. Volatilization and chemical degradation of PCBs in soils have not received sufficient attention. The effect of different soils with a wider range of OC and clay mineral content should be examined under different water saturation conditions. It is also important to determine the degradation products and not merely the extent of 'loss' since loss can be due to a number of nondegradation processes.

6. Migration of PCBs as an adsorbed phase (i.e., transport on particles) and as an immiscible phase (i.e., as a pure compound or as a compound/organic solvent phase) also should be considered in any attempt to predict the transport of these compounds.

Future work on PCB sorption, volatilization, and abiotic degradation is needed to establish a more comprehensive data base. Attenuation models, when incorporated into solute and multiphase transport models, will yield predictive tools for describing migration of PCBs and related nonionizable hydrophobic compounds from the near-field region of initial contact with the soil to the far-field region of the adjacent groundwater aquifer and beyond. Based on these predictive tools for describing migration, the associated risk assessment and subsequent decisions can be made as to whether cleanup is required.

MONS 018665

Section 1

INTRODUCTION

Polychlorinated biphenyls (PCBs) have been manufactured and used industrially since the early 1930's. Their thermal stability, chemical stability (e.g., general inertness to oxidation and hydrolysis), and dielectric properties have made them very useful in a variety of industrial applications. They have been used as coolant-insulation fluids in capacitors and transformers; for impregnation of cotton and asbestos in braided insulation of electrical wiring; as plasticizer in wire, cable coatings, and vinyl chloride polymer films; as lubricants and gasket sealers; as high-pressure hydraulic fluids; as heat transfer agents; as machine tool cutting oils; as protective coatings for wood, metal, and concrete; for adhesives; and for carbonless reproducing paper (Gustafson 1970).

Polychlorinated biphenyls have been found in environmental and biological samples in many locations and are thought to have a tendency to bioaccumulate (Pal et al. 1980). Their widespread distribution has been attributed to volatilization or aerosol formation and atmospheric transport followed by wet or dry deposition. Evidence of chronic toxicity in birds and in man has been presented (Gustafson 1970), though recent research has questioned whether the toxicity may be caused or enhanced by other compounds such as polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs) (Josephson 1984; Yuceta et al. 1983).

The properties and environmental persistence of PCBs depend on their degree of chlorination. For example, PCBs with fewer than four chlorine atoms can be biodegraded fairly readily by a number of microorganisms, whereas PCBs with greater than four chlorine atoms are resistant to biodegradation (Callahan et al. 1979). Less chlorinated PCBs tend to be more volatile, while the more chlorinated PCBs tend to be more readily sorbed to suspended solids or sediments or incorporated into biota. Polychlorinated biphenyls are extremely resistant to oxidation and to acidic and basic hydrolysis. The more highly chlorinated species have been shown to undergo photolysis in organic media, with the possible formation of PCDFs as well as dehalogenated products (Safe et al. 1976 in Callahan et al. 1979). However, photolysis is probably not a significant factor affecting PCBs sorbed on soils in natural systems. PCBs are sorbed rapidly onto soils because of their low water solubilities

MONS 018666

and high octanol-water partition coefficients. Of even more environmental significance is the evidence that PCBs are desorbed slowly from sediments and may contribute to long-term degradation of water quality (Callahan et al. 1979). Much less is known about the environmental behavior of PCDDs and PCDFs; both are susceptible to photolysis, but, as with PCBs, this mode of degradation is relatively unimportant in soils. Tetrachlorodibenzodioxin (TCDD) is strongly sorbed by and is very persistent in soils, is resistant to biodegradation, is not bioaccumulated, and is thought to be immobile in all but very sandy soils (Yuceta et al. 1983).

Because of the ubiquity and persistence of PCBs, and the toxicity and persistence of PCDDs and PCDFs, it would be useful to be able to quantitatively predict their behavior in the soil-water environment so that their potential for environmental migration can be determined. Based on these predictions and on associated risk assessments, a decision can be made as to whether clean-up is required and is cost-effective. To attain this goal, specific data are needed for a variety of soil and water conditions as well as predictive models. In this report the literature on PCBs has been reviewed, and the available data are summarized in Section 2 in a format that will be useful for modeling efforts. In addition, information related to PCDD attenuation in soils is included at the end of Section 2. Because of the virtual absence in the literature at the time of this review of attenuation data on PCDFs in soils, no discussion for PCDF attenuation is included. The literature on available models is reviewed in Section 3 to determine which may be applicable to PCBs and other related hydrophobic organic compounds. Based on the findings in Sections 2 and 3, Section 4 recommends an integrated program of experimental work and model development.

MONS 018667

Section 2

LITERATURE REVIEW OF PCB ATTENUATION IN SOILS

This section reviews the available literature on PCB attenuation in soils, with an emphasis on sorption. Additional information was sought on two closely associated hydrophobic compounds, namely the PCDDs and PCDFs, however because of the dearth of published literature on PCDD sorption and an almost total lack of literature concerning PCDFs in soils, this report focuses on PCB data in soils. The available published PCDD data are discussed separately at the end of this section.

The general topics covered in this section for PCBs include linear partition coefficients or distribution ratios in soils and sediments; Freundlich isotherms; Langmuir isotherms; organic carbon partition coefficients (K_{oc}); water solubility; octanol-water partition coefficients (K_{ow}); reversibility of sorption; kinetics of sorption; mobility studies in aqueous and organic solvent systems (soil thin layer chromatography, soil column, and other migration studies); field studies; and the effect of soils on volatilization, plant uptake, and degradation. In some cases, the published literature deals with individual PCB congeners; in others, with mixtures, usually one or more of the Aroclors; and for still other cases, with spills of actual capacitor fluids. In this section the available information is sorted and summarized so that contradictions and deficiencies in the data can be determined and the data can be organized in a format that makes it more readily accessible for modeling.

EQUILIBRIUM SORPTION: PARTITION COEFFICIENTS AND SORPTION ISOTHERMS

Reasonable agreement between theoretically derived partition coefficients and actual (laboratory or field) values suggests that equilibrium sorption is a good method for describing accumulation of nonpolar organic compounds on soils, sediments, and particles (Pavlou 1980). Almost all of the PCB sorption data in the literature have been described in terms of the Freundlich isotherm, the partition coefficient or the distribution ratio. In one exception, Weber et al. (1983) also apply the Langmuir model, though they conclude that this model fits the data poorly, especially at "high" solution concentrations.

MONS 018668

The partition coefficient (K_p) is defined as the ratio between the amount of compound sorbed on a sorbent surface and that in solution at equilibrium:

$$K_p = \frac{S}{C} \quad (2\text{-}1)$$

where S is the amount of compound sorbed per unit weight of sorbent (μg/g) and C is the equilibrium concentration of compound in solution (μg/mL). When such ratios are determined for a range of solution concentrations, the plot of S versus C is termed a sorption isotherm.

The distribution ratio, K_D, is the appropriate sorption parameter for describing a mixture of congeners and is defined by

$$K_D = \frac{S_{an}}{C_{an}}$$

where S_{an} and C_{an} are the total analytical concentrations of all sorbed and solution congeners, respectively.

The Freundlich isotherm model represents an empirically derived relationship between the amount sorbed and the equilibrium solution concentration:

$$S = K_F C^{1/n} \quad (2\text{-}2)$$

where K_F is the Freundlich sorption coefficient and 1/n is an empirical constant. When 1/n = 1, the Freundlich isotherm reduces to a linear partition coefficient.

The Langmuir isotherm is theoretically derived by assuming that the sorption at a given site is independent of the number of other sites already occupied. Its mathematical expression is

$$S = \frac{S^{max} K_L C}{1 + K_L C} \quad (2\text{-}3)$$

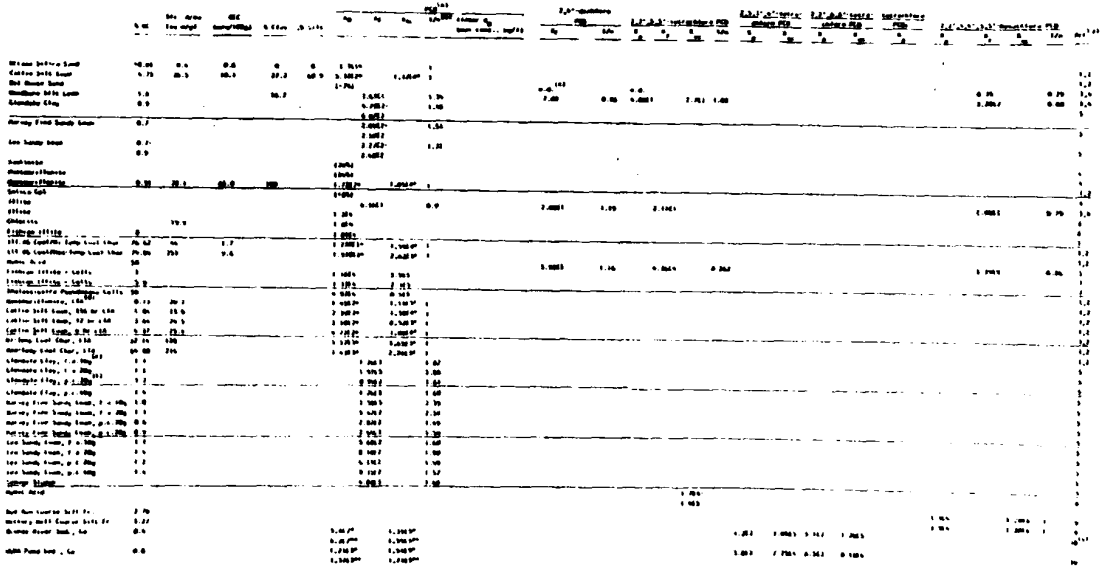
where S^{max} is the monolayer sorption capacity and K_L is the Langmuir sorption coefficient (Weber et al. 1983).

Partition coefficients are frequently normalized to the organic carbon content of the soil (Karickhoff et al. 1979). In this report we have calculated the organic carbon partition coefficient, K_{OC}, from both K_p and K_D values according to the formula $K_{OC} = \frac{K \times 100}{\%OC}$, where K is either K_p or K_D. For more information about the derivation and characteristics of these various partition coefficients, see Section 3 of this report.

MONS 018669

Table 2-1

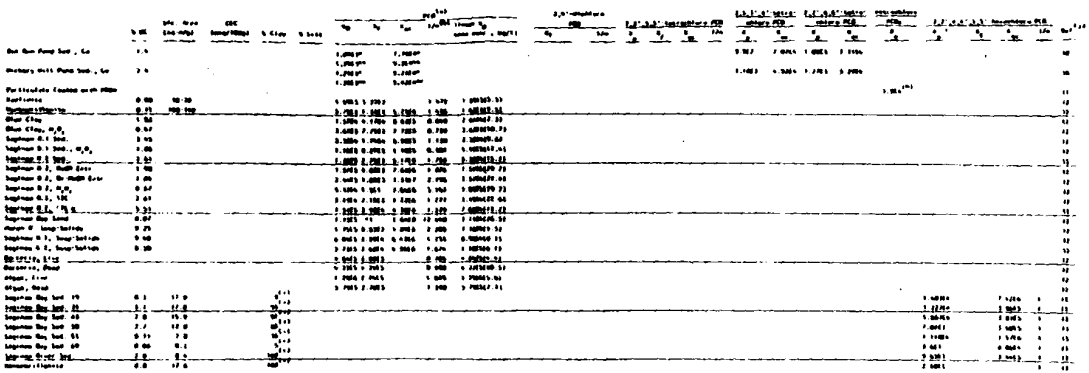
SORPTION COEFFICIENTS OF PCBs



MONS 018670

Table 2-1

(cont'd)



[1] PCB is Aroclor 1254 except a = Aroclor 1242; m = Aroclor 1016

[2] Koc values in grams for 1/n, petroleum modified set of precipitation ratio are determined at soil and sediments, when 1/n =1, $K_{oc} = K_d \times f_{oc}$

[3] n.d. = negligible

[4] 1/n = low temperature adsorption

[5] n.d. HOC = freshly amended with HOC studies

[6] p.d. HOC = preconditioned with HOC studies

[7] Range in K_d and K_{oc} values for PCB are in chronological sequence Aroclor 1242 and Aroclor 1016

[8] Calculated from model

[9] Values are for clay + silt

[10] References for Table 2-1

References for Table 2-1

1. Griffin and Chou (1982)
2. Lee et al. (1979)
3. Hagen and Tomlinson (1964)
4. Hagen et al. (1967)
5. Fairbanks and Wheeler (1983)
6. Mackay and Gorder (1982)
7. Mackay et al. (1982)
8. Mackay et al. (1983)
9. Karickhoff et al. (1979)
10. Means et al. (1979)
11. Perlow (1982)
12. Voice et al. (1983)
13. Karickhoff and Brown (1978)

MONS 0169810

The results of studies designed to determine the sorption coefficients of various PCB isomers or mixtures are shown in Table 2-1. The sorbent matrices studied include soils, sediments, clays, coals, sewage sludge, and biological organisms. Some of the sorbents have been treated by a variety of means (low-temperature ashing, solvent extraction, peroxidation) in an attempt to vary their organic carbon content. Unfortunately, such treatments may also affect the inorganic constituents and other properties of the sorbents (such as surface area, pore distributions). Because most of these parameters are not usually determined or reported in the reviewed papers, changes in sorption coefficient cannot be attributed solely to changes in organic carbon content. Thus, results with such treated sorbents must be interpreted with caution.

The organic carbon contents of the sorbents in Table 2-1 varied from <0.01% for a silica sand to 76.6% for a coal char; most soils were above 0.5%. The organic carbon contents were not given for most of the clays. Surface areas (SA) were noted in four references and ranged from 0.2 to 253 m^2/g. Cation exchange capacity was determined in two references and ranged from 0.0 to 85.0 meq/100 g. The observed variations in K_D, Freundlich parameters, and K_{oc} for the PCB mixtures in Table 2-1 are summarized in Table 2-2a. Isotherm linearity generally applied at low solution concentrations, the exact concentration depending on the sorbent (Weber et al. 1983). At higher concentrations, the nonlinear relationship fits the Freundlich model (Weber et al. 1983). K and K_{oc} increased with decreased temperatures (Weber et al. 1983). It should be noted that most of the PCB sorption data in Table 2-1 were obtained for PCB mixtures (Aroclors) containing several PCB congeners. Because

Table 2-2a

RANGE OF DISTRIBUTION RATIOS FOR PCB MIXTURES

Parameters	Range	Number of Sorbents[a]
K_{oc}	1.6E3 to 1.6E7	32
K_D	2.2E1 to 6.1E5	36
K_F	<1 to 4.2E4	34
1/n	0.39 to 12.4	45

[a]Organisms are excluded.

MONS 018672

the partition coefficients for individual congeners differ, the use of K_Ds to describe the PCB mobility in the environment must be interpreted with caution (see page 3-5 of this report).

A few cases are shown in Table 2-1 where individual congeners were studied. The range of partition coefficients and other sorption model parameters for these congeners are summarized in Table 2-2b. The organic carbon content in the sorbents in Table 2-2b ranged from 0.06% to 58%. The variation in K_{oc} values is smaller than for K_p or K_F values. This decreased variability is consistent with the hypothesis that soil organic carbon is a dominant factor in sorption of hydrophobic organic compounds (Karickhoff et al. 1979). While K_{oc} values show some overlap among the different congeners because of the wide range of soil types used, K_{oc} tends to increase with increased degree of chlorination. The relative sorption of individual congeners as part of Aroclor mixtures was also observed using gas chromatography (GC) (Griffin and Chou 1981; Lee et al. 1979). The congeners with fewer chlorine atoms tended to be sorbed less then those with more chlorine atoms (Griffin and Chou 1981; Lee et al. 1979). A comparison was also made between sorption of Aroclor 1242 and used capacitor fluids that had the same congener distribution patterns; no significant differences in sorption were found in the five soils studied (Griffin and Chian 1980).

Table 2-2b

RANGE OF PARTITION COEFFICIENTS FOR INDIVIDUAL CONGENERS

Parameters	Dichloro PCB	Tetrachloro PCB	Hexachloro PCB
K_{oc}	--	2.7E3-1.3E5 (n=5)[a]	6.1E4-7.4E6 (n=9)
K_p	--	4.9E1-1.3E3 (n=5)	3.6E1-1.5E4 (n=10)
K_F	7.0-4.0E3 (n=3)	2.1E1-4.4E4 (n=2)	3.5E1-3.4E9 (n=4)
1/n	0.85-1.19 (n=3)	0.26-1.09 (n=2)	0.26-0.80 (n=4)

[a] n = number of sorbents studied.

MONS 018673

Further analysis of Table 2-1 points out a number of gaps in the sorption data available for PCBs. (Also, see Section 4 of this report for recommendations.) First, few data are available dealing with sorption of the individual congeners or the congeners as part of the mixture (with the exceptions noted above). Such data are needed both for a single soil as a function of chlorine number and for a number of soils with varying organic carbon and swellable clay contents. Second, while most authors include numbers for sorbent organic carbon content, these data are generally lacking for the clays. Other potentially important soil parameters, such as surface area measurements (including determination of the appropriate methodology to use for these measurements) and clay mineralogy, are too frequently unavailable. And third, while the sorbent organic carbon content covers a wide range of values above 0.5%, very few soil samples with organic carbon <0.1% have been examined. Such low organic carbon soils are typical in the subsurface environment or in highly oxidized surface soils, both of which may influence the transport of PCBs. In these low carbon soils, the presence of swellable clays is considered especially important in sorption (see Section 3 of this report).

The information presented in Table 2-1 may be used to determine whether initial attempts (with even smaller data sets) (Griffin and Chou 1981; Lee et al. 1979; Steen et al. 1978) to correlate K_p for PCBs with sorbent organic carbon content and surface area are valid. These studies show that linear correlations for PCBs exist between K_p and OC for the soil types examined (usually four to five soils, sometimes of limited OC range): for example, $K_p = 255 + 18.5$ OC ($r^2 = 0.87$) (Lee et al. 1979). Steen et al. (1978) observed that partitioning of two tetrachlorobiphenyl isomers was linear with OC for four soils (0.4% to 2.5% OC). However, using the same soils, Steen et al. (1978) observed that partitioning of the Aroclors was independent of OC, which he attributed to the narrow OC range. Data in the available literature are too limited for any definite conclusions to be drawn, but one can speculate that correlations that are valid for individual PCB isomers may not be applicable to Arocior mixtures. In general, the sorbent organic carbon content is thought to be the dominant factor controlling PCB sorption. It is not known at what threshold levels of organic carbon this relationship breaks down for PCBs. The existence of such a threshold dependent on the ratio of organic carbon content to clay mineral content has been suggested by Karickhoff (1984) for hydrophobic organic compound sorption (see Section 3 of this report). This hypothesis needs further examination specifically directed at PCBs.

Parameters other than the OC may also be important in sorption. Significant linear correlations were also found between K_p and sorbent surface area (measured by the

MONS 018674

BET gas-adsorption method with CO_2 as adsorbate, which gives a measure of external surface area as well as micropore area) (Griffin and Chian 1980); for example, $K_p = 230 + 6.64\ SA$ ($r^2 = 0.82$) (Lee et al. 1979). It is interesting to note that the correlation was much weaker when sorbent surface area was measured by the BET gas-adsorption method with N_2 as adsorbate. Strek (1980) observed that the quantities of sorbent required to sorb 50% of the applied PCBs increased in the following order: a peaty muck < montmorillonite < sand < peroxide-treated sand. This sequence incorporates variations in both organic carbon content and specific surface area. The relative amounts of sorbent required indicate that while both parameters play a role, the OC predominates, a relationship also observed by Griffin and Chian (1980); for example, $K_p = 188 + 3.36SA + 11.4\ OC$ ($r^2 = 0.82$) (Lee et al. 1979). Hassett et al. (1984) point out that the molecular weight of the organic matter (humic acids in water) may also make a difference in the degree of sorption; these authors showed a general increase in K_{oc} with molecular weight above 50,000 daltons. Scharpenseel et al. (1978) similarly showed that PCBs attach preferentially to humic acid rather than to fulvic acid but also indicated that PCBs bind to nonhumic organic constituents. Fairbanks and O'Connor (1984) also observed that sorption properties of sewage sludge differ from native soil organic matter; therefore, correlations of K_{oc} with organic carbon content for sewage sludge may not be at all valid for use with soils. Thus, a knowledge of the properties of the organic matter (molecular weight, functional groups, hydrophobicity, structure) is also important in studying sorption characteristics.

PHYSICAL CONSTANTS: WATER SOLUBILITY, K_{ow}, VAPOR PRESSURE

A number of studies deal with determination of the physical constants of PCBs that influence their migration in soils. Attempts have been made to use some of these physical constants such as water solubility (S) and octanol-water coefficients (K_{ow}) to predict partition coefficients and environmental migration (see Section 3). The largest amount of data is available for K_{ow}, less is available for water solubility, and still less for vapor pressure. The octanol-water partition coefficient, K_{ow}, is defined as the ratio of the concentration of a chemical in octanol to that in water in an equilibrated octanol-water system:

$$K_{ow} = \frac{\text{concentration in octanol phase}}{\text{concentration in aqueous phase}} \qquad (2\text{-}4)$$

It has been measured for a large number of PCB congeners by a reverse-phase high-pressure liquid chromatography (RPHPLC) technique (Rapaport and Eisenreich 1984). Water solubilities are given in mg/L or ppm, vapor pressures are in torr, and K_{ow}s

MONS 018675

are dimensionless. Literature values found for these physical constants are summarized in Table 2-3 for the various individual congeners and mixtures of PCBs.

The reported water solubilities of the congeners range from 0.40 to 5.9 ppm for the three monochloro isomers, from 0.06 to 1.9 ppm for four dichloro isomers, from 0.08 to 0.25 ppm for four trichloro isomers, from 0.027 to 0.17 ppm for seven tetrachloro isomers, from 0.01 to 0.031 ppm for three pentachloro isomers, from 0.00095 to 0.0088 ppm for one hexachloro isomer, 0.007 ppm for one octachloro isomer, and 0.015 ppm for the decachloro isomer (Chiou et al. 1977; Griffin and Chian 1980; Haque and Schmedding 1976; Kalmaz and Kalmaz 1979; Kilzer et al. 1979). Although there is considerable overlap in the solubilities from one set of isomers to the next, the general trend is for a decrease in water solubility with an increase in number of chlorine atoms as expected. In each set of congeners with the same number of chlorines, certain congeners were relatively soluble compared to others (Griffin and Chian 1980). These include 2-monochloro-, 2,4'-dichloro-, 2,2',5-trichloro-, 2,2',3,5'-tetrachloro-, and 3,3',4,4'- tetrachloro-biphenyls. The water solubilities of a few congeners as components of Aroclor 1242 were also measured (Griffin and Chian 1980). The water solubilities of these 'component congeners' were typically less than the corresponding solubilities of the individual congeners, sometimes by as much as one and one-half orders of magnitude. The Aroclor solubilities themselves ranged from 3×10^{-3} to 15.0 ppm, depending on the relative amounts of PCB congeners (Griffin and Chian 1980; Kalmaz and Kalmaz 1979; Pal et al. 1980). One problem with some of these data is that the temperature at which the water solubility was measured is not always given in the literature.

The log K_{ow} values for the individual congeners follow a similar pattern as the water solubilities; that is, while there is considerable overlap from one group of isomers to the next, the general trend is for an increase in log K_{ow} with increasing chlorine content starting from ~4.4 for the monochloro isomers and continuing to 7.75 for one hexachloro isomer (Chiou et al. 1977; Rapaport and Eisenreich 1984). The Aroclor trend is also similar, with the less chlorinated Aroclor 1221 having a log K_{ow} of 2.81 and the more highly chlorinated Aroclor 1260 having a log K_{ow} of 4.34 (Pal et al. 1980). Octanol-water coefficients have been correlated with water solubilities for 34 organic compounds with a range of structures, including three PCBs (Chiou et al. 1977); for example, log K_{ow} = 5.00 - 0.670 log S (r^2 = 0.97). Organic carbon partition coefficients for a range of organic compounds have also been correlated with K_{ow} values and with water solubilities for ten hydrophobic compounds including one PCB using a coarse silt sediment (Karickhoff et al. 1979); for example, K_{oc} = -0.63 K_{ow} (r^2 = 0.96); log K_{oc} = -0.54 log S + 0.44 (r^2 = 0.94).

MONS 018676

Table 2-3

PHYSICAL PROPERTIES OF PCBs

	Water Solubility (ppm) [Temperature in ( )]				Log K_{ow}	Vapor Pressure (mm Hg) [Temperature in ( )]
	Ref. [1][a]	Ref. [2]	Ref. [3]	Other Refs.	(Ref.)[b]	
Aroclor 1221		15.0	3.5(23C)		2.61(2); 4.1-4.7(11)	7E-3(2)
Aroclor 1232		1.45			3.23(2); 4.3-5.2(11)	
Aroclor 1242	2.4E-1	2.4E-1	7.03E-1(23C)		3.30(2); 4.3-5.8(11)	4.06E-4(11)
Aroclor 1248	5.4E-2	5.4E-2			3.81(2); 5.0-6.3(11)	4.06E-4(11); 3.75E-4(25C)(9)
Aroclor 1254	1.2E-2	1.2E-2	7.0E-2(23C)	5.0E-1[6]	4.08(2); 4.7-6.4(11)	7.79E-5(11)
Aroclor 1260	2.7E-3	2.7E-3			4.34(2); 6.3-7.3(11)	4.05E-5(11); 4E-5(2)
Aroclor 1016		3.4E-1	9.06E-1(23C)		3.40(2); 4.6-5.8(11)	
PCB, general				7.0E-1[5]		
1-chloro	5.9				4.60	
2-chloro	1.5				4.41	
4-chloro	1.19		1.0E-1	1.5E-2[b]	4.60	
2,2'-dichloro	1.50		1.0E-1	1.1E-2[b]	4.99	
2,4'-dichloro	1.00		6.37E-1	1.39E-1[b]	5.10	
2,3'-dichloro					5.07	
2,4-dichloro	1.40				5.30	
2,5-dichloro					5.30	
2,6-dichloro					5.31	
4,4'-dichloro	0E-2			6.2E-3(120C)[7]	4.83;5.30[6;7]	
2,2',3-trichloro					5.31	
2,4',6-trichloro					5.78	
2,2',5-trichloro	1.40E-1		2.40E-1	6.1E-2[b]	5.55	
2,3',4-trichloro					5.44	
2,3,6-trichloro					5.67	
2',3,4-trichloro					5.57[6]	
2,4,4'-trichloro					5.53	
2,3,3'-trichloro					5.76	
3',3,4-trichloro	7.0E-2					
2,4,6'-trichloro	8.5E-2				5.00	
2,4,5-trichloro					6.25	
2,4',5-trichloro				1.1E-1(25C)[9]	5.09	4E-4(9)
2,6',6-trichloro					5.75	
2,3',5-trichloro					6.15	
3,4,4'-trichloro					6.09	
2,2',3,3'-tetrachloro	3.4E-2				5.96	
2,2',3,4-tetrachloro					6.17	
2,3',3,5'-tetrachloro	1.7E-1				5.81	
2,3',4,4'-tetrachloro	6.8E-2				6.29	
2,2',4,5'-tetrachloro					6.22	
2,3',3,5'-tetrachloro	4.0E-2		2.65E-2	2.23E-2[b]	6.00	
2,3,4,4'-tetrachloro					6.09	
2,3',4,4'-tetrachloro	3.0E-2				6.37	
2,3',4',5-tetrachloro	4.1E-2				6.23	
2,4,4',5-tetrachloro					6.67	
2,3,3',4',5-pentachloro	1.7E-1				5.62;6.53[6]	
2,3',4,4',5-pentachloro					6.61	
2,2',3,4,5-pentachloro	2.2E-2				6.37	
2,2',3',4,5-pentachloro					6.67	
2,3',4,4',5-pentachloro					6.31;6.45[6]	
2,2',3,3',5'-pentachloro					6.97	
2,3',3,4',5-pentachloro					6.55	
2,2',4,4',5-pentachloro					7.27	
2,2',4,5,5'-pentachloro	3.1E-2			1.0E-2(25C)[7]	7.07;6.11[6;7]	
2,2',4,5',6-pentachloro				3.1E-2(25C)[9]		
2,3',4,4',5-pentachloro					7.12	
2,3',3,4',6-pentachloro					6.66;6.16[6]	
2,3',3,4',5-pentachloro					6.69	
2,2',3,3',4,4'-hexachloro					6.96	
2,2',3,3',4,5-hexachloro					7.32	
2,2',3,3',4,5'-hexachloro					7.19	
2,2',3,3',4,6'-hexachloro					7.15	
2,2',3,3',5,6'-hexachloro					6.91	
2,2',3,4,4',5-hexachloro					7.44;7.71	
2,3,3',4,5,5'-hexachloro					7.37	
2,2',4,4',5,5'-hexachloro	0.0E-3			9.3E-4(25C)[7;10]	7.75;8.72[6;7]	
2,2',3,4',5',6-hexachloro					7.18	
2,2',3,3',5,5'-hexachloro					7.59[6]	
2,2',3,3',4,4',5,5'-octachloro	7.0E-3					
Octachloro biphenyl	1.3E-3			7.40(23C)[9]	8.19	9.0E-6(25C)[9]
Transformer fluid			6.30E-1			

[a] Reference for low K_{ow} is [6] unless specified

[b] Water solubility of isomer in Aroclor 1242 [Ref. 3]

[c] References for Table 2-3:

1. Haines and Haines (1979)
2. Pal et al. (1980)
3. Griffin and Chian (1980)
4. Rapaport and Eisenreich (1984)
5. Griffin and Chau (1981)
6. Hawke et al. (1979)
7. Chiou et al. (1977)
8. Rapaport & Eisenreich (1985)
9. Miller et al. (1979)
10. Hawke and Schmedding (1979)
11. Mackay et al. (1980)

MONS 018677

Similar correlations have not yet been attempted for an extensive series of PCBs (see Section 4). Because PCBs constitute a much more closely related group of compounds than was used in the previous correlation studies, it would be valuable to determine whether these correlations remain valid. Such correlations may yield a useful method for extrapolating sorption data from a small number of PCB congeners to the full complement of PCB congeners found in Aroclors.

Very few vapor pressure data appear to be available in the literature studied. The Aroclors have vapor pressures of 7×10^{-3} to 7×10^{-5} torr (Kalmaz and Kalmaz 1979), though one reference (Griffin and Chou 1981) indicates that Aroclor 1248 has a vapor prassure of 0.375 torr, illustrating considerable disagreement in the literature.

KINETICS/REVERSIBILITY OF SORPTION

As discussed in Section 3 of this report, kinetics and reversibility of sorption of hydrophobic compounds such as PCBs is an open, controversial issue. While the background and theory are discussed in Section 3, the conflicting results of research on PCBs are summarized in this section.

Several authors have noted that the amount of desorption of PCBs from various sediment types was minimal. For example, in Haque and Schmedding (1976), the maximum desorption of 2,4'-dichloro-, 2,2',5,5'- tetrachloro-, and 2,2',4,4',5,5'-hexachloro-biphenyl isomers is 4%. Desorption of PCBs from Glendale soil with or without sludge treatment was <2% at the two lowest equilibrium solution concentrations (0.3 and 0.6 µg/L) and 4.4% to 9.5% at the highest equilibrium solution concentration (5 µg/L) (Fairbanks and O'Connor 1984). The partition coefficient for sorption (K_a) is thus less than that for desorption (K_d), again suggesting incomplete reversibility of sorption. For example, Horzempa and DiToro (1983) show a range in K_a between 9,000 and 14,000 for 2,2',4,4',5,5'-hexachloro-biphenyl, while the corresponding range of K_d is 20,000 to 30,000. One exception is a washed sand in which K_a ~40 and K_d ~60. The same authors show a range of K_a from $2.1\ 10^3$ to 1.48×10^4 for another set of sediments and a corresponding range of K_d from 7.23×10^3 to 3.01×10^4. DiToro and Horzempa (1982) and DiToro et al. (1982) suggest that sorption can be divided into reversible and resistant components. The partition coefficient for the reversible component, K_r, corresponding to K_a above, ranges from 3.49×10^2 to 9.15×10^2, whereas the partition coefficient, K_o, for the resistant component ranges from 1.79×10^3 to 1.40×10^4. Their experiments suggest that the resistant component may decrease as a result of a large number of consecutive desorptions, suggesting in turn that the sorption is not irreversible, but instead desorption kinetics are very slow. Gschwend and Wu (1985), however,

MONS 018678

attribute the resistant component to an experimental artifact. The typical experimental protocol involves a sorption step, followed by the removal of the aqueous phase and its replacement by a fresh aqueous phase during the desorption step. When the original soil/aqueous phase is not centrifuged sufficiently, the aqueous phase contains nonsettling microparticles to which PCBs are bound; these bound PCBs are thus removed from the system before desorption under most experimental protocols used to date. Thus, this removal creates the appearance of decreased desorption and higher K_d (Gschwend and Wu 1985). This would explain why the K_a decreases as sorbent concentration (and suspended microparticles) increases (Weber et al. 1983). Gschwend and Wu (1985) found that in experiments with prewashed sediments, the sorption and desorption isotherms are essentially identical.

There is also disagreement concerning the rate of sorption. Several authors suggest that sorption and desorption equilibria are rapid. Equilibrium is reached within 3 hours (Mau-Ritter et al. 1982; Weber et al. 1983), though small increases may occur during the next 24 hours (Horzempa and DiToro 1983). Little subsequent change occurs thereafter, for up to 96 hours (Horzempa and DiToro 1983). However, Karickhoff (1984) suggests that equilibrium is not attained so rapidly. The rate of PCB desorption from illite and chlorite has been calculated as 0.029/hour, using a first-order rate constant (Mau-Ritter and Wurster 1983).

MOBILITY IN AQUEOUS AND ORGANIC SOLVENT SYSTEMS

Several experimental techniques have been used to study the mobility of PCBs in aqueous and organic solvent systems. These methods, discussed below, include soil thin layer chromatography, soil column studies, and microcosm studies.

Soil Thin Layer Chromatography

Soil thin layer chromatography (soil TLC) is a method for estimating the mobility of a compound through a soil using a specified leachate. It is analogous to the standard analytical TLC method except that the typical silica gel or cellulose adsorbent phase is replaced by a thin layer of soil. The leachate or developing solvent may be water, an organic solvent, a landfill leachate, etc. The distance moved by the compound relative to the distance moved by the solvent is defined as the r_f value or retardation factor, where

$$r_f = \frac{\text{distance compound moved}}{\text{distance solvent moved}} \qquad (2\text{-}5)$$

MONS 018679

This r_f value is indicative of the mobility of a compound in a given soil-solvent system. (It should be noted that this definition of r_f, commonly used in the chromatography literature, is the reciprocal of the retardation factor, R_f, defined in Eq. 3-3 below and used in the hydrologic literature describing solute transport in aquifer systems).

The mobility of PCBs as determined by soil TLC has been addressed by Griffin and Chian (1980) and Griffin and Chou (1981). The five soils studied had a range of organic carbon content between <0.01% and 74.04%, specific surface area between 0.4 and 253 m^2/g, cation exchange capacity between 0.0 and 29.4 meq/100 g, and a clay content between 0% and 31.6%. Despite the major differences among these soils, the r_f values of Aroclor 1242 and 1254 are close to 0 (0.02 to 0.06) using either deionized water or a landfill-derived (aqueous) leachate as the developing solvent (Griffin and Chian 1980; Griffin and Chou 1981). On the other hand, when carbon tetrachloride is the developing solvent, the r_f values are close to 1.00 (0.96 to 1.00) (Griffin and Chian 1980; Griffin and Chou 1981). Based on these experimental results, the Aroclors appear to be immobile in soils when water is the solvent, but are highly mobile when a (nonpolar) organic solvent is present. This is consistent with the solubility parameter model of desorption from soils discussed in Section 3 because the PCB is more soluble in the organic solvent and because the organic solvent swells the soil organic matrix thus speeding desorption. These results point out a potential problem in mixed waste landfill systems. Organic solvents may significantly mobilize PCBs that might otherwise remain fairly immobile if water were the only solvent.

Scharpenseel et al. (1978) also refer to this potential problem when they determined the sorption of PCBs by clays and humic acids from hexane solution. In contrast to PCBs in water solution, which have very high partition coefficients, PCBs in hexane solution were minimally sorbed onto clays and humic acids. Interestingly, the sorption of PCBs from hexane solution (in contrast to water solution) was greater onto clays than onto humic acid. This was attributed to the competition between solute (PCB) and solvent (hexane) for the humic acid surface (Scharpenseel et al. 1978). PCB sorption and mobility in the presence of organic solvents or mixed aqueous-organic solvent systems (see Section 3) is an important aspect of the problem which has not been sufficiently addressed (see Section 4).

Soil Column and Microcosm Studies

Soil column and microcosm studies are other sources of information about the mobility of PCBs. In soil column studies, a known weight of soil is packed in a

MONS 018680

column, a PCB component is added, and the column is then leached with successive amounts of water, simulating intermittent rainfall. In PCB soil column experiments, only minimal amounts of PCB were leached from the soil by percolating water. The highest values noted were 0.73% PCBs leached after 1700 mm of total rainfall equivalent; in this case, the PCBs consisted of 30.3% dichloro and 69.7% trichloro congeners (Scharpenseel et al. 1978). When Aroclor 1016 was used as the PCB, it was observed by gas chromatography that only the less chlorinated PCBs were leached (Tucker et al. 1975). Incremental leaching of PCBs by water results in decreasing amounts being leached (Farquhar et al. 1979). In the case of three soils with relatively similar organic carbon content (1% to 6%) but different clay contents (5.5% to 35.8%), breakthrough of the Aroclor 1016 decreased with increased clay content of the soil (Tucker et al. 1975). In a soil column that was extruded and analyzed by autoradiography, PCBs were found to be associated with rotting organic matter, mainly plant remnants, suggesting that PCBs were sorbed and retained by organic matter (Scharpenseel et al. 1978).

One microcosm study was done to determine the movement of PCBs from a silt/clay sediment (2.9% organic carbon) into overlying water (Fisher et al. 1983). Differences in mobility among the various congeners were attributed to differences in sorption. Surprisingly, the less chlorinated congeners (trichloro- and tetrachloro-) exhibited lower diffusivities than the more chlorinated congeners. The diffusivity values ranged from 1.2×10^{-9} to 8.5×10^{-7} cm^2/day for the different congeners, all very low values. At these rates, sedimentation would rapidly bury the PCB-contaminated surface layer, removing it from immediate contact with the overlying water. However, this does not take into account bioturbation or physical disturbance. In the case of such disturbances, the extent of PCB contamination of the overlying water would be dependent on the kinetics of desorption. As mentioned earlier, this topic is currently the subject of much debate.

FIELD STUDIES

Polychlorinated biphenyl spills from transformers have occurred at a number of sites. Several studies have monitored the soils and water at these sites in an attempt to determine and predict the migration and degradation patterns of the PCBs. In one of the earlier studies, Smith et al. (1976) and Moein (1976) observed the effects of an Askarel* spill in eastern Tennessee over a 2-year period (1500 gal of Askarel were spilled and cleaned up by excavation of soil). Soil cores, which consisted mainly of clays with chert (cryptocrystalline quartz) fragments, and well

*The Askarel transformer fluid consisted of Aroclor 1254 and chlorobenzenes.

MONS 018681

water samples from below and around the excavation site were analyzed for both PCBs (Aroclor 1254) and polychlorinated benzenes (the solvent in Askarel). The soil core samples contained 0 to 67 ppm PCB; the water samples contained < 0.5 ppb. These values remained approximately the same after 2 years, indicating no significant reduction in Aroclor 1254 resulting from migration, and no significant migration patterns were observed. Gas chromatography analysis indicated that the ratio of congeners remained the same; therefore, no degradation occurred or all congeners degraded at the same rate. In contrast to the PCBs, the polychlorinated benzenes (solvent) did undergo migration. Specifically, the trichlorobenzenes migrated whereas the higher homologs were retained by the soil. Since this constitutes a mixed-solvent system, it is interesting to note that the PCBs apparently did not migrate with the organic solvent in this case. It is reasonable to assume that dilution effects played a major role here since the bulk of the spill had been cleaned up by excavation.

In another field study in which 6,800 to 21,000 L of Askarel were spilled when an underground pipe broke at a transformer manufacturing plant in Saskatchewan, the distribution and migration of PCBs were studied before major cleanup (Roberts et al. 1982; Schwartz et al. 1982). The study area consisted of granular fill which was underlain by Regina clay, Condie silt, till, glacial sands and gravels. The Regina clay and Condie silt both have an abundant fracture system. These authors found that the distributions of PCBs were extremely heterogeneous, both horizontally and vertically. Surface samples showed large concentrations of PCBs in a number of locations. The PCBs evidently seeped to the surface and were transported on particles during runoff--an important migration mechanism. The surface samples tended to show a decrease in the less chlorinated PCBs relative to the original Aroclor 1254, suggesting preferential degradation or other loss (e.g., resulting from volatilization or faster migration). These authors found that the contaminants spread more laterally than vertically, suggesting that the permeability of the fractured Regina clay was considerably less than the fill. They hypothesized that the Askarel moved as a separate liquid phase along the largest fractures. As an oily phase, Askarel would not wet the rock, but would form droplets that would be trapped as the fractures became smaller. Capillary forces would have to be overcome to force entry of this oily phase into pore openings saturated with water. The force needed would become greater as porosity and permeability decreased. A high head in the system would be needed to overcome this force, making it unlikely that the Askarel would continue to migrate downward as a distinct phase. However, the Askarel does have a finite, though low, solubility in water which would allow it to migrate slowly downward through the low-permeability zone as a dissolved phase in

MONS 018682

water. A field study such as this dramatically emphasizes the need to study PCB migration in three phases: as a dissolved phase (which is how most of the laboratory experiments have been performed), as a sorbed phase (transportation on particles during runoff), and as a pure PCB or PCB/organic solvent phase (an area which has barely been explored).

EFFECTS OF SOILS ON VOLATILIZATION, PLANT UPTAKE, AND DEGRADATION

The transport of PCBs in soils is affected by several processes that can lead to an attenuation of the PCBs in the soil environment. Such processes include volatilization of PCBs from soils, plant uptake, bioaccumulation, and chemical or biological degradation. In turn, the soil environment can significantly affect these removal processes.

Volatilization

Volatilization from soils is a function of the (air and soil) temperature and moisture content, the vapor pressure of the compound, concentration of the compound, the degree to which it is bound to the soil (Haque et al. 1974), and the gas velocity in the soil and air (Thibodeaux 1981). Volatilization is much lower from soils than from water (Kilzer et al. 1979); even the presence of soil particulates or soluble humic substances reduces the volatilization of PCBs from aqueous solution (Griffin and Chian 1980). The mass transfer coefficient is three and one-half orders of magnitude less in soil than in air, though it increases by an order of magnitude as gas is generated in a landfill and gas velocity is thereby increased (Thibodeaux 1981). Thus, for PCBs in a landfill, the greatest barrier to volatilization is the fill cover material. A calculated emission flux rate is on the order of 9×10^{-4} g/m^2/day (Thibodeaux 1981). At an uncontrolled landfill containing leaking capacitors, the fugitive emissions of PCBs into the air were found to be one to three orders of magnitude above background levels; at an unspecified distance downwind from these sites, the emissions were up to an order of magnitude above background (Lewis et al. 1984). At a controlled chemical waste landfill, the average PCB emission rate was determined to be 12.1 ng/s (under conditions of -1° to 14°C, 0.4 to 6.6 m/s wind speed, and 46% to 96% relative humidity). These concentrations were insufficient to be detected downwind (Lewis et al. 1984).

The vapor loss of Aroclor 1254 from soil surfaces was considered negligible during a 4-week interval (Haque et al. 1974). However, Pal et al. (1980) point out that while the volatilization rate is low, the total loss by volatilization over time may be significant because of the persistence and stability of the PCBs. These authors also reference a study in which 40% to 50% of Aroclor 1254 (0.05 to 5.0 ppm in soil)

MONS 018683

was lost from three soils in 2 to 4 months. The type of soil will also influence volatilization, with sands allowing more and humus less (Kilzer et al. 1979). Increasing amounts of organic matter, activated carbon, or clay in the soils may decrease volatilization loss as a result of increased sorption.

The different PCB congeners exhibit different volatilization rates. For example, Aroclor 1242 was found at higher concentrations than Aroclor 1260 above a landfill, even though it was present in the landfill in smaller quantities (Lewis et al. 1984). Hexachloro and heptachloro PCBs volatilize much more slowly than do pentachloro PCBs which, in turn, volatilize at half the rate of tetrachloro PCBs from a sand (Pal et al. 1980). A substantial percentage of dichlorobiphenyl was lost from soils after 1 and 2 years (54% and 79%, respectively), presumably as a result of volatilization (Moza et al. 1976). Kilzer et al. (1979) caution, however, that the relative ranking of volatilization of compounds from water is not predictive for volatilization from wetted soils. For example, while one trichlorobiphenyl isomer volatilized from sand at a rate two and one-half times that observed for a pentachlorobiphenyl, their volatilization rates from humus were very similar.

Plant Uptake

Plant uptake of PCBs is also influenced by soil properties. Addition of 10 to 1000 ppm of PCBs to the soil resulted in up to 100% inhibition of soybean, beet, and redroot pigweed growth (Strek 1980). However, if activated carbon is added to the soil, there is an 81% to 100% reduction in PCB uptake by the plants, and no inhibition occurs (Strek 1980). This result is consistent with the findings by Lawrence and Tosine (1976) that activated carbon added to waters strongly sorbs PCBs (though, incidentally, they found that PVC is a more effective sorbent of PCBs from raw sewage). Strek and Weber (1982) also demonstrated with a series of treated soils that removal of organic carbon from the soil causes greater inhibition of plant growth, addition of clay decreases inhibition, and addition of organic carbon decreases inhibition further. This is, of course, consistent with the relative degrees of sorption of PCBs by these treated soils. Bioaccumulation of PCBs in crops appears to be inhibited in aerobic soils. For example, carrot roots have a bioaccumulation factor of two and sugar beets exhibit no bioaccumulation (Moza et al. 1976). This is in marked contrast to flooded soils and aquatic areas where bioaccumulation is pronounced (Pal et al. 1980).

Degradation

Degradation of PCBs in soils is another mechanism of removal of PCBs from the soil that is affected by the soil environment. Iwata et al. (1973) showed major

MONS 018684

differences in losses of Aroclor 1254 congeners from six soil types in 1 year. In two soils (with 0.3% and 11.3% OC), 95% of the Aroclor 1254 was recovered with no preferential losses of different congeners. In the other four soils (with 0.06% to 1.9% OC), varying degrees of preferential loss of the less chlorinated congeners were observed. Losses were attributed to degradation or sorption since leaching and volatilization were minimized by experimental conditions. Strek (1980) found that the presence of activated carbon (3333 ppm) in soils decreased the loss of the applied PCB by a factor of almost two in 1.5 years.

Other studies have also observed the relative ease of degradation of less chlorinated congeners. For example, monochloro isomers in Aroclor 1242 were 100% degraded in 6 hours by a mixed culture of soil microorganisms, whereas tetrachloro isomers in Aroclor 1242 were ~42% degraded after 15 days (Griffin and Chian 1980). The position of the chlorine atoms also affects the rate of degradation; PCBs with a preponderance of chlorine atoms on one ring degrade more readily relative to those with equal numbers of chlorine atoms on both rings (Pal et al. 1980). Biodegradation is an important attenuation mechanism for monochloro, dichloro, and trichloro PCBs, but it is much less significant with pentachloro and more highly chlorinated PCBs; however, the presence of the less chlorinated congeners may help induce the degradation of the more chlorinated congeners (Pal et al. 1980). It should be noted that high concentrations of PCBs (on the order of 10,000 ppm) inhibit soil microbial activity. Metabolism of PCBs requires aerobic conditions (Pal et al. 1980).

For a dichlorobiphenyl, degradation in 1 year resulted in 8.8% soluble metabolites and 42% unextractable residues (Moza et al. 1976). Metabolites include monochlorobenzoic acids, monohydroxydichlorobiphenyls, and hydroxyoxo(chlorophenyl)chlorohexadienoic acid (Baxter and Sutherland 1984). Metabolism of Aroclor 1242 results in analogous metabolites that are more highly chlorinated. Photodegradation of PCB metabolites yields monochloroacetophenones (Baxter and Sutherland 1984). Photodegradation may also initiate the destruction of highly chlorinated PCBs (Pal et al. 1980). However, in soils, photodegradation would only be possible to a 1-mm depth (the penetration depth of UV radiation) and would require localized anaerobic areas to mitigate the quenching effect of oxygen (Pal et al. 1980).

PCDD ATTENUATION IN SOILS

Despite the tremendous amount of recent public attention to PCDDs, especially 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), in the environment, it appears from the published literature that relatively few laboratory studies have dealt with PCDD attenuation in soils. This may be because safety precautions and specially designed

MONS 018685

laboratories are required for this type of research. Field studies are rather more numerous, but, not surprisingly, are generally more concerned with cleanup and containment of spills than with controlled studies. Most work has dealt with TCDD, though a few studies have also considered 2,7-dibenzo-p-dioxin (DCDD).

Field Study

One fairly extensive field study has occurred in conjunction with the industrial accident in Seveso, Italy, which resulted in the TCDD contamination of a large area. In a series of studies, Di Domenico et al. (1980a, 1980b, 1980c, 1982) made the following observations:

- TCDD concentration was highly variable in the soil surface layer.
- The highest TCDD concentration was not in the top 0.5 cm of soil, but was usually found at 0.5- to 1.5-cm depth; this was postulated to be a result of photodegradation, volatilization, or penetration and binding of TCDD to the lower soil layers.
- The amount of TCDD found at depths greater than 8 cm was at least an order of magnitude lower than that found in the upper layer. The concentration at greater depths increased slightly in 1 year; this was considered significant.
- TCDD concentrations decreased rapidly in the first 5 months, dropping by about half; this was attributed to photodegradation or volatilization in the soil surface layer. After 5 months, the rate of decrease in TCDD concentration declined significantly, with little further decrease apparent. Thus, predictions of persistence of TCDD in the soil increased with elapsed time after the incident; for example, 1 month after the incident, persistence was thought to be 1 year, whereas by 17 months after the accident, persistence was thought to be 10 years.
- Wipf et al. (1982) observed that plant uptake was minimal for apples, pears, peaches, corn, and carrots, though the outer layers of the vegetation did accumulate TCDD from local dust.

Equilibrium Sorption

None of the papers reviewed have yielded any data on sorption isotherms or partition coefficients for PCDDs. However, Hutter and Philippi (1982) estimate a sorption coefficient of 1×10^4 from data in Isensee and Jones (1975). They observed that TCDD becomes strongly sorbed to soils during long-term incubations and becomes more difficult to extract with time, leading to potential experimental extraction artifacts. At least one study by Walters and Means is currently under way that deals with determination of kinetic and equilibrium characteristics of sorption and desorption of TCDD on soils.

Physical Constants: Water Solubility, K_{ow}, Vapor Pressure, Henry's Law Constant

Some physical constants for TCDD are summarized in Table 2-4.

Table 2-4

PHYSICAL PROPERTIES OF TCDD

Property	Value	References
Water Solubility (ppm)	2E-4	Kearney et al. (1972), Helling (1971)
	3.17E-4 (25°C)	Schroy et al. (1984)
Log K_{ow} (unitless)	6.15	Schroy et al. (1984)
Vapor Pressure (torr)	1.7E-6	Schroy et al. (1984)[a]
	1.49E-9 (25°C)	Schroy et al. (1984)
Henry's Law Constant ($atm\text{-}m^3$/mole)	2.1E-6 (25°C)	Schroy et al. (1984)[a]

[a]Estimated from the general literature.

Soil TLC

The mobility of TCDD and OCDD as determined by soil TLC has been addressed by Helling (1971) and Kearney et al. (1973a). The five soils studied had a range of organic carbon between 0.08% and 52.4%, a clay content between 0% and 39.5%, and a cation exchange capacity between 0.2 and 33.8 meq/100 g. As with the PCBs, the r_f values of both PCDDs, using water as the developing solvent, were 0.0 for all soils, despite their diversity.

Soil Leaching Studies

Five studies indicate that there is little or no leaching of TCDD in soils. For example, in an aquatic ecosystem, TCDD added to the water was found in only the uppermost organic soil layer after 2 years (Tsushimoto et al. 1982). In a highly porous sandy soil, Young (1983) observed that the TCDD remained in the top 15 cm of soil 14 years after application. Kearney et al. (1973a) claim that vertical movement of TCDD did not occur in a wide range of soil types; however, they do not document this statement. In a column study by Matsumura and Benezet (1973), almost no TCDD leached from sand to soil in 7 days. However, Yockim et al. (1978) did find some desorption of TCDD into water from a silt loam soil (0.9% OC, 12.2% clay) after

MONS 018687

1 day. During a period of 275 days, Nash and Beall (1980) also observed minor leaching of TCDD which reached a (low) concentration maximum in the leachate water after 126 days and then declined.

Degradation

Degradation studies include a determination of the half-lives of PCDDs in soils and an attempt to explain their loss by mechanisms that include volatilization, photodegradation, and biodegradation. Half-lives of TCDD have been determined in soils as well as in a number of other media (see Table 2-5). In another study, Yockim et al. (1978) found that soil TCDD levels decreased by 18% in 5 months.

Table 2-5

HALF-LIVES OF TCDD

Matrix	Half-Life	References
sediment and water	600 days	Ward and Matsumura (1978)
soil and organic compost	2.5 years	Camoni et al. (1982)
loamy sand (0.5% OC)	420-540 days	Kearney et al. (1972)
silty clay loam (1.5% OC, 39.5% clay)	530-650 days	Kearney et al. (1972)
soils	10-12 years[a]	Young (1983)
soils (with high herbicide/ microbial concentrations)	< 200 days	Young (1983)
moist soils (1-100 ppm TCDD)	1 year	Kearney et al. (1973a)
soils	variable	Nash and Beall (1980)
grass	5 days	Nash and Beall (1980)
leachate water	57-65 days	Nash and Beall (1980)
air	7-24 days	Nash and Beall (1980)

[a]Measure of persistence rather than half-life.

MONS 018688

Volatilization

Hutter and Philippi (1982) summarize the conflicting information about TCDD volatilization by stating that it is negligible over short time periods, but that some TCDD losses have been attributed to volatilization (e.g., Cameni et al. 1982; Young 1983). Plimmer (1978) observed TCDD on thin layer chromatography plates in the dark. In his experiments, 16% of the applied TCDD was volatilized from silica gel plates in 8 hours (32% in 20 hours) and 6% was volatized in 8 hours from a plate coated with a silty clay loam. Young (1983) suggests the possibility of water-mediated evaporation from soils.

Photodegradation

Plimmer (1978) also compared the decomposition of TCDD on TLC plates in the dark and in sunlight. When the TLC plate was coated with silica gel, 31% of the TCDD decomposed in sunlight compared to 1% in the dark, suggesting substantial photodegradation. However, when the TLC plate was coated with a silty clay loam, negligible photolysis of the TCDD occurred. The photolysis products on the silica gel plate were more polar than the TCDD. Nash and Beall (1980) also found that TCDD on leaves, grass, and in air (but not in soil) degraded more readily in the sun than in the shade in a microagroecosystem chamber and field plot. More TCDD was also lost by volatilization from the nonshaded plot (50°C) than from the shaded plot (30°C). The photolysis reaction includes dechlorination to mono-, di-, and tri-chlorinated dibenzo-p-dioxins. Kearney et al. (1973b) also concluded that TCDD does not photodecompose on wet or dry soil surfaces. Both Crosby et al. (1973) and Liberti et al. (1978) suggest that the photodecomposition of TCDD is a reductive dechlorination process that requires a hydrogen donor. Thus, photodecomposition is negligible for thin films of pure TCDD on dry, irradiated soil surfaces (Crosby et al. 1973). However, the presence of organic solvents or other organic compounds may photosensitize TCDD. Liberti et al. (1978) treated a sieved soil with a hydrogen donor solvent and noted 100% decay to a depth of 10 mm and 40% to 60% decay to a depth of 30 mm after 9 days in the sun. (It is possible that part of this decay could be attributed to volatilization.)

Biodegradation and Plant Uptake

TCDD does not appear to be readily biodegradable (Hutter and Philippi 1982). Little CO_2 evolution was measurable from TCDD after 1 year. In a test of 100 microbial strains, Matsumura and Benezet (1973) found only five with some ability to degrade TCDD. DCDD, on the other hand, is metabolized to the extent of ~5% in 10 weeks; the major metabolite is more polar than the parent compound (Kearney et al. 1972).

MONS 018689

The uptake of TCDD from soil by oats and soybeans is negligible (Isensee and Jones 1971; Kearney et al. 1973a). As with PCBs, there seems to be a greater uptake of TCDD from solution than from soils. Oats and soybeans took up two to ten times as much TCDD from solution than from soils, averaging 13% in the roots, though little in other parts of the plants.

MONS 018690

Section 3

SORPTION MODEL REVIEW

The objective of Task 2 of this study was to review available literature on models that describe the role sorption plays in the attenuation of hydrophobic organic compounds, specifically PCBs, in soils, sediments, and groundwater aquifer materials during the solute transport of these compounds in natural waters. This section documents the results of this review. Because PCBs fall within the broad class of hydrophobic organic compounds, models describing hydrophobic sorption are emphasized in this review. It was beyond the scope of this study to review the models describing attenuation of these compounds via volatilization or microbiological degradation processes, or models describing their transport via immiscible multiphase fluid flow and/or suspended particulate and sediment movement.

Hydrophobic organic compounds are typically those that are relatively insoluble in water (water solubility <100 ppm) and whose octanol/water partition coefficients, K_{ow}, (defined in Eq. 3-15 below) are greater than 10^2 to 10^3. For example, the water solubility and K_{ow}s of PCB isomers fall within the range 5.9 ppm < S (PCBs) < 7.0 ppb and 4.4 < log K_{ow} (PCBs) < 8.13. In general, hydrophobic solutes are not involved in strong specific interactions (e.g., coulombic attraction, ligand exchange, or hydrogen bonding) with the sorbent (Hamaker and Thompson 1972). Sorption of hydrophobic solutes results, not because of a large sorbate-sorbent bonding energy, but rather, because the sorbate-solvent and sorbent-solvent interaction is weak relative to the solvent-solvent (i.e., the tendency of water to bond to itself) interaction. Hydrophobic bonding is a long-range attraction which describes the enhanced interaction between sorbate and sorbent resulting from the presence of a solvent with strong self-bonding interactions (Adamson 1982). Hydrophobic sorption increases as the sorbate becomes less polar or as its water solubility decreases (Gustafson et al. 1968; Gustafson and Paleos 1971).

The models and related estimation methods for describing hydrophobic sorption reviewed in this section have been developed using, and are applicable to, a broad range of hydrophobic compounds. In most cases, these models have not been explicitly applied to PCB sorption, although in a few cases the hydrophobic compounds

MONS 018691

modeled included two or three PCB congeners. Thus, in this section examples taken from the literature consider other hydrophobic compounds as well as PCBs.

The soil/subsurface mobility and fate of organic compounds such as PCBs, PCDOs, and PCDFs are ultimately described by solute transport models. This section provides a brief description of how sorption models are incorporated into and used in solute transport models. Mathematical descriptions of sorption isotherm models, linear organic-carbon-referenced models, and gel models of equilibrium sorption are reviewed. The emphasis in the literature centers around sorption of dilute solutes from an aqueous solvent phase. However, where available, mathematical descriptions of sorption from nonaqueous or mixtures of aqueous/organic solvents are included. A mathematical description of sorption on low carbon soils, the reversibility of the sorption process, and sorption kinetics are also discussed.

SOLUTE TRANSPORT MODELS INCLUDING SORPTION

Currently, models used to predict or simulate the transport of organic and inorganic compounds through porous media are based on an advective-dispersive (AD) equation (described in Eq. 3-1 below). For most organic solutes, additional terms or equations which describe the chemical or microbiological reactions must be added to the AD equation. In general, these reactions retard or attenuate the advance of the solute relative to the movement of the bulk fluid. For PCBs, sorption is the dominant attenuation mechanism because these compounds are relatively resistant to chemical and microbiological transformation. Thus, to describe the transport of PCBs in soils, sediments, and groundwater aquifer materials (henceforth referred to as sorbents), it is necessary to incorporate a mathematical representation of the sorption/desorption process into the AD equation.

The AD equation used to describe one-dimensional advective-dispersion of a solute in uniform porous media at steady hydraulic flow with constant water content can be written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \qquad (3\text{-}1)$$

where C is the concentration of the mobile organic solute, S is the sorbed phase concentration, D is the dispersion coefficient in the direction of flow (Bear 1972), x is the direction of flow, v is the average velocity of fluid (solvent) phase, ρ is the bulk density of the porous media and θ is the volumetric water content.

MONS 018692

Sorption is usually incorporated into the AD equation by assuming that S is a function of C [i.e., by the sorption isotherm $S = f(C)$]. In general, sorption cannot be adequately represented by a single function because S depends on other variables in addition to C. This dependence on other variables can, in some cases, be highly complex (e.g., if the organic solute is ionizable and forms complexes with other ions in solution). However, PCBs are relatively inert and generally undergo no significant side reactions (ionization, complexion, etc.) with other constituents in solution. Thus, representation of PCB sorption with a single isotherm equation is valid.

Based on the local equilibrium assumption (James and Rubin 1979), it is possible to replace $\partial S/\partial t$ in Eq. 3-1 by $(dS/dC)\cdot(\partial C/\partial t)$. The last term on the right-hand side of Eq. 3-1 becomes

$$-\frac{\rho}{\theta} K' \frac{\partial C}{\partial t}$$

where $K' = dS/dC$ and is physically represented by the slope of the sorption isotherm. This expression represents the solute mass which is lost from solution as a result of sorption. The resultant AD equation is applicable only when sorption reactions are fast relative to the velocity, v, and sorption equilibrium is attained.

For many organic sorbates and PCBs in particular, the isotherm is linear for a wide range of soil types and typical environmental concentrations. In such cases the slope, K', of the isotherm is a constant and is typically referred to as the distribution coefficient, K_d, or partition coefficient, K_p. For PCBs the latter terminology is more appropriate. Under these circumstances the AD equation for PCB transport can be expressed as

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 C}{\partial x^2} - v' \frac{\partial C}{\partial x} \qquad (3\text{-}2)$$

where D' is the effective dispersion coefficient ($D' = D/R_f$) and v' is rate of advance of the PCB front ($v' = v/R_f$) in the absence of dispersion. This PCB front is retarded relative to the rate of advection of the front (v) of a nonreactive solute; R_f is the PCB retardation factor, defined as v/v' or as

MONS 018693

$$R_f = v/v' = 1 + \frac{\rho}{\theta} K_p \qquad (3\text{-}3)$$

Many types of sorption isotherms have been used to describe the sorption of organic compounds on soils, and a few of these are discussed in the following subsections.

ISOTHERM AND PARTITION CONSTANT (K_p) MODELS

Sorption isotherm models consist of 1) a functional relationship, or isotherm equation, relating the surface density of sorbed organic compound to its solution activity (C) at equilibrium; and 2) a set of assumptions on which the isotherm equation is based. Ideally, S could be expressed as the surface activity of the sorbent per unit mass of the solid sorbent. However, because no adequate theory exists for calculating the surface activities of organic compounds, S is typically expressed in units of concentration per unit mass of solid. The solution activity, C, can also be expressed in terms of concentrations rather than solution activities when the compound behaves ideally (e.g., in dilute sorbate solutions). A plot of S versus C is referred to as the sorption isotherm. The Linear, Langmuir, BET, Frumkin, and Freundlich models are briefly described below.

Linear Isotherm Model

By far the simplest model of sorption is the linear sorption model where the amount sorbed (S) is related to the equilibrium solution concentration (C) by a constant and a linear isotherm results. This constant is the slope of the isotherm and referred to as the partition coefficient,

$$K_p = \frac{S}{C} \qquad (3\text{-}4)$$

Applications of this model have been extensively described in the PCB sorption literature (see Section 2 of this report). Each of the models discussed below reduces to this linear relationship for low solution concentration of the sorbate. Low solution concentration is typically encountered for hydrophobic organic compounds, such as PCBs, under natural environmental conditions. Because of its mathematical simplicity, the linear isotherm model is easily incorporated into, and allows easy solution of, the advective-dispersive solute transport equations (Cherry et al. 1984).

When describing the sorption of organic compounds which consist of a number of individual species or congeners, a distinction must be made between the partition

MONS 018694

coefficient, K_p^i, for sorption of individual congeners and the distribution ratio, K_D, for PCB mixtures defined by,

$$K_D = \frac{\sum_i S_i}{\sum_i C_i} = \frac{\sum_i K_p^i C_i}{\sum_i C_i} = \frac{S_{an}}{C_{an}} \qquad (3\text{-}5)$$

where S_{an} and C_{an} are the total analytical concentrations of all sorbed and solution congeners, respectively, and the sum is over all congeners present.

This distinction is particularly important when describing PCB mobility in soils (e.g., Eq. 3-3). Since K_p^is for individual congeners differ, K_D changes as congeners are chromatographically separated from each other along the migration path of the Aroclor. When modeling PCB transport, K_D is not an adequate parameter for describing attenuation via sorption; individual K_p^is should be used.

Langmuir Model

The Langmuir model is based on the following assumptions: 1) the free energy of sorption (ΔG) is constant and independent of S (i.e., the extent of surface coverage); 2) no surface heterogeneity exists (i.e., all regions of surface are energetically identical); 3) no interactions occur between sorbed species; and 4) the maximum monolayer sorption density (S^m) is that of a complete monolayer. The Langmuir isotherm equation is described by the expression

$$S = \frac{K_L S^m C}{1 + K_L C} \qquad (3\text{-}6)$$

where the Langmuir constant K_L can be related to the free energy of sorption (ΔG) by the expression $K_L = \exp(-\Delta G/RT)$, where R is the gas constant and T is the temperature in degrees Kelvin.

If more than one organic sorbate is present in solution, the individual sorbates will compete for the available surface in relation to their individual binding constants, K_Ls. This competition reduces the sorption of each individual sorbate. For the case of two Langmuirian sorbates, '1' and '2', Eq. 3-6 can be generalized to account for the competitive effect of each sorbate on the sorption of the other, that is,

$$S_1 = \frac{K_{L1} S_1^m C_1}{1 + K_{L1} C_1 + K_{L2} C_2} \qquad (3\text{-}7)$$

MONS 018695

$$S_2 = \frac{K_{L2}\, S_2^m\, C_2}{1 + K_{L1}\, C_1 + K_{L2}\, C_2}$$

where S and C for sorbates '1' and '2' are as defined above, and the S^ms and K_Ls are the single-sorbate sorption maximum and Langmuir adsorption constants for each sorbate. The competitive Langumir Model (Eq. 3-7) has also been used for describing sorption of single sorbates onto heterogeneous soils containing more than one type of sorption site. For example, if two Langmuirian sites, 1 and 2, exist on the sorbent surface, with binding constants K_{L1} and K_{L2}, respectively, then S_1 and S_2 describe the amount of sorbate on each site.

In the single application of the Langmuir model to PCB (Aroclor 1254) sorption found in the literature, Weber et al. (1983) measured S_{an} and C_{an} and found that Eq. 3-6 did not provide a good fit to the data. This is not surprising, however, because Eq. 3-6 assumes a constant free energy of sorption (or a single K) and, as Eq. 3-5 shows, an Aroclor mixture by necessity is characterized by several K^is. Use of a 'competitive type' Langmuir model or a 'composite' K_D may have provided a better fit to the data. Weber et al. (1983) found that the Freundlich isotherm (described below) provided a good fit to the Aroclor 1254 data. The competitive Langmuir model (Eq. 3-7) has been used as the basis of a model that treats the 'apparent' irreversible sorption of single PCB isomers on soils that are presumed to possess two distinct sorption sites with K_{L1} and K_{L2} (Curl and Keoleian 1984).

BET Model

Ample evidence in the soils literature of non-Langmuirian sorption behavior suggests that one or more of the Langmuir assumptions are violated. If, for example, the monolayer assumption is relaxed, multilayer Langmuirian sorption can be described by the Brunauer, Emmett and Teller (BET) isotherm. The sorption of the first monolayer of sorbate molecules with a constant average heat of sorption, E, forms a new surface layer to which additional molecules sorb with an average heat of sorption, E_2. Each layer is assumed to follow a Langmuir equation. No limit to the number of successive layers is imposed, and thus, the adsorption density approaches that of a saturated vapor condensing on the surface of the saturated solution in contact with the solid. If the heats of adsorption on all successive layers are assumed equal, the BET equation is,

$$S = \frac{K_B S^m C}{(C_s - C)[1 + (K_B - 1)(C/C_s)]} \qquad (3\text{-}8)$$

where C_s is the saturation concentration of the solute, S^m is the maximum adsorption density of the first layer corresponding to complete monolayer coverage, K_B is a constant related to the difference in sorption energies ($E_1 - E_2$) and the ratio of evaporation/condensation coefficients for sorbed layers (Bailey and White 1970). The BET equation reduces to the Langmuir equation if $K_B >> 1$ and $C/C_s << 1$. The BET isotherm differs from the other isotherm equations considered in this section by allowing for the creation of new surface as the existing surface becomes occupied. We are not aware of any application of the BET model to PCB sorption data; however, at high solute concentrations, this model may be applicable. The curvature of the experimental isotherm at PCB concentrations greater than 50% of its solubility limit will provide an indication of whether the BET model is applicable.

Frumkin Model

If either attractive or repulsive interactions between sorbed species become significant as the fractional surface coverage ($\theta = S/S^m$) increases, the energy of sorption becomes an explicit function of surface coverage, S. Frumkin extended the original Langmuir formulation to include a term describing long-range surface interaction energy among surface species. The Frumkin isotherm equation can be expressed as

$$S = \frac{S^m K_f C \exp[-\alpha(S/S^m)]}{1 + K_f C \exp[-\alpha(S/S^m)]} \qquad (3\text{-}9)$$

where α is a parameter that expresses the way in which increased sorption changes the sorption energy of the sorbate (Parsons 1964; Bard and Faulkner 1980). If $\alpha > 0$, the interactions between two surface species are attractive and sorption is enhanced (i.e., the slope of the Frumkin isotherm is greater for all values of C than in the Langmuir case). Conversely, if $\alpha < 0$ (repulsive surface interactions), sorption is retarded with respect to the Langmuir case. As α approaches zero, Eq. 3-9 reduces to the Langmuir isotherm equation. The Frumkin isotherm model has been widely used to describe sorption of both polar and hydrophobic compounds onto electrode surfaces. It has been applied to the modeling of the sorption to soils of hydrophobic organic compounds by Koopal (1984). We find no evidence that it has

MONS 018697

been applied to PCB sorption on soils, although at high sorption densities where lateral attractive hydrophobic interactions may occur on the surface, this model may be useful.

Freundlich Model

Other possible isotherm equations can be derived if 1) the condition that a maximum sorption capacity, S, exists is relaxed and 2) the free energy of sorption (ΔG) decreases as S increases. This decrease in sorption energy could occur if the surface is heterogeneous in structure or composition and the most energetically favorable regions of the surface are initially occupied. For example, if we assume that the sorption energy varies as log (S) and that the distribution of ΔG on the surface is Gaussian, then the Freundlich isotherm equation can be derived (Sposito 1981; Adamson 1982) and expressed as

$$S = K_f C^{1/n} \tag{3-10}$$

where K_f and n are empirical constants. For dilute solutions n is typically 1, but as the sorption density increases, $n > 1$. Examples of typical Freundlich isotherms are compared to a linear isotherm in Figure 3-1a. The linearized form of Eq. 3-10 (Figure 3-1b),

$$\ln (S) = \ln K_f + (1/n) \ln C \tag{3-11}$$

is used to derive the parameters (1/n) and K_f from experimental data. Note that no physical basis exists for assuming the log (S) or the Gaussian energy distribution. Indeed, Eq. 3-10 was originally used by Freundlich because it frequently described experimental data better than Langmuir, BET, and other models. Repeated attempts to attach physical significance to the constants, K_f and n, have generally been unsuccessful. However, K_f has been considered by some to be a relative indicator of sorption capacity (Weber 1972), although this interpretation is questionable. The literature shows that the Freundlich model has been widely used for describing PCB sorption (see Section 2 of this report).

MONS 018698

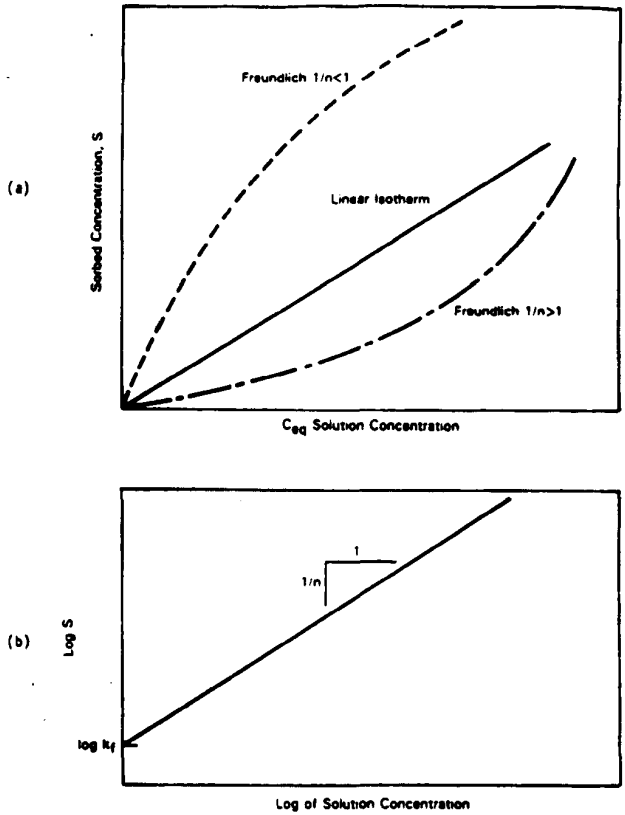


Figure 3-1. (a) Examples of Linear and Freundlich isotherm commonly used to describe PCB sorption/desorption data. (b) Linearized Freundlich isotherm from which Freundlich constants K_F and n may be determined.

It should be emphasized that the empirical observation that a given set of adsorption data can be fitted to a Langmuir, Freundlich, or Frumkin equation does not necessarily establish a constant or logarithmic dependence of adsorption energy on adsorption density, S, nor the existence of interactions between surface sorbate species.

The isotherms or partition coefficients described above are expressed in terms of the concentration of the total sorbate (C) in solution. This implicitly assumes that the free energy of adsorption for all solution species is equal. For ionizable organic sorbates, this assumption may not be correct. However, for individual PCB congeners, this assumption is valid. The use of sorbate activities, rather than concentrations, in the above isotherms would, however, extend their applicability to higher solute concentrations and to mixed aqueous/organic solvents where variations in the ratio of miscible components may significantly alter the activities of the sorbate species (Chiou et al. 1982).

CARBON-REFERENCE SORPTION MODEL

The linear isotherm model discussed by Karickhoff (1981, 1984) describes sorption of hydrophobic organic solutes at low environmental concentrations for a wide variety of soils and sediments. This model, which is probably the most applicable model for existing PCB data, can be derived from the following thermodynamic condition: the sorbate fugacities (F)* in the solution and sorbed phases are equal at equilibrium (i.e., $F_s = F_w$). The subscripts "s" and "w" refer to the sorbent and solution phases, respectively. In each phase, the fugacity and concentration are related; in aqueous solution, for example,

$$F_w = \gamma_w F_w^0 C_w = \phi_w C_w$$

where γ_w is the activity coefficient, F_w^0 is the corresponding reference state fugacity and their product is termed the fugacity coefficient, ϕ_w. For hydrophobic compounds the reference state is usually taken as the pure liquid solute at STP or the supercooled liquid when the solute has a melting point greater than 0°C (as is

*The fugacity can be thought of as the 'escaping tendency' of a chemical compound from a phase and has units of pressure. In terms of a thermodynamic driving force, fugacity is to mass diffusion as temperature is to heat diffusion. At equilibrium, the fugacities of a compound in air, solution, soil, and biotic phases are equal (Mackay 1979).

MONS 018700

the case for PCB congeners). This relation is valid for mole fraction units; however, for low concentrations conventional units (moles/L) can be used. Using a similar expression for F_s, the equality of fugacities yields the isotherm:

$$S = K_p C \tag{3-12}$$

where,

$$K_p = \frac{\gamma_w F_w}{\gamma_s F_s} = \frac{\phi_w}{\phi_s} \tag{3-13}$$

More generally, for composite sorbents consisting of several components (e.g., organic carbon, expandable clay), K_p can be expressed as a linear combination of the sorption onto individual components

$$K_p = \phi_w \sum_j (Y^j/\phi_s^j) \tag{3-14}$$

where Y^j denotes the weight-fraction of component j. This combination assumes no interactions among components exist, and $K_p^j = \phi_w/\phi_s^j$ varies linearly with the quantity of each component. In general, because the activity coefficients, and thus K_p, are functions of solute concentration, this sorption isotherm, Eq. 3-12, is nonlinear. However, for dilute conditions, the values of ϕ_s^j approach limiting values, and Eq. 3-12 reduces to a linear isotherm with a constant partition coefficient, K_p.

Organic sorption on natural sediments and soils usually yields linear isotherms when the organic sorbate is present in solution at concentrations below 10^{-5} M or below 50% of the compound water solubility, whichever is lower (Karickhoff et al. 1979; Rogers et al. 1980; Brown and Flagg 1981; Chiou et al. 1982; Hassett et al. 1980a, 1980b; Means et al. 1980, 1982). This is typically the case for PCBs in natural waters. Solute speciation changes (protonation, chemical complexion, coagulation, or degradation) represent a significant source of isotherm nonlinearity for ionizable hydrophobic compounds. PCBs however, are relatively resistant to degradation and undergo virtually no chemical side reactions in solution. In this respect, the linear isotherm model is ideally suited to the description of PCB sorption.

MONS 018701

Based on extensive data for pesticides and neutral hydrophobic organic compounds Karickhoff (1984) concluded that soil organic carbon content (OC) dominates observed variations in K_p for surface soils, while particle size distribution and swellable clay content (CM) are of secondary importance, for most sorbents with OC > 0.1% (by weight). Thus, to a first approximation, K_p in Eq. 3-14 reduces to

$$K_p = \phi_w \frac{f_{oc}}{\phi_{oc}} = K_{oc} f_{oc} \qquad (3\text{-}15)$$

where f_{oc} is the weight fraction of organic carbon in the soil, ϕ_{oc} is the fugacity coefficient of the sorbate in the soil organic carbon, and the carbon-referenced partition coefficient, K_{oc}, is

$$K_{oc} = \frac{\phi_w}{\phi_{oc}} = \frac{K_p}{f_{oc}} \qquad (3\text{-}16)$$

Based on extensive data for a wide variety of hydrophobic organic compounds and natural sorbents, Karickhoff (1984) concluded that for nonionizable, hydrophobic organic compounds, whose water solubility is $<10^{-3}$ M, sorption is typically 'controlled' by soil organic carbon (humin-kerogen), and sorption can be adequately described using the carbon-referenced partition coefficient K_{oc} (i.e., for this class of sorbate, K_{oc} is essentially independent of soil type).

Estimation of K_{oc}

In Eq. 3-16, the dominant variation in K_{oc} is due to the variation in the fugacity coefficient of the sorbate in the solvent, ϕ_w. On the other hand, the fugacity coefficient of the sorbate in the soil organic carbon, ϕ_{oc}, remains relatively constant (Karickhoff 1981). For the case of dilute hydrophobic organic sorbates in an aqueous or mixed aqueous/organic solvent, existing techniques for estimating K_{oc} from basic physical properties of the sorbate are described below.

Relations Between K_{oc} and Water Solubility. Based on the reciprocal relationship between ϕ_w and mole-fraction solubility (X_w), Karickhoff (1981, 1984) has shown that for hydrophobic sorbates

$$\log K_{oc} = - a \log X_w - \frac{\Delta S_f (T_m - T)}{2.303\ RT} + b \qquad (3\text{-}17)$$

MONS 018702

where a and b depend on ϕ_{OC} but are treated as regression parameters, ΔS_f is the entropy of fusion, T_m is the melting point of the sorbate in °K, R is the gas constant, T is absolute temperature. The ΔS_f term is a "crystal energy" or "melting point" correction to the solubility for sorbates which, like PCBs, are solids at ambient temperatures. For solutes that are liquids at temperature T, the ΔS_f term approaches zero. Reasonable estimates of ΔS_f can be made for families of structurally similar compounds (Yalkowsky and Valvani 1980; Yalkowsky 1981). Karickhoff (1981) evaluated the parameters in Eq. 3-20 using a set of K_{OC}-solubility data for a sequence of condensed ring aromatic compounds. Estimates based on this correlation equation agreed within a factor of 2 to 3 with independent data for several families of hydrophobic compounds. However, using the same correlation equation for highly chlorinated, high molecular weight compounds, such as DDT or hexachlorobiphenyl, yielded estimates that were high by as much as an order of magnitude. In general, it is not advisable to use a correlation equation for estimation outside the immediate class of compounds for which it was derived. Within the family of 209 PCB congeners, this approach should be useful but has not appeared in the literature.

Relation Between K_{OC} and K_{OW}. The octanol-water partition coefficient (K_{OW}) is the ratio of the solute concentration in octanol to that in water. Because fugacities in the two phases are equal, this ratio can be expressed in terms of either fugacity or activity coefficients,

$$K_{OW} = \frac{C_O}{C_W} = \frac{\phi_W}{\phi_O} = b\,\frac{\gamma_W}{\gamma_O} \qquad (3\text{-}18)$$

where b is a constant for converting molar to mole fraction units, and "o" refers to octanol. The partition coefficient, K_{OC}, can be related to K_{OW} by combining Eqs. 3-16 and 3-18,

$$K_{OC} = \frac{\phi'_O}{\phi'_{OC}}\,K_{OW} \qquad (3\text{-}19)$$

Here the primes on the solute fugacity coefficient for the octanol and the organic carbon sorbent refer to water-saturated octanol and sorbent, respectively. It is important to note here that the ratio (ϕ_O'/ϕ_{OC}') must not depend on the solute if a linear relation between K_{OC} and K_{OW} is to exist. Regression equations of the form,

$$\log K_{OC} = a \log K_{OW} + b \qquad (3\text{-}20)$$

MONS 018703

based on this assumption of linearity have been extensively used in the literature (Hassett et al. 1980a; Karickhoff 1981; Schwarzenbach and Westall 1981; Rao at al. 1982). The values of a and b, as data-fitted coefficients, and the accuracy of this linear regression differ depending on the structure and functionality of the sorbate included in the regression. The accuracy of K_{oc} estimated using Eqs. 3-19 and 3-20 depends on 1) the predominance of organic carbon as the soil sorbent and hydrophobic interactions as the dominant sorbate-sorbent interaction and 2) sorption isotherm linearity. The applicability and accuracy of Eqs. 3-19 and 3-20 should be established among PCBs.

Structural Estimates from Molecular Fragments. In general, linear free energy theory treats the solute molecule as an array of fragments and assumes that each of these fragments make independent (linear) contributions to the total free energy, ΔG, of the molecule. The linear free energy relations (LFERs) of interest here describe the partitioning coefficients, K_{ow} and K_{oc}, for solutes in terms of the contributions of individual structural components of the solute.

The incremental change in K_{ow} or K_{oc}, caused by the substitution of a functional group X for a hydrogen atom on the base molecule R-H can be written

$$\pi_{oc}^{X} = \log K_{oc}^{(R-X)} - \log K_{oc}^{(R-H)} \qquad (3\text{-}21)$$

$$\pi_{ow}^{X} = \log K_{ow}^{(R-X)} - \log K_{ow}^{(R-H)}$$

The substituent constants, π_{oc}^{X} and π_{ow}^{X}, for X are derived from experimental sorption data and octanol-water partitioning data. These πs are relatively constant within a family of structurally similar organic compounds. For a family of compounds, say PCBs, Eq. 3-21 can be used to extrapolate values of K_{ow} or K_{oc} for isomers for which no Ks are available using the πs for that family and values of experimentally determined Ks for other isomers.

Because K_{oc} and K_{ow} are linearly related via Eq. 3-19, π_{ow}^{X} can be shown to be proportional to π_{oc}^{X} if the ratio (ϕ_o'/ϕ_{ow}') is independent of solute (sorbate). This result is very useful because existing data for π_{ow}^{Cl} (Leo 1975; Leo et al. 1971) could be used to estimate K_{oc}s for PCBs without developing a separate body of data for substituent constants for chlorine, π_{oc}^{Cl} (Karickhoff 1984).

MONS 018704

The application of K_{OC}-K_{OW} and K_{OC}-solubility relations defined above and the use of Eq. 3-21 in practical problems has been described by Lyman et al. (1982) in a handbook of estimation methods. In general, it is advised that estimation of K_{OC} for a given compound should be derived from a correlation equation derived for a family of structurally similar compounds. A similar caveat applies to substituent constant equations for π. We find no evidence that K_{OC}-K_{OW} and K_{OC}-solubility relations for PCBs, as a family of compounds, have been derived or the linearity of π_{ow}^{Cl}, as a function of the number of substituted Cl atoms, has been examined among PCB congeners.

MIXED SOLVENTS

The K_{OC}-solubility relation, Eq. 3-17, expresses sorption of dilute solute (or sorbate) from aqueous solvents. This relation has been generalized for other solvents and mixed aqueous/organic solvents by Amidon et al. (1974) and Yalkowsky et al. (1975) using a solviphobic cavity model. This model describes the solubility of hydrophobic solute molecules which may contain distinct hydrophobic and polar fragments or moieties. Although this approach has not been applied to estimate aqueous PCB solubility, it may be applicable to the estimation of PCB solubility/sorption from aqueous, nonaqueous, and miscible aqueous/organic solvents.

In the cavity model, solubility is dominated by the energy required to create a cavity in the solvent. This energy depends on the molecular surface area of solute hydrophobic and polar moieties and the interfacial surface tensions between the solvent and these moieties. The mole fraction solubility (X_w) in aqueous solvent is expressed by Amidon, Yalkowsky and coworkers by

$$\log X_j = -\frac{[\gamma_j (HSA) + \phi_j (PSA)]}{2.303\ kT} - \frac{\Delta S_f}{2.303\ RT}(T_m - T) \qquad (3\text{-}22)$$

where j denotes the solvent, k is Boltzman constant, T and R have been defined above, γ_j and ϕ_j are interfacial free energies at the aqueous interface with the hydrophobic and polar segments of the sorbate molecule, whose respective interfacial surface areas are (HSA) and (PSA). The ΔS_f term is the same crystal energy term used in Eq. 3-17. Substitution of Eq. 3-22 into Eq. 3-17 results in a generalization of the expression for K_{OC}^{W}.

$$\log K_{OC}^{W} = a\frac{[\gamma_j (HSA) + \phi_j (PSA)]}{2.303\ kT} + b \qquad (3\text{-}23)$$

MONS 018705

where w refers to water as the solvent. Based on the work of Yalkowsky et al. (1975, 1976) for binary solvent mixtures, Rao et al. (1982) showed that for a mixture of water and water-miscible organic solvent, the K_{OC} for sorbate j in the mixture can be written

$$\log K_{oc}^{m} = \log K_{oc}^{w} - a P_c f_c \tag{3-24}$$

where a is a constant, the superscript m refers to the mixed solvent, and K_{oc}^{w} is defined in Eq. 3-23 for an aqueous solvent that does not contain the organic cosolvent C. The fraction of organic cosolvent is denoted by f_c ($0 < f_c < 1$). The expression for P_c is given by

$$P_c = \frac{[\Delta\gamma_c\ (HSA) + \Delta\phi_c\ (PSA)]}{2.303\ kT} \tag{3-25}$$

where $\Delta\gamma_c$ and $\Delta\phi_c$ are the differences in surface tension between water and the cosolvent

$$\Delta\gamma_c = (\gamma_w - \gamma_c) \text{ and } \Delta\phi_c = (\phi_w - \phi_c) \tag{3-26}$$

Note the PSA term in Eqs. 3-23 and 3-25 vanishes for sorbates containing no polar moieties, as is the case with PCBs. For this reason this description of K_{OC} for mixed solvents should be applicable to PCBs. A further generalization to ternary or quaternary aqueous-organic mixtures was proposed by Rao et al. (1982),

$$\log K_{oc}^{m} = \log K_{oc}^{w} - \sum_k a_k P_k f_k \tag{3-27}$$

where the summation is over cosolvents k, and $f_w + \Sigma f_k = 1$. The theoretical approach on which these mixed-solvent expressions for K_{OC} are based assumes, as Yalkowsky and coworkers do, that solubility can be treated as a linear combination of pair-wise interactions of each solvent with each moiety of the solute molecule. Based on this development, the sorption coefficients, log K_{OC} or log K_p, would be expected to decrease linearly as a function of the cosolvent fraction f_c or Σf_k. This linear decrease has significant implications for the mobility of PCBs in soils contacting mixed solvents.

Nkedi-Kizza et al. (1982), Hornsby et al. (1982) and Rao et al. (1983) have reported data for the sorption of unsubstituted and substituted polycyclic aromatic hydrocarbons from mixed aqueous-organic solvents using reversed-phase high-performance liquid chromatography, batch, and column techniques, which are consistent with the formal description of mixed-solvent sorption presented above. The applicability of this formalism for describing PCB sorption data and/or the a priori estimation of PCB sorption from physical solubility data and surface areas should be evaluated.

The sorption of hydrophobic organic compounds from mixed solvents is being actively researched; however, we found no evidence of current or past research on PCB sorption from mixed solvents.

GEL PARTITION MODEL

Sorption/desorption on soil organic matter (gel) has been described by Freeman and Cheung (1981) using solubility parameter theory for solute-gel and solvent-gel interactions. The humin-kerogen particles and coatings on mineral surfaces responsible for the K_p-f_{oc} correlation in soils are considered to be arrays of highly branched polymer chains that form a three-dimensional network. Interaction of this polymer lattice with the solvent(s) controls the initial polymeric swelling to form a porous gel phase (polymer-solvent system) and its subsequent expansion and contraction. This expansion and contraction, in turn, influences 1) sorption (desorption) rates of solutes into (out of) the gel via diffusion through the gel matrix and 2) apparent reversibility of sorption reactions via 'trapping' or 'lock-in' mechanisms (Johnson and Starr 1972; Ogner and Schnitzer 1971).

Hydrophobic (lipophilic) solutes diffusing into the gel phase will be sorbed depending on the relative solute affinities for the bulk solvent and gel phases. By combining both molecular sieve effects with a solubility theory description of solvent-gel and solute-gel interactions (Hildebrand et al. 1970), Freeman and Killion (1977) are able to describe equilibrium and kinetic sorption processes. An expression for K_{oc} was derived for solute, i:

$$\ln K_{oc} = A - B L_i + \frac{V_i}{RT} f(\delta) \qquad (3\text{-}28)$$

where A and B are soil parameters describing gel phase pore structure; L_i and V_i are the size and molar volume of solute, 'i', respectively; and the solubility parameter function

MONS 018707

$$f(\delta) = (\delta_l - \delta_s)^2 - (\delta_l - \delta_s)^2 \qquad (3\text{-}29)$$

describes the solute preference for the solvent versus the gel phases, based on competing solute-solvent and solute-gel attractive interactions (hydrophobic bonding). Here, δ is the solubility parameter (Hildebrand et al. 1970; Shinoda 1978) and subscripts s and g refer to solvent and gel, respectively.

Maximum gel expansion is expected when gel and solvent solubility parameters are matched, (i.e., $\delta_s = \delta_g$). Diffusion of the solute through the gel will be a maximum for this matched condition and will decrease as the difference between δ_s and δ_g increases (mismatched). The rate of desorption of the solute from the sorbent gel will be a maximum for a solute-gel matched system (i.e., $\delta_l = \delta_g$). However, desorption of a solute is also a function of its solubility in the solvent phase (extracting liquid) and will be favored when solute and solvent are matched. The rate and the extent of the desorption process is maximized when $\delta_l \simeq \delta_s \simeq \delta_g$.

Freeman and Cheung (1981) show that desorption of di(2-ethylhexyl) phthalate (DEHP, $\delta_l = 8$) from a single clay-silt sediment (obtained from an industrial wastewater holding pond, assumed $\delta_g = 10$) into several organic solvents of variable δ_s is consistent with their gel partition model. When δ_s was within the band $\Delta\delta$, whose limits are defined by δ_l and δ_g, rapid and complete desorption of DEHP was observed. When δ_s differed by one or more units from $\Delta\delta$, an initial rapid desorption step occurred, followed by a slow diffusion-controlled desorption step that plateaued well below 100% desorption. Kitchens et al. (1984) reported Aroclor 1260 desorption from a "clay-soil" (2.0% OC) to be between 90% to 92% complete after two successive extractions (10 min each) with an isopropanol solvent ($\delta_s = 11.4$) depending on whether the soil was air-dry or wet (23% water by weight).

For water, $\delta_s = 23$ (Burrell and Immergut 1975), while for natural soil organic carbon (humin) δ_g values of between 10 and 13 have been estimated (Freeman and Cheung 1981; Chiou et al. 1983). Because of magnitude of $\delta_g - \delta_s$ and the formulation of the gel model, it can be concluded that in aqueous systems (or mixed aqueous-organic solvent systems where water is the major cosolvent), sorption equilibrium may be particularly difficult to obtain, requiring days to months. For shorter time periods, the sorption process would appear to be irreversible. In successive batch desorption experiments of PCBs from a "high-clay" soil and a "potting soil" Weitzman (1984) concluded that desorption into aqueous and mixed aqueous/isopropanol solvents was linear with time, extremely slow (days to months), and would be incomplete after

MONS 018708

several hundred successive extractions; desorption of PCB from "pure sand" was more rapid, but still on the order of days to weeks. Indeed, for grossly mismatched solvents, a sorbed component which is highly resistant to desorption may exist similar to that reported by DiToro and Horzempa (1982) for PCBs and by other investigators for a variety of pesticides and hydrophobic sorbates.

Although a δ_1 data base for hydrophobic pollutants such as PCBs is not currently available and the variability of the A, B, and δ_g parameters for different soils has not been established, a major advantage of this gel model is its inherent ability to treat nonaqueous and mixed aqueous/organic solvents through variation of the solvent solubility parameter, δ_1.

SORPTION ON LOW-ORGANIC-CARBON SOILS

The sorption of hydrophobic solutes on low organic carbon soils ($f_{oc} < 0.001$) is not well understood, and thus, no qualitative predictive model is available. However, it has been repeatedly pointed out (Hassett et al. 1980a, 1981a; Mingelgrin and Gerstl 1983; Karickhoff 1984) that the influence of mineral surfaces, particularly expandable clay surfaces, cannot be neglected in low-organic-carbon soils, as they can be in the majority of cases in soils where $f_{oc} > 0.001$. The influence of expandable clay minerals and a description of a crude qualitative model describing their influence on K_p is summarized below.

It is known that surface area is an important parameter influencing sorption of hydrophobic solutes on minerals containing only trace amounts of organic carbon. The expandable clay minerals (e.g., montmorillonite) dominate sorption in natural mixed-mineral assemblages (Hassett et al. 1980a; Karickhoff and Brown 1978). Hassett et al. (1980a) found, for a wide range of soils and organic sorbates, that the large deviations in the observed K_p (K_p^{obs}) with respect to the carbon-referenced K_{oc} depend on the ratio of the expandable clay to organic carbon content of the soil (i.e., f_{cm}/f_{oc}), where f_{cm} is the weight fraction of expandable clays. For sorbates with polar moieties and varying hydrophobicity ($3 < \log K_{ow} < 5$), these deviations in K_p [$K_p = (K_p^{obs}/f_{oc} - K_{ow})$] have been observed when the ratio (f_{cm}/f_{oc}) exceeds some threshold value, f_T (Hassett et al. 1980a, 1981b; Means et al. 1982; Karickhoff 1984). An additional CM contribution to K_p becomes significant at this threshold value.

Examination of the relative importance of the OC and CM soil fractions is facilitated by the simple two compartment model discussed by Karickhoff (1984) in which

MONS 018709

soil organic carbon (humin) and expandable clay surfaces compete for the sorbate. Based on Eq. 3-14, Karickhoff expresses K_p as

$$K_p^{obs} = K_{oc} Y_{oc} + K_{cm} Y_{cm} \tag{3-30}$$

$$= K_{oc} f_{oc} a_{oc} + K_{cm} f_{cm} a_{cm}$$

where K_{oc} and f_{oc} have been defined previously. K_{cm} is an expandable clay-referenced partition constant, f_{cm} is the fractional quantity of expandable clay in the soil, and a_{oc} and a_{cm} are availability fractions ($0 < a_i < 1$) indicating what fraction of the total mass of OC or CM is available for sorption. This simplistic model assumes that the two sorbent compartments act independently (i.e., there is no covariant interaction between sorbents). We have found no evidence of experimental data justifying this assumption for hydrophobic organic sorbates. However, for inorganic sorbates, it is known that mineral surfaces and natural polymeric organic coatings do not behave according to Eq. 3-30 (Altmann 1984). Nevertheless, insight can be obtained by making this assumption and rearranging Eq. 3-30 so that,

$$K_p' = \frac{K_p^{obs}}{f_{oc} a_{oc}} = K_{oc} + K_{cm} \frac{f_{cm}}{f_{oc}} \frac{a_{cm}}{a_{oc}} \tag{3-31}$$

The ratio (a_{cm}/a_{oc}) can be considered as an availability or permeability parameter, λ, describing the ability of the solute to diffuse through the humin coating to the underlying mineral surface. λ can account for the "blockage or masking" (Walker and Crawford 1968; Edwards and Bremner 1967) of clay mineral surfaces by soil organic carbon, which renders them unavailable to organic sorbates. Using Eq. 3-31, Karickhoff analyzed published pesticide data and proposed that a possible threshold value, $f_T = 30$, exists for hydrophobic organic sorbates containing polar moieties. For soils below this threshold, the clay mineral components contribute little to sorption, and $K_p' = K_{oc}$. As f_{cm}/f_{oc} increased above this threshold, K_p' increased significantly relative to K_{oc}. This increase in K_p' is presumed to be a result of the increased accessibility of clay surfaces. Expandable clays are known to contain nonpolar hydrophobic surfaces, ≡Si-O-Si≡, in addition to polar surfaces, -OH (Chen 1976). One can hypothesize that both hydrophobic sorption [attraction of the non-polar solute moieties to hydrophobic clay surfaces (Hassett et al. 1981a) and specific sorption (attraction of polar solute moieties to polar mineral surfaces]

MONS 018710

would contribute to this increase in K_p'. For soils or unconsolidated aquifer materials where $f_{oc} < 0.001$ or $(f_{cm}/f_{oc}) > 30$, Karickhoff concluded that sorption on mineral surfaces should be considered.

It should be emphasized that the value of this threshold must be regarded as tentative and probably depends on the structure and functionality of the solute. In addition, for mixed aqueous-organic solvents, the threshold for a given solute may vary with the fraction of organic cosolvent, f_c. This variation is plausible because 1) the availability parameter, λ, depends on swelling of the humin and thus on the solubility parameter, δ, (Freeman and Cheung 1981) which changes with f_c and 2) hydrophobic sorption on humin decreases exponentially with increasing f_c (see Eq. 3-24). Nothing is known about the sorption behavior of PCBs in low organic carbon soils. Because PCBs contain no polar moieties through which specific sorption to polar clay surfaces could occur, the intensity of hydrophobic sorption to hydrophobic clay surfaces, K_{cm}^{hyd}, may not differ substantially from that of the humin, K_{oc}^{hyd}. Thus, depending on the relative magnitude of K_{cm}^{hyd} and K_{oc}^{hyd} for individual PCB congeners, the observed K_p' may increase, remain constant, or decrease as a function of CM/OC among different soils. For mixed solvents, both the relative increase or decrease in K_p' and the CM/OC thresholds may depend on the type and fraction of the cosolvent. Therefore, an adequate description of sorption in low organic carbon soils of highly hydrophobic, nonpolar, nonionizable compounds such as PCBs may require that the carbon-referenced K_{oc} model be modified as for the less hydrophobic polar compounds described by Eq. 3-30.

SORPTION REVERSIBILITY AND ISOTHERM NONSINGULARITY

The reversibility of organic sorption processes on soils is an important unresolved issue typified by conflicting literature reports. The reversibility of sorption reactions on soils is a key factor both in developing a conceptual understanding of the underlying sorption/desorption mechanisms and incorporating a mathematical description of sorption/desorption into advective/dispersive solute transport equations. If, under equilibrium conditions, successive sorption/desorption experiments can be described by a single isotherm, the term singular isotherm is used and the sorption process is considered to be reversible. However, numerous studies have indicated that successive desorption experiments do not retrace the original sorption isotherm but rather follow a distinct isotherm (more sorption); the term nonsingular isotherm or nonsingularity is used to characterize the observed hysteresis on the plots, S versus C (Figure 3-2). When this nonsingularity is observed, as it often is, it can be attributed to 1) experimental artifacts [e.g., nonattainment of

MONS 018711

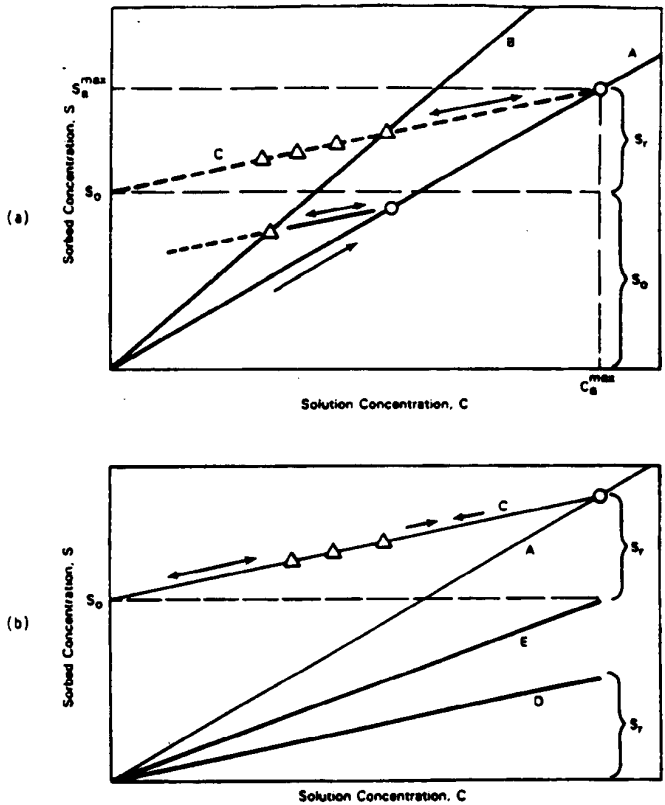


Figure 3-2. Linear sorption-desorption isotherms. (a) Curve A and B are the sorption and first desorption isotherms, respectively. Curve C is the consecutive desorption isotherm which describes the sorption/desorption path followed as the sorbate concentration, C, is cycled between 0 and C_a^{max}. (b) Curve D and E are the isotherms for the easily reversible (S_r) and resistant (S_0) sorbed components, respectively.

equilibrium in the sorption and/or desorption experiment because diffusion-controlled migration of the sorbate through the porous or gel structure of the solid (Freeman and Cheung 1981; Karickhoff 1984)] 2) the existence of a nonsettleable fine-particulate or macromolecule phase in solution that competes with the settleable solids for the sorbate (Voice et al. 1983; Gschwend and Wu 1985), or 3) the existence of a fraction of the bound sorbate that is highly resistant to desorption (DiToro and Horzempa 1982). In tha latter case, the sorption process would appear to be irreversible. Several approaches for describing nonsingular behavior are described below. However, resolution of divergent observations and the basic issue of reversibility remain topics of current research.

The degree of the nonsingularity in many cases is directly proportional to the amount of the sorbate sorbed before initiation of desorption (Van Genuchten et al. 1974), the rate of sorption, the hydrophobicity of the sorbate, and the duretion of the desorption experiment (Mukhtar 1976). Karickhoff (1984) points out that the magnitude of the nonsingularity in K_p is inversely proportional to the rate of desorption (i.e., slow desorption results in a nonsingular isotherm unless the duration of the desorption experiment is sufficiently long to ensure that equilibrium is reached). For the first or single desorption step following the initial sorption step, this nonsingular behavior can be expressed using a pair of Freundlich isotherms,

$$S_a = K_a C^{N_a} \tag{3-32}$$

and

$$S_d = K_d C^{N_d} \tag{3-33}$$

where the subscripts a and d refer to sorption and desorption, respectively, where $K_d > K_a$ and the Freundlich constant 1/n in Eq. 3-10 has been redefined (1/n = N). As can be seen for the linear isotherms in Figure 3-2a, the magnitude of the hysteresis depends on the maximum amount of sorbate sorbed, S_a^{max}, at the maximum solution concentration, C_a^{max}, before initiation of desorption. Van Genuchten et al. (1974), among others, derived the useful relation

$$K_d = (K_a)^{\beta} (S_a^{max})^{1-\beta} \quad \text{or} \quad K_d = K_a (C_a^{max})^{N_a - N_d} \tag{3-34}$$

MONS 018713

Here, $\beta = N_d/N_a \simeq 1/2.3$ for a wide range of compounds. Using the latter expression for K_d, S_d can be written in terms of K_a and C

$$S_d = K_a (C_a^{max})^{N_a - N_d} C^{N_d} \tag{3-35}$$

Eqs. 3-32 and 3-35 constitute a simple model describing hysteretic sorption. This model has been incorporated into a solute transport model similar to Eq. 3-1 to describe pesticide sorption/desorption processes in soil column breakthrough and leaching studies (Van Genuchten et al. 1974). Good agreement was achieved between predicted and observed pesticide breakthrough curves at low, average pore-water velocity; however, for higher pore-water velocities, this simple sorption-transport model failed to describe experimental data.

DiToro and Horzempa (1982) report the existence of both a readily reversible component (S_r) and a highly resistant component (S_o) for PCB sorption to sediments (Figure 3-2). This highly resistant component does not desorb upon successive desorption steps, lasting up to 48 hours each. Within the context of DiToro's model, these successive desorption steps are assumed to trace a linear path intercepting the S-axis at a point which defines S_o. This path is termed the consecutive desorption isotherm (curve C Figure 3-2). The linear sorption isotherm and linear first desorption isotherm are labeled A and B, respectively, in Figure 3-2a and given by

$$S_a = k_a C \tag{3-36}$$

$$S_d = k_d C \tag{3-37}$$

Here, k_a and k_d are the sorption and desorption partition constants, respectively. When cycling the solution concentration such that $C < C_a^{max}$, DiToro and Horzempa found that the system traced out a path along curve C with only minor hysteresis. This line, with respect to an origin located at S_o along the S-axis in Figure 3-2a, is referred to as the reversible component isotherm:

$$S_r = k_r C \tag{3-38}$$

The partition coefficient for the reversible component, k_r, is given by

MONS 018714

$$k_r = \frac{k_a}{1 + m\,(k_d - k_a)}$$

where m is the mass of sorbent in solution. Alternatively, this reversible isotherm can be viewed as curve D in Figure 3-2b. The resistant component isotherm is shown as curve E and given by

$$S_o = k_o\, C_a^{max} \tag{3-39}$$

where C_a^{max} is defined as above and k_o, the partition coefficient for the resistant component is given by

$$k_o = \frac{m\, k_a\, (k_d - k_a)}{1 + m\,(k_d - k_a)}$$

which remains constant as long as $C < C_a^{max}$. The consecutive desorption isotherm (curve C) is simply the sum of Eqs. 3-38 and 3-39 (curves D and E) and is given by

$$S = S_o + k_r\, C \tag{3-40}$$

Isotherm Eqs. 3-36 and 3-40, together with the constants k_a and k_d and the definitions of k_r and k_o, define a model for describing nonsingular PCB sorption/desorption cycling on natural sediments. If, after successive cycling the solvent phase concentration C exceeds C_a^{max}, S_o is no longer constant, and Eq. 3-40 must be replaced by $S = (k_o + k_r)\, C$. This model is easily incorporated into the mass balance equations of a solute transport model, although we find no evidence that this has been done.

The expressions defining k_r and k_o above are based on the assumption that the sorption and the first desorption isotherms are linear and that all of the adsorbate mass is associated with the solid at the start of desorption. If, however, the sorption and first desorption isotherms (Eqs. 3-32 and 3-33, respectively) are nonlinear, this analysis of nonsingular sorption can be generalized by substituting the Freundlich isotherms from 3-32 and 3-33 for the linear isotherms 3-36 and 3-37. Using Eqs. 3-32 and 3-33 and the approximation $N_a/N_d \simeq 2.3$, k_o and k_r can be redefined in terms of the Freundlich constants N_a, N_d, K_a, and K_d. This analysis is

MONS 018715

strictly limited, however, to that region of the consecutive desorption isotherm, (Eq. 3-40 or curve C in Figure 3-2), that is linear. If the consecutive desorption isotherm curves toward the origin as the sorbate concentration in the solvent decreases or approaches zero, the linear analysis fails. Then, either the magnitude of a highly resistant component depends on the solution concentration C, the number of desorption steps, and the time involved in each desorption step, or the concept of a highly resistant component loses its meaning (see discussion of Figure 3-3 on p. 3-27).

This analysis identifies a major research question: does a totally resistant component continue to exist as C approaches zero. That is, does a truly nonreversible sorbed component exist, and under what conditions does it exist? From a practical standpoint, the more important question for PCB-contaminated soils is the possibility of prolonged cleanup and treatment necessitated by slow desorption of the 'resistant' component. Without prolonged treatment or PCB source removal, PCBs would migrate from the near-field region of initial PCB contact with the soil to the far-field region of the adjacent groundwater aquifer and beyond.

The decrease in observed values of K_p with the increase in the solid to solution ratio (S:S) of the sediment/solvent suspension (O'Conner and Connolly 1980; Voice et al. 1983) and the nonsingularity or irreversibility of the hydrophobic sorption process (Swanson and Dutt 1973; Peck et al. 1980; Rao and Davidson 1980; DiToro and Horzempa 1982) represent two important examples of nonideal sorption behavior for hydrophobic organic solutes. The debate regarding the dependence of K_p on S:S and isotherm nonsingularity has for a long time centered on whether these observations are experimental artifacts or real behavior (Rao and Davidson 1980). Recently, Gschwend and Wu (1985) have presented new experimental evidence for PCB sorption on sediments that strongly suggests that both the S:S dependence of K_p and nonsingular behavior are indeed experimental artifacts.

Gschwend and Wu (1985) propose a model of sorption that includes the effects of sorbate bonding to nonsettling microparticulates and neutrally buoyant organic macromolecules, which in previous studies have not been distinguished from the sorbate that remains in true solution. These nonsettling particulates (NSP) are removed from natural sediments as the sediments are dispersed or suspended in the solution phase, and because of their small settling velocities or near-neutral buoyancy, resist separation from the true solution phase via centrifugation, which is by far the most common method of solid-solution phase separation in organic sorption studies.

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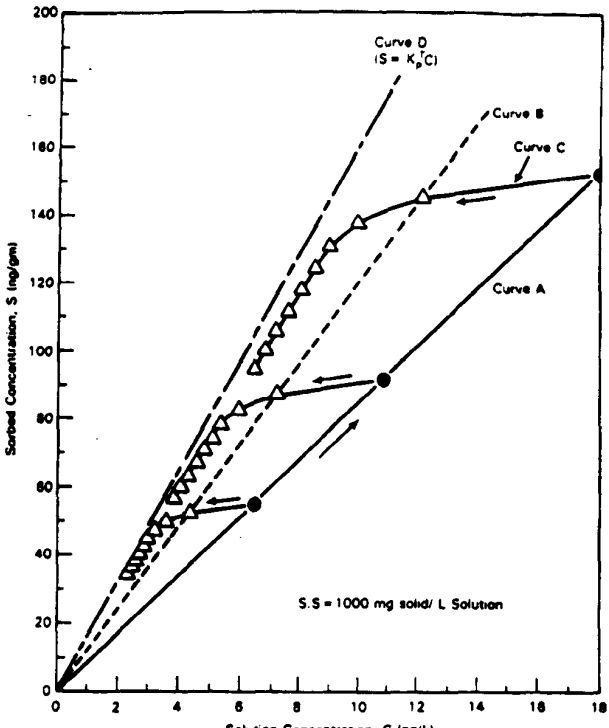

Figure 3-3. Sorption/desorption isotherms when sorption to nonsettling particulates and neutrally buoyant macromolecules (NSP) is accounted for. Curves A, B and C are the sorption, first desorption and consecutive desorption isotherms, respectively. Curve D is the 'true' isotherm in the absence of NSP.

Gschwend and Wu show that a noncentrifugable NSP phase typically occurs in batch sorption experiments unless precautions are taken to minimize NSP effects. This may be particularly important for the highly hydrophobic PCBs. Determination of partitioning constants must include not only the fraction of the sorbate associated with

MONS 018717

the true dissolved and settleable solid phases but also with this NSP phase. They express the observed partition coefficient K_p^{obs} as

$$K_p^{obs} = \frac{S}{C(dis) + C(NSP)} \tag{3-41}$$

where C(dis) and C(NSP) are the true dissolved concentration of the sorbate and the concentration of the sorbate bound to the NSP, respectively. The true partition coefficient is defined as

$$K_p^T = \frac{S}{C(dis)} \tag{3-42}$$

These two equations can be combined to yield

$$K_p^{obs} = \frac{K_p^T}{1 + K_{NSP}^T \left(\frac{\text{wt. NSP}}{\text{volume of solvent}}\right)} \tag{3-43}$$

or in terms of K_{oc} ($K_p = f_{oc} K_{oc}$)

$$K_{oc-p}^{obs} = \frac{K_{oc}^T}{1 + K_{oc-NSP}^T (DOC)} \tag{3-44}$$

where the dissolved organic carbon (DOC) is

$$DOC = \frac{(f_{oc})\ (\text{wt. NSP})}{(\text{volume of solvent})}$$

From Eq. 3-41 it can be seen that when C(NSP) << C(dis) K_p^{obs} approaches K_p^T. Eqs. 3-43 and 3-44 suggest that this condition occurs when [(wt. NSP)/volume] or DOC are such that $[K_{NSP}^T[(\text{wt. NSP})/\text{volume}]]$ or $(K_{oc-NSP}^T\ DOC) << 1$. In addition, when the S:S ratio or the hydrophobicity of the sorbate increases, C(NSP) will increase and K_p^{obs} will decrease relative to K_p^T. This apparent dependency of the partitioning coefficient on S:S is not a property of the sorption or partitioning mechanism, but rather an artifact resulting from failure to account for sorbate bonding to the NSP

MONS 018718

phase. The value of K^T_{NSP} or K^T_{oc-NSP} can be established by independent experiment or set equal to K^T_p. K^T_p or K^T_{oc-p} are determined from data at low values of S:S (curve D Figure 3-3).

Apparent irreversible or hysteretic sorption behavior is also shown by Gschwend and Wu (1985) to result from neglect of the NSP phase. They found that for the first, and each successive desorption experiment, C(NSP) decreases relative to the original quantity of NSP present during the original sorption experiment in which K^a_p is determined. Hence, by transposing Eq. 3-41 for desorption, it can be seen that the observed K^d_p will be greater than the initial K^a_p, which has often been interpreted as irreversible binding of the sorbent. Further, the extent of this hysteresis was thought to be a function of the initial dissolved concentration (Figure 3-2 and 3-3). With the consideration of NSP, Gschwend and Wu show that the consecutive desorption isotherm (curve C in Figure 3-3) bends towards the origin and asymptotically approaches the true isotherm which has slope K^T_p (curve D). This true isotherm is obtained using low S:S suspensions.

Although this model provides a reasonable interpretation of two important types of nonideal sorption behavior, it was developed and tested for two PCB congeners using only two natural sediments. Additional PCB congeners, organic compounds, and soils must be examined before any general resolution of the divergent observations regarding the reversibility and rates of hydrophobic sorption on natural sediments will emerge.

SORPTION KINETICS

Karickhoff (1984) noted that "a great deal of confusion exists in the sorption literature regarding the speed of attainment of sorption equilibrium." Reports abound which claim rapid and readily reversible organic sorption reactions in aqueous suspensions. Yet, others report highly release-resistant 'nonlabile' fractions, comprising 50% to 80% of the sorbed organic (Di Toro and Horzempa 1982), that require extended and often harsh extractions for complete removal of the sorbent from the solid phase (Karickhoff and Brown 1978; Karickhoff 1980; Freeman and Cheung 1981). These reports and others note that the nonlabile fraction and the difficulty of extraction usually increase with the duration of the sorption step.

The nonlabile component may indeed result not from the actual nature of the sorption/desorption process but rather from mass transfer or diffusion processes that control the migration of the sorbate between the bulk solvent phase and regions of the sorbent not in direct contact with the bulk solvent (Van Genuchten et al. 1974;

MONS 018719

Van Genuchten and Wierenga 1976a, 1976b; Rubin 1984). Based on observations that magnitude of the kinetic rate coefficients for 2,4-D sorption on kaolinite and montmorillonite were typical of those observed for diffusion coefficients (0.2 to 0.05 $days^{-1}$), Haque et al. (1968) concluded that the rate-limiting step in sorption/desorption was diffusion of the pesticide to the reactive sites within the clay matrix and not the kinetics of reaction at the site. Leenheer and Ahlrich (1971) suggest that for times exceeding a few minutes, the rate-limiting step was pesticide diffusion to sorption sites in the interior of the soil organic matter. Observations of initial rapid reactions (for both sorption and desorption reactions), followed by a slow reaction over long times, have been reported by many authors (Hamaker et al. 1966; Freeman and Cheung 1981). It is likely that both mass transfer of the sorbate to reactive sites and reaction kinetics of the sorbate at the sites contribute to the general macroscopic observation that sorption (or desorption) is a combination of a fast plus a slow step. Experimentally, mass transfer and reaction kinetics contributions cannot be distinguished. Examples of each approach are presented below.

Mass Transfer as the Rate-Limiting Step

A two-stage kinetic model of sorption was proposed by Karickhoff (1980) where sorption was considered to be the sum of a 'labile' component (S_ℓ) and a 'nonlabile' component (S_n). The labile component reaction, which occurs rapidly (usually within an hour), is treated as an equilibrium process and characterized by an equilibrium constant, K_L. The migration of the sorbate to and from the 'nonlabile' compartment is described by a mass transfer coefficient (k_n). The combined process is denoted

$$C \underset{K_L}{\overset{}{\rightleftharpoons}} S_\ell \underset{k_n}{\overset{}{\rightleftharpoons}} S_n$$

where C is the concentration of the sorbate in the bulk solvent phase and S_ℓ and S_n are the quantities of bound sorbate associated with labile and nonlabile sorbent sites. Karickhoff (1984) notes that the magnitude of k_n varies widely among sediments; however, he concludes that, as a rule, "the characteristic time ($1/k_n$) for diffusive release from the 'nonlabile' compartment approximates the K_{OC} (in minutes)." This model is limited in that it will not describe changes in sorption for times that are short relative to the characteristic time of nonlabile sorbate exchange.

A similar diffusion-limiting model for treating sorption was proposed by Van Genuchten and Wierenga (1976a,b) in which the soil-water phase was assumed to

MONS 018720

consist of mobile and immobile phases. The mobile phase (phase 1) participated in the advective-dispersive movement of the soil water through the soil. The immobile phase (phase 2) was considered stationary, residing for example in stagnant or dead-end pore spaces. Solute movement between phases 1 and 2 was assumed to be diffusion controlled:

$$\frac{\partial C_2}{\partial t} \propto d\,[C_1 - C_2]$$

where d is the diffusion coefficient and C_1 and C_2 are the solute concentrations in phases 1 and 2. In each phase, sorption/desorption was considered to be instantaneous and described in both regions by either linear or Freundlich isotherms. This treatment was applied by the authors to simulate pesticide migration through soil columns.

Reaction Rate as the Rate-Limiting Step

Selim et al. (1976) describe a mixed, nonlinear, equilibrium-kinetic model in which the soil was assumed to consist of two types of reaction sites or compartments: Type 1, which react rapidly relative to the average velocity of the bulk solvent and Type 2, which react slowly. Sites where the reaction rate is limited by diffusion are assumed to be Type 2. For Type 1 sites, the local equilibrium assumption is valid and a linear Freundlich was used to describe sorption

$$S_1 = KC^N \tag{3-46}$$

The rate of change of Type 2 sites is described by a first-order reversible kinetic equation

$$\frac{\partial S_2}{\partial t} = \frac{\theta}{\rho} k_1 C^N - k_2 S_2 \tag{3-47}$$

where k_1 and k_2 are the forward and reverse (sorption and desorption) rate coefficients ($days^{-1}$) and θ and ρ are the volumetric water content and the density of the porous media (soil), respectively. The total quantity sorbed, S_T, is assumed to be the sum on S_1 and S_2 (i.e., the equilibrium and kinetic processes are assumed to be independent). The macroscopic rate of total sorption can be written

MONS 018721

$$\frac{\partial S_T}{\partial t} = \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \tag{3-48}$$

Combining this with Eqs. 3-46 and 3-47 yields

$$\frac{\partial S}{\partial t} = (KNC^{N-1}) \frac{\partial C}{\partial t} + \frac{\theta}{\rho} k_1 C^N - k_2 S_2 \tag{3-49}$$

Substitution of Eq. 3-49 into the advective-dispersive mass balance equation (Eq. 3-1) constitutes a one-dimensional solute transport model that contains a nonlinear, combined equilibrium-kinetic description of sorption. Cameron and Klute (1977) used linear sorption isotherms (N = 1) in Eqs. 3-46 to 3-49. They obtained analytical solutions for the transport model (Eq. 3-1 and 3-49) and used these to describe soil column breakthrough and leaching data. Numerical and analytical solutions for the case where N = 1 have also been obtained for various boundary and initial conditions (Ogata 1964; Cho 1971; Lindstrom and Boersma 1970). If $k_2 S << (\theta/\rho)k_1 C$, and N = 1, Eq. 3-47 reduces to an irreversible, first-order kinetic model where $\partial S/\partial t$ is dependent only on the forward rate constant and C and independent of S. Analytic solutions for Eq. 3-1 containing this equilibrium-kinetic irreversible sorption model have been obtained (Ogata 1964; Cho et al. 1970). This nonlinear ($N \neq 1$), mixed, equilibrium-kinetic model was used by Selim et al. (1976) and Rao et al. (1979) to model pesticide breakthrough data in saturated soil column experiments.

Rao et al. (1979) have compared the ability of the mass transfer model (Van Genuchten and Wierenga 1976a) and the reaction kinetics model (Selim et al. 1976; Cameron and Klute 1977) to describe both batch sorption uptake-rate data and soil column breakthrough data at various initial concentrations of three pesticides on three soils. These authors concluded that for the soil column experiments, the sorption/desorption processes were diffusion-controlled and not limited by reaction kinetics at individual sites within the solid/solution interface. On the other hand, the concept of mobile and immobile soil-water phases in the mass transfer model was not a reasonable hypothesis because the fraction of immobile water differs for the nonadsorbing tritium tracer and the pesticides. It may be concluded that adequate descriptions of nonequilibrium organic sorption/desorption during organic solute transport do not currently exist. This is an area of active debate and research from both the chemical and hydrologic perspective.

MONS 018722

Yet another approach to describing nonequilibrium sorption that allows sorption and desorption energies to vary as a function of surface coverage was proposed by Lindstrom et al. (1970). This first-order, reversible kinetic model of sorption is expressed by

$$\frac{\partial S}{\partial t} = [k_2 \exp(\alpha S)] \left[\frac{k_2}{k_3} \frac{\theta}{\rho} C \exp(-2\alpha S) - S\right] \quad (3\text{-}50)$$

where α is related to surface stress coefficients. At equilibrium ($\partial s/\partial t = 0$), this equation reduces to

$$S = \left[\frac{\theta}{\rho} \frac{k_2}{k_3}\right] [C \exp(-2\alpha S)] \quad (3\text{-}51)$$

which can be rearranged into

$$\ln (S/C) = \ln \left[\frac{\theta}{\rho} \frac{k_2}{k_3}\right] - 2\alpha S \quad (3\text{-}52)$$

Plots of (S/C) versus S for different equilibrium sorbate concentrations provide a means to evaluate the parameters α and $(\theta\ k_2)/(\rho\ k_3)$. This model has been used to describe pesticide breakthrough and leaching in saturated soil columns (Van Genuchten et al. 1974). To our knowledge, these models for describing nonequilibrium sorption/desorption processes along with others described in reviews by Travis and Etnier (1981) and Kirackhoff (1980) have not been applied to PCB sorption/desorption in flow-through soil systems.

Returning finally to Eq. 3-49 for the mixed linear equilibrium-kinetic model ($N = 1$), the total sorption at equilibrium (i.e., for prolonged contact times) becomes

$$S = \frac{\theta}{\rho} (k_1/k_2 + K) C \quad (3\text{-}53)$$

This equation basically represents a linear isotherm. After some critical time, t_c (the value of which will depend upon both the sorbate and sorbent and experimental conditions), the equilibrium component can be shown to begin to dominate. At that

MONS 018723

point, equilibrium will appear to have been reached, when in fact the kinetic component continues to contribute. This is consistent with the observation of Karickhoff (1984) that "if one measures simply changes in aqueous phase and sorbed phase concentrations, the [sorption] process appears to be complete after a few hours, but in reality [it] may proceed indefinitely." This issue of sorption equilibrium (i.e., the time to reach equilibrium) is at the center of the confusion regarding reversibility of sorption reactions. This and the related issue of adequately describing nonequilibrium sorption/desorption processes remain topics of active research.

Section 4

RECOMMENDATIONS

The two preceding sections have described the data in the literature on PCB attenuation in soil and the conceptual models that may be applicable for describing PCB sorption/desorption in soils. The second section also provided a brief review of the PCDD data available in the literature. Data have been tabulated for water solubility, K_{ow}, K_p, K_F, and K_{oc} (Section 2). Equations have been presented linking these parameters for hydrophobic organic compounds, in general (Section 3). Using a much more limited data set than that described in Tables 2-1 and 2-3, several empirical equations have been found to describe the correlation among some of these parameters for PCBs (Section 2). For example, K_{ow} has been used to estimate K_{oc} values which, in turn, can be used to determine K_p values when the fraction of organic carbon in the soil is known. The K_p values are related to the retardation factor (p. 3-4), which relates PCB movement to solvent movement. While several empirical or derived relationships have been proposed, available data are insufficient to accurately predict PCB movement in soils.

Furthermore, results of both laboratory and field studies present conflicting conclusions regarding PCB attenuation within soils, subsoils, and groundwater systems. The commonly held belief that PCBs are environmentally immobile is overly simplistic. Transport models describing PCB migration within these environmental systems must include adequate descriptions of dominant attenuation processes (e.g., sorption, volatilization, etc.) if they are to serve as accurate predictive tools upon which risk assessments can be based. Quantitative risk assessments are an essential part of the process for evaluating environmental contamination and deciding whether and what site remediation is warranted. However, quantitative predictive models and the requisite data for describing these attenuation processes for PCBs, are not currently available.

The review of the available literature on PCB attenuation in soils discussed in Section 2 revealed a number of deficiencies or gaps in the data. Even less data were found for PCDD and virtually no data were found for PCDF attenuation in soils. The review of sorption models and semiquantitative methods for estimating sorption constants in Section 3 described a number of conceptual and mathematical approaches,

MONS 018725

as well as their strengths and limitations that are available for describing hydrophobic organic compound sorption in soils. Some of these models have been used for PCBs; many have not or have only incorporated one or two PCBs along with other hydrophobic compounds. Conditions for which models are needed, but for which none are available, are also identified. In both Sections 2 and 3, issues for which conflicting information exists in the literature are discussed. Based on the observations in these sections, we recommend a combined program of experimental and model development work. The basic goals of this program are to 1) amplify the PCB data base by filling in some of the data gaps on their attenuation in soils, and 2) determine and test the appropriate models for quantitative prediction of their sorption in soils, using both currently available data as well as data to be generated in the future. As in Sections 2 and 3, the recommendations in this section emphasize sorption data and models, though research needs in other areas related to abiological attenuation are addressed. Because EPRI is currently examining the role of biological degradation as part of a separate study, it has not been addressed here. Our recommendations for PCBs can be divided into several categories as described below.

STUDY OF PCBs IN AQUEOUS SOLVENT/SOIL* SYSTEMS

1. Establish the applicability and accuracy of models and estimation techniques of the type described in Section 3 to PCB congeners using both the limited data currently available and new data as it becomes available. Examples of models that should be tested include the relationships between K_p and percent of OC, K_{oc} and K_{ow}, K_{oc} and water solubility, and K_{oc} and surface area.

2. Because low organic carbon soils are typical in subsurface aquifer materials, it is important to determine the sorption/desorption behavior [K_ps, rates, reversibility, dominant soil parameters: e.g., surface area, expandable clay content (CM), etc.] for a broad range of low organic carbon (OC < 0.1%) sorbents. Appropriate estimation and modeling techniques for sorption/desorption on low-carbon soils should be developed. The levels of OC at which these other parameters become important for PCBs should be determined.

3. The related and controversial issues of reversibility/hysteresis/rate of approach to equilibrium for soils where OC > 0.1% (and possibly for low organic carbon soils, if similar effects are found to exist) need to be resolved. The dependence of reversibility/kinetics on soil aggregation properties, contact time, and other parameters should be established. Models are needed for describing sorption/desorption cycling. A major research question must be considered here; that is, is there a truly nonreversible sorbed component? For PCB contaminated soils, this addresses the important question of whether prolonged cleanup and treatment, or source

*The term soil is used here in a general sense to indicate soils, sediments, subsurface aquifer materials, and engineered backfill materials.

MONS 018726

removal is necessitated by slow desorption of the 'resistant' component. If this theory regarding slow desorption of the resistant component is accurate, PCBs might migrate in the presence of water from the near-field region of initial PCB contact with the soil to the far-field region of the adjacent groundwater aquifer and beyond, unless source removal is performed. On the other hand, if the sorption is truly irreversible, source removal may not be necessary.

4. The existing limited data base for PCBs should be enhanced by measuring K_p for 1) a range of individual isomers varying in chlorine number on a single soil; 2) repeating (1) for a wide range of soil types (e.g., differing OC/CM); and 3) repeating (1) and (2) for PCB mixtures, paying special attention to individual congeners that are part of the PCB mixtures. Model and estimation techniques should then be tested using these data.

5. The dependence of K_p or K_{ow} on temperature and the salt concentration of the solute should be determined because these geochemical parameters may vary in groundwater systems and from site to site.

6. Because differences in organic matter in soils have been observed to influence K_{oc}, the role of molecular weight, functional groups, structure, hydrophobicity of the soil organic matter, and the origin of the soil organic matter should be examined as they affect the ability to sorb PCBs.

STUDY OF PCBs IN ORGANIC OR MIXED AQUEOUS-ORGANIC SOLVENT-SOIL SYSTEMS

1. The sorption/desorption and reversibility/hysteresis behavior needs to be examined for selected mixed solvent/soil systems as outlined in recommendations 1, 2, and 3 for PCBs in aqueous solvent/soil systems. The role of expandable clays may be of special interest here.

2. The applicability of the generalized K_{oc}/solubility relationships and the gel model approach for describing hydrophobic sorption for organic and mixed-solvent systems described in Section 3 should be tested.

3. Estimation techniques and models should be generalized or new ones developed for describing sorption in organic solvent and mixed solvent/soil systems because the nature of the solvent plays a major role in PCB attenuation and transport. Adequate estimation techniques and models are either untested or nonexistent.

GENERAL PCB SORPTION RECOMMENDATION

The applicability and utility of 'C-18' or 'soil column' reverse-phase, high-pressure liquid chromatography techniques for rapid measurement of PCB solvent/soil partitioning parameters should be investigated. This method allows flow rate effects on sorption to be determined.

MONS 018727

RESEARCH NEEDS IN OTHER AREAS OF ATTENUATION

1. A wide disparity exists in literature values for water solubility, vapor pressure, and octanol-water partition coefficients for individual PCB congeners. A critical review and evaluation of literature data are urgently needed to determine 'best' values of these physical constants and to determine where additional experimental effort is most needed to correct this situation.

2. Volatilization data from soils are needed for a wider range of PCB congeners, especially those that are more highly chlorinated. The effect of different soils with a wider range of organic carbon content and clay mineral content should be examined under different water saturation conditions. The effect of the presence of organic solvents on volatilization from soils should also be determined because organic solvents will likely be present in a surface spill.

3. The effect of soils on chemical degradation is another area that has not received sufficient attention. Here, it is important to determine the degradation products and not merely the extent of loss of the PCBs, because loss can be due to a number of processes not related to degradation. These studies should be done on single congeners or simple mixtures of congeners whose decomposition can be more readily followed experimentally. Again, a number of soils with a wide range of organic carbon and clay mineral contents should be examined under different water saturation conditions.

4. The migration of PCBs as a sorbed phase (i.e., transport on particles) and as an immiscible phase (i.e., as pure compound or as a compound/organic solvent phase) also should be considered in any attempt to predict PCB transport.

SUMMARY OF RECOMMENDATIONS

The recommendations made above are presented with the needs of the electric utility industry in mind. Polychlorinated biphenyls while of themselves important to the utility industry, also represent an ideal tool for investigating the important hydrophobic interactions which play a major role in the attenuation process of a wide variety of organic compounds significant to a much broader spectrum of researchers and industries. Results from PCB research may be 1) applied to other nonionizable hydrophobic compounds with relatively unreactive functional groups, and 2) potentially extrapolated to the hydrophobic component of interaction associated with polar and/or slightly ionizable organic compounds. Model compounds other than PCBs might require a greater effort in the separation of sorption phenomena from other pathways of loss, e.g., biodegradation, chemical reaction, or volatilization.

A coordinated experimental and modeling approach should be used to address this series of recommendations. The development of predictive tools for describing the attenuation mechanisms governing PCB movement in soils, sediments, and subsurface aquifer materials must, by necessity, include both laboratory studies and field

MONS 018728

testing. During the initial laboratory phase, batch sorption/desorption experiments, soil column breakthrough, leaching and volatilization experiments, and degradation studies should be conducted. These experiments should study aqueous, mixed aqueous-organic and organic solvents, and a range of congeners (e.g., those found in utility Aroclor mixtures should be emphasized). In addition, well-characterized soils should be used which cover a range of organic carbon and expandable clay content and which typify soils where utility cleanup may be an issue. Information obtained at contaminated sites that further defines the practical limits of attenuation processes should be integrated into laboratory studies during all stages of research.

Field testing of the data base and attenuation models developed during the initial phase should begin as soon as feasible and technically profitable at well-characterized field sites. The objective of this testing is to identify deficiencies in the predictive capability resulting from inadequacies in the process models (e.g., sorption, volatilization, etc.) and/or in the requisite data base and site characterization. These deficiencies should, in turn, be resolved by either laboratory or field experiments or a combination of both.

Future work on PCB sorption, volatilization, and abiotic degradation will establish the data base. Attenuation models can be incorporated into solute and multiphase transport models to yield predictive tools. Such models can then be used to describe migration of PCBs and related nonionizable hydrophobic compounds in the presence of solvents from the near-field region of initial contact with the soil to the far-field region of the adjacent groundwater aquifer and beyond. Then based on these predictive tools for describing migration, the associated risk assessment and subsequent decisions can be made as to whether cleanup is required and/or cost-effective.

MONS 018729

Section 5

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MONS 018730

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MONS 018740

REPORT SUMMARY

SUBJECTS: Hazardous/toxic substances / Solid-waste studies / T&D: Substations

TOPICS: PCBs; Hydrology; Adsorption; Mathematical models; Literature reviews

AUDIENCE: R&D scientists / Environmental engineers

Attenuation of Polychlorinated Biphenyls in Soils: Literature Review

Computer models that accurately predict the long-term behavior and transport of PCBs in soils would help utilities make correct and cost-effective decisions about cleaning up contaminated sites. However, inconsistencies and deficiencies in the data on PCB sorption processes hinder the development of such models.

BACKGROUND

Regulatory agencies restrict the use of polychlorinated biphenyls (PCBs) because of their perceived toxicity to humans and other organisms and their persistence in soil and water. However, the degree of concern with which PCB-contaminated soil should be regarded remains unclear because little is known about the behavior and long-term migration of these compounds in various types of soil and water. The utility industry is particularly interested in resolving this question, since these chemicals are widely used as insulating fluids and coolants in capacitors and transformers.

OBJECTIVES

To review and summarize the scientific literature on the attenuation of polychlorinated biphenyls in soils and on conceptual and mathematical approaches to modeling PCB sorption and desorption in soils.

APPROACH

Researchers reviewed laboratory and field measurements of PCB behavior in soils, identified mechanisms of interaction between PCBs and soils, and identified and evaluated several mathematical approaches to modeling PCB sorption and desorption. Because recent research suggests that toxicity attributed to PCBs may be caused or intensified by chlorinated dibenzofurans and dioxins, project personnel reviewed literature on the attenuation of those compounds also.

RESULTS

The study findings indicate that further research is required for a clear understanding of the mechanisms of PCB sorption and the differences in behavior of the 209 possible PCB compounds.

- The collected data support the qualitative conclusion that PCBs are sorbed into the organic carbon in the soil. However, insufficient quantitative data exist on PCB sorption under equilibrium conditions in aqueous solvents and soils containing typical concentrations of organic carbon. It is therefore not

MONS 018741

yet possible to verify existing sorption models for the 209 individual PCB compounds or to make accurate, scientifically defensible predictions of PCB mobility in soils.

- Conflicting information exists on the rates and reversibility of the PCB sorption and desorption process in typical organic compound soils and aqueous solvents. Such conflicts hinder modeling.

- The literature contains no data on PCB sorption, desorption, and reversibility under equilibrium and nonequilibrium conditions in aqueous solvents and soils containing organic carbon levels of less than 0.1%. Nor do verified mathematical models exist. Such low organic carbon levels are typical of subsoils and subsurface groundwater aquifer materials. The mobility of PCBs in such materials may differ significantly from that in typical organic carbon soils.

- The report includes a summary of existing PCB data on sorption coefficients.

EPRI PERSPECTIVE

This study shows that utilities are addressing the cleanup of PCB spills and contaminated sites on the basis of very limited data on PCB behavior in the environment and little understanding of the molecular processes involved in PCB interaction with soil. Models that accurately predict PCB migration in soil would enable utilities and regulators to agree on the proper corrective action for a specific PCB spill. Before such models become a reality, utilities need reliable data on the long-term behavior of PCBs in a variety of soil and water conditions.

PROJECT

RP1263-22
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Coal Combustion Systems Division
Contractor: Battelle, Pacific Northwest Laboratories

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MONS 018742

Attenuation of Polychlorinated Biphenyls in Soils: Literature Review

CS-4396
Research Project 1263-22

Final Report, January 1986

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MONS 018743

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Prepared by
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MONS 018744

ABSTRACT

Polychlorinated biphenyls (PCBs) have found their way into a wide variety of industrial applications, a major one being coolant-insulation in capacitors and transformers. Perceived toxicity to humans and other organisms in conjunction with environmental persistence has led to a highly regulated climate of PCB use. Because of the ubiquity and persistence of PCBs, the ability to predict their long-term mobility in the soil-water environment is of particular interest to the electric utility industry and regulatory agencies.

This report has two main objectives: to review and summarize available literature data on the attenuation of PCBs in soil and to review the current literature on the conceptual and mathematical approaches that may be applicable to modeling PCB sorption/desorption in soils. Because research has suggested that toxicity attributed to PCBs may be caused or enhanced by other closely associated hydrophobic compounds such as polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs), literature on PCDD and PCDF attenuation data in soils has also been briefly reviewed; these data are amenable to the same modeling approaches as described for PCBs. Sorption/desorption data have been emphasized, but information on other attenuation mechanisms has been included as well. Major deficiencies in the data are identified and, based on these deficiencies, recommendations are made for a combined program of experimental work and model development. These recommendations identify specific areas for research which in the near future would allow the development of a predictive capability.

MONS 018745

CONTENTS

Section		Page
1	INTRODUCTION	1-1
2	LITERATURE REVIEW OF PCB ATTENUATION IN SOILS	2-1
	Equilibrium Sorption: Partition Coefficients and Sorption Isotherms	2-1
	Physical Constants: Water Solubility, K_{ow}, Vapor Pressure	2-8
	Kinetics/Reversibility of Sorption	2-11
	Mobility in Aqueous and Organic Solvent Systems	2-12
	Soil Thin Layer Chromatography	2-12
	Soil Column and Microcosm Studies	2-13
	Field Studies	2-14
	Effects of Soils on Volatilization, Plant Uptake, and Degradation	2-16
	Volatilization	2-16
	Plant Uptake	2-17
	Degradation	2-17
	PCDD Attenuation in Soils	2-18
	Field Study	2-19
	Equilibrium Sorption	2-19
	Physical Constants: Water Solubility, K_{ow}, Vapor Pressure, Henry's Law Constant	2-20
	Soil TLC	2-20
	Soil Leaching Studies	2-20
	Degradation	2-21
	Volatilization	2-22
	Photodegradation	2-22
	Biodegradation and Plant Uptake	2-22
3	SORPTION MODEL REVIEW	3-1
	Solute Transport Models Including Sorption	3-2
	Isotherm and Partition Constant (K_p) Models	3-4
	Linear Isotherm Model	3-4
	Langmuir Model	3-5
	BET Model	3-6

MONS 018746

Section		Page
	Frumkin Model	3-7
	Freundlich Model	3-8
	Carbón-Reference Sorption Model	3-10
	Estimation of K_{oc}	3-12
	Mixed Solvents	3-15
	Gel Partition Model	3-17
	Sorption on Low-Organic-Carbon Soils	3-19
	Sorption Reversibility and Isotherm Nonsingularity	3-21
	Sorption Kinetics	3-29
	Mass Transfer as the Rate-Limiting Step	3-30
	Reaction Rate as the Rate-Limiting Step	3-31
4	RECOMMENDATIONS	4-1
	Study of PCBs in Aqueous Solvent/Soil Systems	4-2
	Study of PCBs in Organic or Mixed Aqueous-Organic Solvent-Soil Systems	4-3
	General PCB Sorption Recommendation	4-3
	Research Needs in Other Areas of Attenuation	4-4
	Summary of Recommendations	4-4
5	REFERENCES	5-1

MONS 018747

ILLUSTRATIONS

Figure		Page
3-1	(a) Examples of Linear and Freundlich Isotherm Commonly Used to Describe PCB Sorption/Desorption Data. (b) Linearized Freundlich Isotherm from Which Freundlich Constants K_F and n may be Determined.	3-9
3-2	Linear Sorption/Desorption Isotherms	3-22
3-3	Sorption/Desorption Isotherms when Sorption to Nonsettling Particulates and Neutrally Buoyant Macromolecules is Accounted for	3-27

MONS 018748

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Chemical analysis
Fires
Transformers
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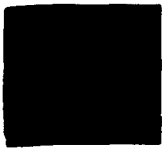
Electrical insulation

EPRI EL-4503
Project 2028-12
Final Report
March 1988



State-of-the-Art Review: Pyrolysis and Combustion of PCB Substitutes

Prepared by
SCS Engineers, Inc.
Long Beach, California

MONS 018749

REPORT SUMMARY

SUBJECTS Hazardous/toxic substances / T&D: Substations

TOPICS

PCB	Transformers
Chemical analysis	Capacitors
Fires	Electrical insulation

AUDIENCE Environmental managers / Distribution engineers

State-of-the-Art Review: Pyrolysis and Combustion of PCB Substitutes

Utilities are concerned about the possible long-term toxic effects of trace combustion products of potential PCB substitutes. This literature review turned up much information on the bulk combustion products of replacement compounds that are already in wide use but few data on either the trace or bulk products of relatively new materials.

BACKGROUND Several compounds are under consideration as substitutes for polychlorinated biphenyls (PCBs) in transformers and capacitors. To ensure that these insulating materials do not pose problems similar to those encountered with PCBs, utilities need to determine not only their electrical, thermal, and physical characteristics but also the bulk and trace materials they produce when pyrolyzed or combusted.

OBJECTIVE To review the literature on the materials produced during the pyrolysis and combustion of several solid, liquid, and gaseous substitutes for PCBs.

APPROACH Researchers focused their review on 18 potential PCB replacement materials—2 solids (epoxy resins and polyvinyl chloride), 2 gases (Freon 113 and sulfur hexafluoride), and 12 liquids, including phthalate esters, benzylneocaprate, silicone, chlorobenzenes, methylated diphenylethene, and perchloroethylene. In particular, project workers sought information on trace products related to those found during PCB thermal decomposition—for example, polyaromatic hydrocarbons, polychlorinated dibenzofuran, and polychlorinated dibenzodioxin.

RESULTS The literature contains a great deal of information on the bulk pyrolysis and combustion products of PCB substitutes that have had wide use in the electricity industry and other industries. Examples of such substitutes are epoxies, sulfur hexafluoride, silicone, phthalate esters, methylated diphenylethene, perchloroethylene, and polyvinyl chloride. However, there is little information on the trace products of concern. Literature on both the bulk and trace combustion products of some of the less familiar replacement compounds is sparse and, in some cases, nonexistent. For example, researchers found no information on the materials generated during thermal

decomposition of benzylneocaprate and alkylbiphenyls. The study concluded that further laboratory work is needed to identify additional trace materials of the better known PCB substitutes and both bulk and trace products of the newer compounds.

EPRI PERSPECTIVE

Concern over the toxicity of PCBs has focused on both its bulk and trace combustion products. To build a database as sophisticated as that for PCBs, researchers must perform intensive analyses of all potential substitutes. EPRI is currently conducting laboratory studies to enlarge the present database. Four such studies are project RP2028-11, which is focusing on the bulk pyrolysis and combustion products of several liquid PCB substitutes, and projects RP2028-15, RP2028-16, and RP2028-17, which are analyzing the bulk and trace products of a group of liquid, solid, and gaseous PCB substitutes.

PROJECT

RP2028-12
EPRI Project Manager: Gil Addis
Electrical Systems Division
Contractor: SCS Engineers, Inc.

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MONS 018751

State-of-the-Art Review: Pyrolysis and Combustion of PCB Substitutes

EL-4503
Research Project 2028-12

Final Report, March 1986

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Prepared by
SCS Engineers, Inc.
Long Beach, California

MONS 018753

ABSTRACT

An extensive literature search was conducted to identify the combustion and pyrolysis by-products of several PCB substitutes. These compounds included phthalate esters, benzylneocaprate, siloxanes, chlorinated benzenes, dixylylethane, alkylbiphenyls, paraffinic hydrocarbons, perchloroethylene, chlorofluorocarbons, sulfur hexafluoride, epoxy resins, and polyvinyl chloride. No information was found on the thermal decomposition of benzylneocaprate or the alkylbiphenyls. Siloxanes decompose to silica, cyclic siloxanes, and hydrocarbons of relatively low toxicity. Paraffinic hydrocarbons decompose into a series of shorter hydrocarbon compounds. Epoxies yield both alkyl and aryl hydrocarbons. Sulfur hexafluoride yields a series of sulfur and thionyl fluoride compounds and unidentified toxic PICs. The phthalate esters produce phthalic anhydride, napnthalene, and biphenyl. Methylated diphenylethane and phenylxylylethane decompose into a series of polynuclear aromatic hydrocarbons. Perchloroethylene produces predominantly hydrogen chloride and chlorine and sometimes phosgene. Chlorofluorocarbons yield these compounds and their fluoride analogs. Polyvinyl chloride decomposes into phosyene, naphthalene, benzene, and chlorinated benzenes. Chlorinated benzenes and possibly butylated monochlorodiphenylether can produce PCDDs and PCDFs.

MONS 018754

ACKNOWLEDGMENTS

It is impossible to do an adequate state-of-the-art review without consulting those individuals and organizations currently engaged in research. Published information is often months to years out of date, and only contacts with researchers can produce a timely review. Consequently, it was necessary to request assistance from many organizations. There is no way to list every company or individual talked to during the course of this effort, but several, because of the extent of their cooperation, deserve special mention.

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MONS 018755

CONTENTS

Section		Page
1	INTRODUCTION	1-1
	Background	1-1
	Objectives	1-1
	Report Organization	1-3
2	DATA ASSESSMENT	2-1
	Introduction	2-1
	Combustion/Pyrolysis Chemistry	2-1
	Toxicity and Exposure Limits	2-3
	Synergism	2-4
3	PROPOSED PCB SUBSTITUTES: LIQUIDS	3-1
	Introduction	3-1
	Esters	3-1
	Siloxanes	3-8
	Aromatics	3-13
	Paraffinic Hydrocarbons	3-24
4	DIELECTRIC GASES	4-1
	Chlorofluorocarbons	4-1
	Sulfur Hexafluoride	4-7
5	PROPOSED PCB SUBSTITUTES: SOLIDS	5-1
	Introduction	5-1
	Epoxy Resins	5-1
	Polyvinyl Chloride (PVC)	5-6
6	REFERENCES	6-1
APPENDIX A	GLOSSARY AND ABBREVIATIONS	A-1
APPENDIX B	GENERIC AND TRADE NAMES	B-1

MONS 018756

ILLUSTRATIONS

Figure		Page
3-1	Phthalate Esters	3-3
3-2	Typical PDMS Pyrolysis Products	3-10
3-3	Chlorinated Benzene Compounds Used in Dielectric Fluids	3-14
3-4	Typical Chlorobenzene Thermal Reactions	3-17
3-5	Formation of PCDFs/PCDDs from PCDPEs	3-22

MONS 018757

TABLES

Table		Page
2-1	Toxicity and Exposure Limits Data of Common Toxicants	2-5
3-1	Chemical and Physical Characteristics of Selected Phthalate Esters	3-2
3-2	Effect of Reaction Temperature on the Thermal Decomposition of Selected Phthalate Esters	3-5
3-3	Toxicity and Exposure Limits of Di-(2-Etnylhexyl)-Phthalate, o-Dioctylphthalate, and Their PICs	3-7
3-4	Chemical and Physical Characteristics of a Typical PDMS Transformer Fluid	3-9
3-5	Chemical and Physical Properties of Selected Chlorinated Benzenes	3-12
3-6	Chlorobenzene Decomposition Temperatures	3-13
3-7	Formation of PCDFs and PCDDs from the Pyrolysis of Chlorobenzenes at 620 °C	3-16
3-8	Toxicities and Exposure Limits of Chlorobenzene Combustion/ Pyrolysis Products	3-18
3-9	Physical and Chemical Properties of Selected Diaryl Alkanes	3-19
3-10	Physical and Chemical Properties of Selected Alkyl Biphenyls	3-24
3-11	Chemical and Physical Characteristics of PAO 13CE	3-25
3-12	Chemical and Physical Characteristics of RTEmp	3-26
3-13	Chemical and Physical Characteristics of Perchloroethylene	3-28
3-14	Toxicity and Exposure Limits of Perchloroethylene and Decomposition Products	3-30
4-1	Toxicity and Exposure Limits of Freon 113 Decomposition Products	4-3
4-2	Chemical and Physical Characteristics of Sulfur Hexafluoride	4-4
4-3	Toxicity and Exposure Limits of Sulfur Hexafluoride Decomposition Products	4-6

MONS 018758

TABLES (continued)

Table		Page
5-1	Volatile Products from Pyrolysis of Epoxy Resin	5-3
5-2	PICs Found in Fire Gases from Two Cast Resin Transformer Fires	5-4
5-3	Toxicity and Exposure Limits of Epoxy Decomposition By-Products	5-5
5-4	Decomposition Yields of Some Aromatics Obtained by the Pyrolysis of PVC (Geon-103 EP) at Various Temperatures	5-8
5-5	Toxicities and Exposure Limits of PVC Thermal Degradation By-Products	5-10

MONS 018759

EXECUTIVE SUMMARY

Since 1976, the manufacture and commercial use of polychlorinated biphenyls (PCBs) have been restricted by law. Proposals have been made to remove existing PCB-containing transformers and capacitors from service. A number of chemicals have been and are being considered for use as PCB substitutes in electrical applications. Although all have been tested for acceptable dielectric, heat transfer, and flammability properties, few have been extensively analyzed for combustion by-products.

PCBs were not restricted for problems with their dielectric properties or heat transfer capabilities, but rather for suspected toxicological properties that were not considered when PCBs were first commercially produced. These toxicological properties are attributed not only to the PCBs themselves, but also to the presence of various toxic chlorinated aromatics in the by-products of PCB/askarel fires. It is thus necessary to examine the chemical behavior of proposed PCB substitutes to identify the potential for similar problems. The purpose of this report was to conduct a state-of-the-art literature review to determine what is known regarding the chemical and toxicological nature of the combustion by-products of various PCB substitutes.

DATA ASSESSMENT

Until very recently, the major concern in any fire or explosion episode was firefighter safety. As a result, tests have focused almost exclusively on major gaseous combustion products such as carbon monoxide, hydrogen cyanide, oxides of nitrogen and sulfur, hydrogen chloride, and so forth. These are the immediate life-threatening combustion products with which one must deal, and they are generally the simplest to detect and measure.

However, it has become evident in the aftermath of several PCB incidents that the toxic trace combustion product problem is concerned more about soot deposits than the vapors formed. Trace products of incomplete combustion (PICs) are produced

MONS 018760

in such low levels that vapor emissions dispersing in the atmosphere rapidly reach inconsequential levels. These same PICs may concentrate in soot, however, and soot provides a reservoir for continued emissions or exposure long after a fire has been extinguished and the gases dispersed.

Furthermore, analysis of soot or even gas samples for trace PICs at the levels typically produced requires very sophisticated analytical instrumentation and highly trained specialists. Even then, complete identification of PICs in a particular sample may take years of work. As the level of sensitivity of analytical instruments increases, even more toxic PICs may become evident. For instance, continued research on PCB combustion by-products has identified not only chlorinated dioxins and dibenzofurans, but also polychlorinated chrysenes, pyrenes, xanthenes, terphenyls, quaterphenyls, and others.

This level of research has been directed at PCB because of its negative publicity and the perceived crises in regards to several PCB incidents. No such crises exist for the proposed PCB substitutes. As a result, with a very few exceptions, comparable research has not been conducted into their PICs. As noted above, existing data tend to focus on the macro combustion products present in the vapor state rather than trace PICs in the soot. Consequently, there is relatively little data on trace PICs comparable to that on dioxins or dibenzofurans. These types of by-products simply have not been identified and studied in most cases.

PROPOSED PCB SUBSTITUTES: LIQUIDS

Two types of esters, phthalate esters and benzylneocaprate, have been considered as PCB substitutes. In general, pyrolysis of esters will produce gases similar to and no more toxic than those obtained from hydrocarbons. One major decomposition product is phthalic anhydride which can react further to form naphthalene and biphenyl. In the presence of chlorobenzenes, PCB and chlorinated naphthalene may be produced.

Polydimethyl siloxane has been widely used as a retrofill fluid. During thermal decomposition, amorphous silica, several cyclic siloxanes, and a variety of simple hydrocarbons are produced. Most of these compounds are not highly toxic, and animal inhalation tests on pyrolyzed siloxanes have generally indicated a low toxicity.

MONS 018761

Chlorobenzenes have generally not been considered PCB substitutes as much as additives to PCBs and other dielectrics. Decomposition of chlorobenzenes can produce a variety of highly toxic compounds. Pyrolysis of monochlorobenzene can yield mono- and dichlorobiphenyls, chloronapnthalene, and vinyl chloride. In the presence of air, chlorobenzenes can produce chlorophenols which can, in turn, dimerize to PCDFs and PCDDs. Many of these combustion/pyrolysis products are very highly toxic.

Methylated diphenylethane and phenylxylylethane are used as components in dielectric fluid mixtures. No information was found on the combustion/pyrolysis products of either compound, but pyrolysis of chemically similar diphenylmethane and 1,2-diphenylethane produces a number of polynuclear aromatic hydrocarbons. Few of these are considered to be highly toxic, but several are known or suspected carcinogens.

There is no information available on the thermal decomposition products of butylated monochlorodiphenylether, another PCB substitute. However, both the unsubstituted diphenylether and polychlorinated diphenylethers have been studied. Diphenylether can break down into phenol, benzene, and dibenzofuran. Polychlorinated diphenylether can produce PCDFs and PCDDs.

There is also no information available on the thermal decomposition products of the alkyl biphenyls, specifically isopropylbiphenyl and n-propylbiphenyl.

Paraffinic hydrocarbons, such as polyalphaolefin and RTEmp, tend to decompose into a variety of short-, medium-, and long-chain saturated and unsaturated hydrocarbons. In the presence of air, organic acids, alcohols, and aldehydes are formed.

Perchloroethylene is being promoted as a transformer fluid neat, mixed with mineral oil, or mixed with fluorocarbons. Chlorine or hydrogen chloride are the principal decomposition products to be expected. Under certain conditions, phosgene or trichloroacetic acid may be produced.

DIELECTRIC GASES

Chlorofluorocarbons are used as dielectrics both neat and mixed with perchloroethylene. Although generally thermally stable, at high temperatures or during

MONS 018762

arcing, decomposition is possible. Chlorine, hydrogen chloride, hydrogen fluoride, phosgene, and carbonyl fluoride are among the by-products which can be expected. Phosgene and carbonyl fluoride, in particular, are highly toxic.

Sulfur hexafluoride can be used alone as a dielectric or in a mixture of gases. It produces a number of long-lived by-products under fire and arcing conditions. The principal by-product is thionyl fluoride; other products include sulfuryl fluoride, thionyl tetrafluoride, and sulfur dioxide. Toxicity tests on sparking gases have yielded a higher toxicity than the above compounds would indicate. Thus, there are one or more unidentified trace decomposition products which contribute significantly to the toxicity of the decomposition gases.

PROPOSED PCB SUBSTITUTES: SOLIDS

Two solids were reviewed: epoxy resins and polyvinyl chloride (PVC). Complicating an assessment of their decomposition is the fact that neither is a pure compound or even a mixture of a few discrete compounds. Rather, each is a mixture of resin, hardener, filler, and various other materials, many of which may have a variable composition. Thus, the decomposition products of these solids can vary extensively, depending on the nature of the additives.

Pyrolysis of epoxy resins can produce a variety of organic compounds including benzene, methyl chloride, ethyl chloride, acetone, propylene, ethane, pentane, toluene, cresol, phenol, and others. Several of these are known or suspected carcinogens.

Decomposition of PVC can yield benzene, toluene, xylene, aliphatic hydrocarbons, β-methylnaphthalene, several chlorinated benzenes, and phosgene. Because of the production of chlorinated benzenes, the formation of PCDDs and PCDFs is a distinct possibility, although none have been identified in PVC pyrolysis gases to date.

MONS 018763

Section 1

INTRODUCTION

BACKGROUND

The U.S. Congress passed the Toxic Substances Control Act in 1976. Under requirements of the Act, the EPA issued restrictions on the manufacture and commercial use of polychlorinated biphenyls (PCBs). PCB production in the United States was halted in 1977, and the production of PCB-containing transformers and capacitors has been limited since then; however, there was no order to take such units out of service. The service life of these units is measured in tens of years, so that the replacement rate is low (about 0.2% per year) (117). However, should the EPA order PCB-containing units removed from service (FR 49(198):39966-39989, 11 October 1984, Proposed Rules), the need to find acceptable PCB substitutes will become critical.

Several possible substitutes for PCBs are readily available (92, 97). PCBs were not restricted for problems with their dielectric properties or heat transfer capabilities, rather for suspected toxicological properties not considered in 1929 when PCBs were first commercially produced (117). These toxicological properties are attributed not only to the PCBs themselves, but also to the presence of polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and other chlorinated aromatics in utility PCB fluids and in the by-products of PCB/askarel fires. It is thus necessary to examine the chemical and toxicological behavior of proposed PCB substitutes and to identify potential problems for each alternative chemical option for transformers and capacitors before its use becomes widespread.

OBJECTIVES

The available PCB substitutes are of widely variant chemical composition. The toxicology and environmental hazard evaluation of most of these compounds has been reported (97). The objective of this study is to review the state of the art regarding the thermal degradation chemistry of PCB substitutes, the formation

MONS 018764

of hazardous products of incomplete combustion (PICs) from these compounds, and the toxicity and environmental hazard of those PICs.

The liquid, gaseous, and solid dielectrics examined in this study are described below.

Liquids

- Phthalic esters di-(2-ethylhexyl)-phthalate and dioctylphtnalate.
- Benzyl neocaprate.
- Polydimethylsiloxane.
- Chlorobenzenes.
- Butylated monochlorodiphenylether.
- Methylated diphenylethane.
- Phenylxylylethane.
- Isopropylbiphenyl.
- Propylbiphenyl.
- Poly(1-octene).
- RTEmp.
- Perchloroethylene.

Gases

- Freon 113.
- Sulfur hexafluoride.

Solids

- Epoxy resins.
- Polyvinyl chloride.

The risk from exposure to these compounds is modified in this study by the assumption that the hazard from the compounds studied occurs only when the compound is in a transformer or capacitor which has failed catastrophically (ruptured) due to internal arcing, which involves temperatures of up to 6000 °C for periods of less than a second, or due to short-circuits which cause internal "hot

MONS 018765

spots," involving temperatures of up to 250 °C for a few minutes before evolution of gas from the fluid ruptures the transformer case, or which has suffered fluid loss as a result of an external fire (15, 71). Any unit which completes its service life without losing fluid to the environment is considered to pose no hazard in the context of this study. Such units may pose a disposal problem; this difficulty is not considered here.

REPORT ORGANIZATION

Section 2 of this report discusses proper assessment of the data. Sections 3, 4, and 5 cover the thermal degradation of the liquid, gaseous, and solid dielectrics, respectively, and the toxicology of their PICs.

MONS 018766

Section 2

DATA ASSESSMENT

INTRODUCTION

If comparative toxicologic action of the combustion products of several materials is to be used, even in part, as a method of preferential selection, available information must include:

- The nature and amount of the toxicologic agents generated when the materials undergo combustion or pyrolysis under specified decomposition conditions.
- The dose-response characteristics of these agents.
- The additive, antagonistic, or synergistic stress from the products generated by the degradation (72).

The available data for each of the above criteria are highly variable, in terms of both quantity and quality. Some chemicals have been studied extensively, some not at all. Before addressing the specific data for each PCB substitute, it is necessary to examine the types of data available and their limitations.

COMBUSTION/PYROLYSIS CHEMISTRY

The ideal way to identify the expected thermal degradation products of a given substance is to combust or pyrolyze it under conditions nearly identical to those which might be encountered in the field, yet in a tightly controlled environment, followed by a full-spectrum analysis of the vapors and soot produced. This is virtually impossible to do for a variety of reasons, not the least of which is the cost of such experiments. In general, available data are based on laboratory tests and incomplete analyses.

Part of the problem is that, until very recently, the major concern in any fire or explosion episode was firefighter safety. As a result, tests have focused almost exclusively on major gaseous combustion products such as carbon monoxide, hydrogen cyanide, oxides of nitrogen and sulfur, hydrogen chloride, and so forth.

MONS 018767

These are the immediate life-threatening combustion products with which one must deal, and they are generally the simplest to detect and measure.

However, it has become evident in the aftermath of several PCB incidents that the toxic trace combustion product problem is concerned more about soot deposits than the vapors formed. This is not to suggest that a compound like a dioxin is less toxic in the vapor state. However, trace PICs are produced in such low levels that vapor emissions dispersing in the atmosphere rapidly reach inconsequential levels. These same PICs may concentrate in soot, however, and soot provides a reservoir for continued emissions or exposure long after a fire has been extinguished and the gases dispersed.

Furthermore, analysis of soot or even gas samples for trace PICs at the levels typically produced requires very sophisticated analytical instrumentation and highly trained specialists. Even then, complete identification of PICs in a particular sample may take years of work. As the level of sensitivity of analytical instruments increases, even more toxic PICs may become evident. For instance, continued research on PCB combustion by-products has identified not only chlorinated dioxins and dibenzofurans, but also polychlorinated chrysenes, pyrenes, xanthenes, terphenyls, quaterphenyls, and others (113).

This level of research has been directed at PCB because of its negative publicity and the perceived crises in regards to several PCB incidents. No such crises exist for the proposed PCB substitutes. As a result, with a very few exceptions, comparable research has not been conducted into their PICs. As noted above, existing data tend to focus on the macro combustion products present in the vapor state rather than trace PICs in the soot. Consequently, there is relatively little data on trace PICs comparable to that on dioxins or dibenzofurans. These types of by-products simply have not been identified and studied in most cases.

A major fraction of the available data was not generated with a view toward utility dielectric applications. Experimental conditions were not designed to match a transformer failure or similar occurrence. The fact that a particular dielectric can, in a laboratory, pyrolyze or combust to a dioxin or dibenzofuran does not, in itself, indicate that a similar reaction will occur in an actual incident. The experimental temperatures to which the dielectric was exposed and the residence time at those temperatures, must be compared to the conditions expected to occur during normal operation of a transformer or capacitor and during catastropnic failure of such a unit.

MONS 018768

It is not the purpose of this report to speculate on potential PICs. Rather, the objective is to report the state-of-the-art. In some cases, where there is little combustion data on a particular compound, there are more data on a structurally analogous compound. Such data are included as guidelines for any future research, although even very closely analogous compounds may not behave identically.

TOXICITY AND EXPOSURE LIMITS

There is no single, universally accepted standard for expressing chemical toxicities; rather, there is a series of terms depending on the nature of the data and how it was obtained. Lethal dose, lethal concentration, toxic dose, and threshold limit value are examples of the types of toxicity data available. Furthermore, within each type there may be variations to describe the lowest recorded value or the value at which a certain percent of a test population died or showed adverse reactions. The data may be expressed in terms of liquid concentration, atmospheric concentration, or concentration per unit body weight, often with a time factor included. Finally, the data are generally identified by the types of organism from which they were obtained, either human, rat, mouse, guinea pig, or other animal.

These different types of data are frequently unrelatable. High oral toxicity, for instance, may or may not accompany an equally high inhalation or dermal toxicity. Toxic dose, lethal dose, and threshold limit value express three different types of data which, even within the same animal species, may be unrelated for a particular chemical. Finally, due to morphological differences, extrapolation from animal toxicities to human may not be possible (22, 68).

Unfortunately, every particular type of data is not available for every chemical. This can make toxicity assessment and comparison a difficult task. There is no way to take an oral TC_{LO} for rats and a dermal LD_{50} for guinea pigs, and project an inhalation TLV for humans. Consequently, it is necessary to establish a few guidelines to the application of the data to be presented later in this report.

In general, this report tries to present inhalation or dermal toxicity data for humans, wherever such were available. As they frequently are not available, inhalation data for rats, oral data for humans or rats, or inhalation or oral data for other animals were used, in the above order of preference. Some attempt was made to qualitatively assess the data.

MONS 018769

It is also recognized that discrete toxicity data values presented in isolation probably mean little to most readers. Sax (95) attempted to describe toxicity data as follows:

- High toxicity: LD_{50} < 500 mg/kg.
- Moderate toxicity: LD_{50} 500 to 7,500 mg/kg.
- Low toxicity: LD_{50} 7,500 to 15,000 mg/kg.
- No toxicity: LD_{50} > 15,000 mg/kg.

These are general descriptions and are not to be relied upon dogmatically. For instance, synergistic effects (to be discussed below) are overlooked entirely.

Table 2-1 presents toxicity data for several common or well-known toxicants. Data comparable to that presented elsewhere in this report are presented in order to provide a general basis for comparison with PCB substitute by-products.

SYNERGISM

The toxicity data, as presented in this report, are specific for individual compounds. In a fire or catastrophic failure situation, a variety of compounds will be produced. Depending on the nature of the toxic effects, a mixture of two equally toxic compounds may be twice as toxic as either compound alone. On the other hand, if the action of the two compounds is sufficiently different, there may be little evidence of this "additive" effect. Furthermore, there is a potential for synergistic effects whereby a mixture of two toxic chemicals is far more toxic than the sum of the individual toxicities. These questions generally have not been studied in regard to PCB substitute thermal by-products; consequently, little data relating to combined toxicities or synergisms are presented. The potential for such should not be overlooked, however.

MONS 018770

Table 2-1

TOXICITY AND EXPOSURE LIMITS DATA OF COMMON TOXICANTS (83)

	LC_{50} (inh-rat)	LD_{50} (orl-rat)	LD_{50} (orl-mus)	TD_{LU} (orl-hum)	LD_{LO} (orl-hum)	TC_{LO} (inh-hum)	LC_{LO} (inh-hum)	TLV-TWA	STEL
Ethanol	20,000 ppm/10H*		7800 ug/kg	1430 ug/kg	2000 mg/kg			1000 ppm	
Hydrogen Cyanide	484 ppm/ 5M				570 ug/kg		120 mg/m^3 1H	10 ppm (TLV-CL)	
DDT		113 mg/kg	135 mg/kg					1 mg/m^3	3 mg/m^3
Hydrogen Sulfide	444 ppm						600 ppm/ 30M*	20 ppm	
Carbon Monoxide	1807 ppm/ 4H					650 ppm/ 45M	4000 ppm/ 30M	50 ppm	400 ppm
2,3,7,8-tetra-chlorodibenzo-p-dioxin		22.5 ug/kg	114 ug/kg						
Benzene	10,000 ppm/7H	4894 mg/kg		130 mg/kg		100 ppm	20,000 ppm/5M	10 ppm	25 ppm

See Glossary for definitions of abbreviations (Appendix A).

* H - Hours.
M - Minutes.

MONS 018771

Section 3

PROPOSED PCB SUBSTITUTES: LIQUIDS

INTRODUCTION

The liquid PCB substitutes can be divided into the following groups based on their chemical structures:

- Esters:
  - --Phthalic acid esters (di-2-ethylhexyl phthalate and dioctyl-phthalate).
  - --Benzylneocaprate.
- Siloxanes:
  - --Polydimethylsiloxane.
- Aromatics:
  - --Chlorobenzenes (mono-, tri-, and tetra-chlorobenzene).
  - --Butylated monochlorodiphenylether.
  - --Methylated diphenylethane and dixylylethane.
  - --Isopropylbiphenyl.
  - --Propylbiphenyl.
- Paraffinic hydrocarbons:
  - --Poly (1-octene).
  - --RTEmp.
- Perchloroethylene.

ESTERS

In general, pyrolysis of esters under high thermal and disruptive charge conditions will produce gases similar to those obtained from the hydrocarbons. The presence of oxygen in the molecule results in the formation of higher levels of carbon oxide gases. The products of disruptive discharge and the volume of gas

MONS 018772

produced per joule of energy dissipated are reported to be less than those produced from mineral oils, askarels, and silicones. The deposit formed is also less carbonaceous, and thus causes less switch contact fouling. The products of decomposition are reported to be no more toxic than those produced by hydrocarbons (119). The structure of the ester molecule greatly influences thermal stability. The stability is greatly improved by the absence of hydrogen atoms on the carbon in the β-position to the hydroxyl and carbonyl group of the alcohol and acid components, respectively.

Phthalic Acid Esters

General. Di-(2-ethylhexyl)-phthalate (Figure 3-1) was marketed in the United States by General Electric under the trade name of Dielektrol II, which is a mixture of di-(2-ethylhexyl)-phthalate, 1,2,4-trichlorobenzene, and small amounts of 1,2,3-trichlorobenzene. It is also sold in Japan under the trade name Selectrol I. Trichlorobenzene was added to raise the corona extinction voltage (35). Chemical and physical properties of these two compounds are shown in Table 3-1.

Table 3-1

CHEMICAL AND PHYSICAL CHARACTERISTICS OF SELECTED PHTHALATE ESTERS (97)

	Di-(2-ethylhexyl)-phthalate	dioctylphthalate
Molecular Weight	390.6	390.6
Melting Point	-55 °C (-67 °F)	-25 °C (-13 °F)
Boiling Point	231 °C (448 °F) at 5 mm Hg	220 °C (428 °F) at 4 mm Hg
Flash Point	215 °C (420 °F)	
Ignition Temperature	390 °C (735 °F)	
Specific Gravity		0.978
Vapor Pressure	1.32 mm Hg (200 °C)	<0.2 mm Hg
Viscosity	81 cps (20 °C)	

Thermal Decomposition of Phthalic Esters. Phthalate esters are most widely used as plasticizers in various plastics such as polyvinyl chloride. Consequently, most of the detailed decomposition data relates to decomposition in plastics under high-temperature processing conditions with a view toward the impact on the stability of the plastic. The degree to which these data apply to neat phthalate esters or phthalate ester/chlorobenzene mixtures is unknown.

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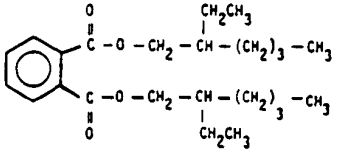
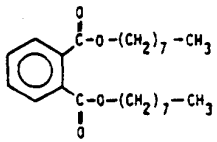


di-(2-ethylhexyl)-phthalate



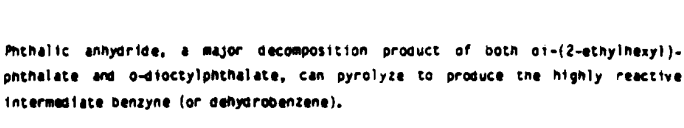
dioctylphthalate

Figure 3-1. Phthalate Esters

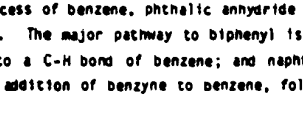
MONS 018774

Table 3-2 presents some of the degradation products of di-(2-ethylhexyl)-phthalate and dioctylphthalate and the effects of temperature on the thermal decomposition of these esters. It should be noted that these are not trace PICs. The smallest weight percent shown is 0.1, which is equivalent to 1000 ppm. No attempt was made to identify any PICs present in the ppb to few-ppm range. This same type of analytical procedure, used on askarels, would fail to detect dioxins or dibenzofurans. No data were found on the decomposition of either ester at higher temperatures.

The thermal decomposition of these compounds is believed to proceed via a cis-elimination that takes place according to a two-step mechanism. In the first step, a six-member intermediate is formed from the abstraction of the β-carbon in the side chain by the carbonyl oxygen. The second step, which is regarded as therate-determining step, involves carbon-oxygen cleavage from the intermediate with a β-carbon radical (47).


(3-1)

Phthalic anhydride, a major decomposition product of both di-(2-ethylhexyl)-phthalate and o-dioctylphthalate, can pyrolyze to produce the highly reactive intermediate benzyne (or dehydrobenzene).


(3-2)

Phthalic Anhydride Benzyne

In the presence of an excess of benzene, phthalic anhydride reacts to form naphthalene and biphenyl (8). The major pathway to biphenyl is probably by overall insertion of benzyne into a C-H bond of benzene; and naphthalene is formed by either 2+2 or 2+4 cyclo addition of benzyne to benzene, followed by elimination of acetylene.

Table 3-2

EFFECT OF REACTION TEMPERATURE ON THE THERMAL DECOMPOSITION OF SELECTED PHTHALATE ESTERS (87, 88)

DI-(2-ETHYLHEXYL)-PHTHALATE

Component	Composition of Decomposition Products, wt%, at:									
	250°C	280°C	300°C	360°C	380°C	400°C	420°C	450°C	480°C	500°C
2-ethyl-1-hexene	0.1	0.1	0.2	1.5	3.3	8.9	19.5	41.9	51.0	52.0
2-ethylhexanal	0.4	0.3	0.6	0.7	0.9	0.3	0.2	0.1	0.2	0.1
2-ethyl-1-hexanol	-	-	0.1	0.4	0.6	3.2	2.2	18.5	35.5	31.4
Phthalic anhydride	0.5	0.2	0.2	0.2	0.8	4.2	7.5	7.4	10.5	18.1
Methyl, 2-ethylhexylphthalate*	0.3	0.1	0.1	1.7	4.2	7.1	8.1	7.2	9.6	0.2
Di-(2-ethylhexyl)-phthalate	98.7	99.3	99.2	95.8	90.2	76.3	55.5	24.8	6.7	0.1

DIOCTYLPHTHALATE

Component	Composition of Decomposition Products, wt%, at:											
	250°C	280°C	300°C	320°C	340°C	350°C	360°C	380°C	400°C	420°C	450°C	480°C	500°C
1-octene	0.4	0.3	0.2	0.5	1.7	2.1	2.0	5.2	8.4	20.3	43.9	0.4	57.2
Octanal	-	-	-	0.1	0.4	-	0.4	0.1	0.1	-	-	-	-
1-octanol	0.4	0.5	0.4	0.4	0.5	0.5	0.6	1.0	3.4	10.0	22.1	24.5	22.6
Phthalic anhydride	0.1	0.1	0.1	-	-	0.2	-	0.5	3.0	6.3	4.3	4.5	8.8
Methyl, octylphthalate*	0.3	0.3	0.5	0.4	2.5	1.3	3.2	4.0	5.0	9.4	8.8	8.9	9.8
Dimethylphthalate*	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.6	0.2	0.1
Dioctylphthalate	99.8	98.7	98.6	98.4	94.7	95.7	93.7	89.1	79.9	53.6	20.4	1.4	1.6

*Components of low heat stability were converted to methyl esters for analysis. The actual decomposition products were 2-ethylhexylphthalate (methyl, 2-ethylhexylphthalate), octyl phthalate (methyl, octylphthalate), and phthalic acid (dimethyl phthalate).

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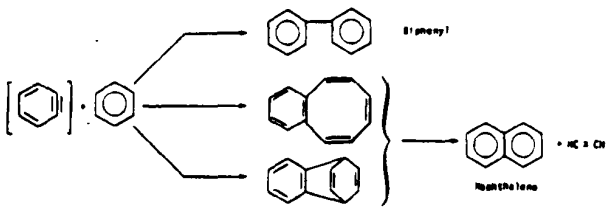


(3-3)

(3-4)

(3-5)

Since the dielectric fluids Dielectrol II and Selectrol I also contain substantial amounts of chlorobenzenes, it is conceivable that these reactions may occur, possibly producing PCB and chlorinated napnthalene.

Decomposition tests on PVC plastics containing phthalic acid esters have yielded basically the same products, although some are chlorinated. Apparently HCl, produced from the PVC, reacts with some of the ester decomposition products to give chlorinated species (88). The same type of Cl- addition reaction is conceivable in the presence of chlorobenzenes.

Toxicity and Exposure Limits of Decomposition Products. Toxicity and exposure limits data for di-(2-ethylhexyl)-phthalate, dioctylphthalate, and their identified PICs are shown in Table 3-3. This table does not include the chlorinated compounds mentioned above, as none of these PICs has actually been identified.

In general, the identified PICs appear to have the same degree of low to moderate toxicity as their precursors. However, an assessment of the toxicities is difficult, as all of the available data relate to animals, and, in most cases, inhalation data are not provided. It is still worth noting the low TLV for phthalic anhydride (TLV-TWA = 1 ppm). Phthalic anhydride is a pyrolysis product of both 2-(diethylhexyl)-phthalate and dioctylphthalate, and is formed in considerable quantities at the higher temperatures.

MONS 018777

Table 3-3

TOXICITY AND EXPOSURE LIMITS OF DI-(2-ETHYLHEXYL)-PHTHALATE, N-DIOCTYLPHTHALATE, AND THEIR PICs (83)*

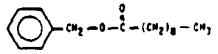
	LC_{LO} (inh-rat)	LD_{50} (inh-mus)	LC_{50} (inh-mus)	TD_{LO} (orl-man)	LD_{50} (orl-rat)	LD_{50} (orl-mus)	TLV-TWA	STEL
di-(2-ethylhexyl-phthalate				143 mg/kg	31 mg/kg		5 mg/m^3	10 mg/m^3
dioctylphthalate			5000 mg/m^3			6513 mg/kg		
phthalic anhydride					4020 mg/kg	2 gm/kg	1 ppm	4 ppm
2-ethyl-1-hexene	4000 ppm/4H	100 mg/kg						
2-ethyl-1-hexanol					2460 mg/kg			
1-octanol						1790 mg/kg		
phthalic acid					7900 mg/kg			

*No data were available for 1-ethylhexyl phthalate, benzyne, octyl phthalate, or 1-octene.

MONS 018778

Benzylneocaprate

General. There is little published information available on benzylneocaprate. It has been marketed by Asea of Sweden as Faradol 100, but the manufacturers have recently discontinued production. The only data found on the chemical and physical characteristics of this compound are its molecular weight (262) and vapor pressure (0.0003 mm Hg at 25 °C).



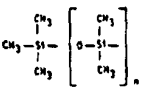
Benzylneocaprate

Thermal Decomposition of Benzylneocaprate. No information was available on the thermal degradation of benzylneocaprate. Benzylneocaprate would be expected to be thermally very stable. The cis-elimination reaction with the six-membered transition ring, by which the phthalic esters decompose, would not be expected to occur. The lack of hydrogen atoms available for abstraction from the β-carbon results in a "hindered" β-carbon. The degradation of such esters presumably follows a free radical mechanism which requires high energy levels, and therefore high thermal degradation temperatures (119).

SILOXANES

General

The principal siloxane used as a transformer insulating liquid is polydimethylsiloxane (PDMS).



Polydimethylsiloxane

PDMS is produced commercially by Dow Corning as DC561 and DC200, General Electric as SF97, Union Carbide as L305, and SWS Silicone as F101 and F190. Table 3-4 lists the important properties of a typical PDMS transformer fluid.

Table 3-4

CHEMICAL AND PHYSICAL CHARACTERISTICS
OF A TYPICAL PDMS TRANSFORMER FLUID (119)

Molecular Weight	2826
Boiling Point	250 °C
Fire Point	360 °C
Flash Point	300 °C
Specific Gravity	0.961 at 25 °C

Thermal Decomposition of PDMS

PDMS begins to thermally decompose at 200 °C. The thermal degradation occurs rapidly at 300 °C with a breaking of the Si-O bond and formation of lower molecular weight compounds such as tri- and tetracyclic siloxanes (D_3 and D_4, respectively) (Figure 3-2) (119). These are volatile, low flash point materials that boil at 150 to 170 °C. Their presence in excess of 2.5% reduces the flash point of the silicone liquid to that of a similar viscosity mineral oil. In addition to the cross-linked volatiles, both gaseous and solid (i.e., amorphous silica) decomposition products are found.

Silicone transformer liquids, after being aged for 4 hours at 350 °C, have been found to generate several cyclic siloxanes, notably D_3, D_4, D_5, and D_6 (in that order, quantitatively) (110). These same compounds can be produced at lower temperatures if the thermal aging process is extended, for instance, 5 months at 240 °C. With increasing time, the rate of formation of D_4 begins to exceed that of D_3 at the lower temperatures.

In one experiment, PDMS was pyrolyzed over the temperature range of 600 to 1200 °C; a rapid temperature rise (60 °C/msec) and a residence time of 20 sec were used (61). The following decomposition products and tendencies were observed:

- 600 to 800 °C - Predominantly cyclic siloxanes arising from siloxane rearrangement. The relative amount of cyclic siloxanes decreased regularly with increasing molecular weight, with the exception of a greater abundance of D_6 compared to D_5 at temperatures below 800 °C.

- 800 to 900 °C - Compared to the lowest temperature range tested, total volatiles increased and the relative fraction of high-volatility material increased. Methane and hydrogen were the major components of the high-volatility fraction; C_2 hydrocarbons (C_2H_2, C_2H_4, C_2H_6) have also been identified.

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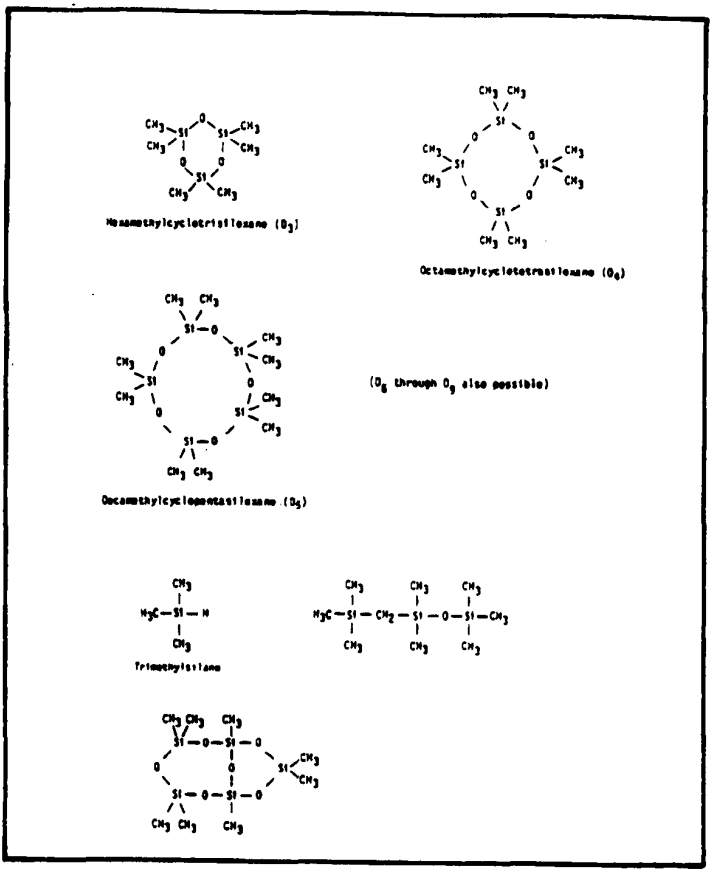


Figure 3-2. Typical PDMS Pyrolysis Products

- 900 to 1200 °C - A number of trace components appear at 900 °C and become more abundant at higher temperatures. The identified trace compounds include those shown in Figure 3-2. They appeared to arise via C-H and Si-C bond cleavage, and contain silylhydride, silmethylene, and monomethyl siloxane structures.

- 1200 °C - At this temperature, the high-volatility fraction accounted for the majority of the volatiles.

In the absence of oxygen and under arcing conditions, a variety of hydrocarbons can be produced, including methane, acetylene, ethylene, ethane, and propylene (21, 61, 112). Thermal oxidation of PDMS leads to the formation of paraformaldehyde and formic acid, as well as carbon oxides (77).

Thermal degradation is catalyzed by trace impurities of materials such as water, metals, and ionic compounds. The manufacture of the siloxanes, via an organic chloride with the production of hydrogen chloride, introduces the possibility of chlorine contamination, although chlorine concentrations probably do not exceed 1 ppm (119).

Toxicity and Exposure Limits of PDMS Decomposition Products

There are no available data on the toxicities of the various cyclic and cross-linked organosiloxanes (Figure 3-2) formed during PDMS decomposition. Of the organic compounds produced, only formaldehyde and formic acid are particularly toxic, and neither is considered highly toxic (formaldehyde LD_{50} (rat-orl) - 800 mg/kg; formic acid LD_{50} (rat-orl) - 1100 mg/kg). Both are irritants, and formic acid can be dangerously caustic to the skin (69). Both are liquids at ambient temperatures, and may therefore be found in the soot as contaminants on surfaces following a fire.

The silica produced is amorphous. Crystalline silica is a known cause of silicosis, and is considered to be far more toxic than the amorphous form. The TLV for crystalline silica (cristobalite, 0.05 mg/m^3) is several orders of magnitude lower than that of amorphous silica (precipitated silica, 5 mg/m^3) for respirable dust. Silicon carbide, formed under arcing conditions, is considered to be a mild irritant when inhaled.

The toxicity of the pyrolysis gas of PDMS (Dow Corning 561 silicone transformer liquid) was evaluated using a method developed by Hilado, where rats are subjected to inhalation of the pyrolyzed compound (44). The toxicity of PDMS was

Table 3-5

CHEMICAL AND PHYSICAL PROPERTIES OF SELECTED CHLORINATED BENZENES (97)

	Mono-Chloro	Trichloro			Tetrachloro		
		1,2,3	1,2,4	1,3,5	1,2,3,4	1,2,3,5	1,2,4,5
Molecular Weight	112.56	181.45	181.45	181.45	215.9	215.9	215.9
Melting Point	-45.2 °C	16.95 °C	63.5 °C	52.6 °C	47.5 °C	54.5 °C	140 °C
Boiling Point	132 °C	213 °C	208.5 °C	221 °C	254 °C	246 °C	243 °C
Flash Point	29 °C	110 °C	107 °C	113 °C	NI*	NI	155 °C
Vapor Pressure	8.8 mm Hg @ 20 °C	1 mm Hg @ 38.4 °C	10 mm Hg @ 78 °C	1 mm Hg @ 40 °C	NI	NI	<0.1 mm Hg @ 25 °C
Specific Gravity	1.1	1.446	NI	1.69	NI	NI	1.858

*NI = No information.

MONS 018783

compared to that of another transformer liquid, a paraffinic hydrocarbon. Under the specific test conditions, the toxicity of the pyrolysis gas from PDMS was found to be less than that of the paraffinic hydrocarbon. The silicone transformer liquid was among the least toxic of over 270 substances tested by Hilado under the same conditions.

AROMATICS

Chlorobenzenes

General. Chlorobenzenes generally were not used independently as dielectric fluids. Rather, they were mixed with other fluids (e.g., di-(2-ethylhexyl)-phthalate or PCBs) to lower pour points. The principal chlorobenzenes used are the tri- and tetra- congeners. These compounds typically make up about 30% of a dielectric fluid mixture. Figure 3-3 shows the different tri- and tetrachlorobenzene isomers possible. Monochlorobenzene has also been considered for use in dielectric fluids. Table 3-5 lists some of the chemical and physical properties of these chlorinated benzene compounds.

Thermal Decomposition of Chlorobenzenes. The chlorobenzenes are relatively thermally stable compounds. Table 3-6 lists the temperatures for the onset of thermal decomposition and 99% decomposition for some of the compounds.

Table 3-6

CHLOROBENZENE DECOMPOSITION TEMPERATURES

	Onset °C	99% Decomposition °C
Monochlorobenzene	540	710
1,2,3-trichlorobenzene	645	780
1,2,4-trichlorobenzene	640	750
1,2,3,4-tetrachlorobenzene	660	800
1,2,3,5-tetrachlorobenzene	655	760

As with other chlorinated organic compounds, the major combustion/pyrolysis products are HCl, hydrogen and methane (no air), and carbon oxides (in air). However, considerable research has been focused on the trace PICs produced.

MONS 018784

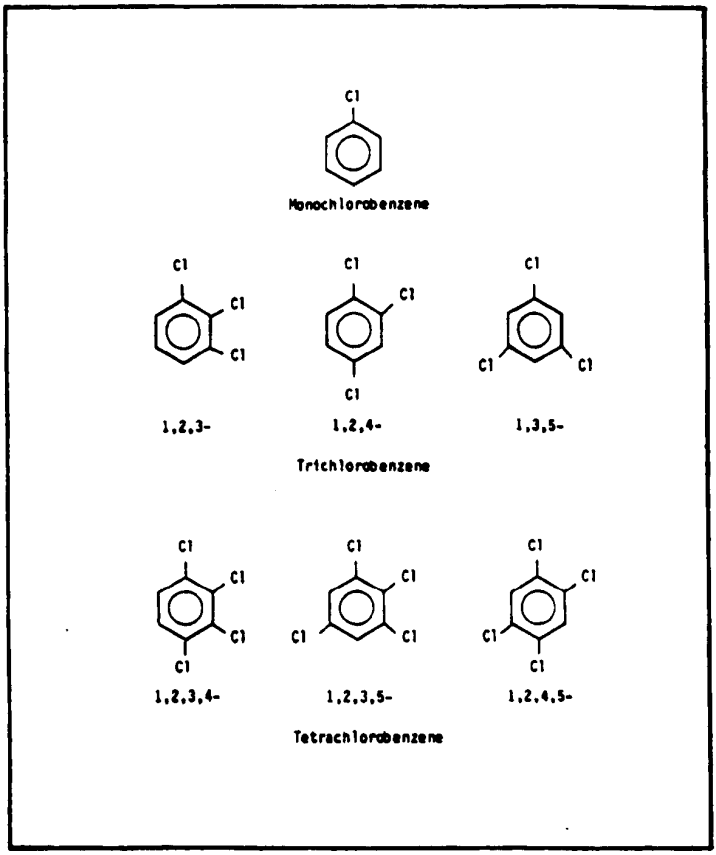
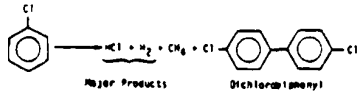


Figure 3-3. Chlorinated Benzene Compounds Used in Dielectric Fluids

Monochlorobenzene, pyrolyzed at 690 °C for 24 sec, can produce chlorobiphenyls, dichlorobiphenyls, naphthalene, and chloronaphthalenes (19). At 770 to 800 °C and 850 to 880 °C, the following reaction has been observed:



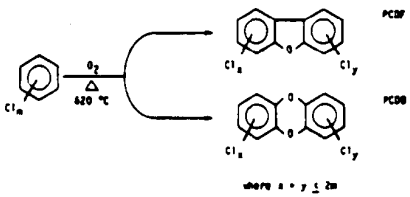
(3-6)

Between 850 and 880 °C, yields of HCl, hydrogen, methane, and chlorinated biphenyl decrease, but considerable quantities of vinyl chloride ($CH_2 = CHCl$) are produced.

Pyrolysis of chlorobenzenes in the presence of air yields chlorophenols which can, in turn, dimerize to PCDFs and PCDDs (17, 27, 113). The degree of chlorination in the chlorophenols tends to be the same or higher than that of the parent chlorobenzene (16). In other words, monochlorobenzene will produce mono-, di-, or trichlorophenols; trichlorobenzene will produce tri-, tetra-, and pentachlorophenols.

Buser (16) pyrolyzed tri-, tetra-, and pentachlorobenzenes at 620 °C in sealed quartz mini-ampules in the presence of air. The pyrolysis gases included higher chlorinated benzenes, chlorophenols, PCDFs, PCDDs, and, in some cases, polychlorinated naphthalenes, polychlorinated styrenes, and small quantities of PCBs. Polychlorinated diphenyl ethers and polychlorinated biphenylenes were identified in other experiments (17, 113).

Table 3-7 lists the quantities of PCDFs and PCDDs produced. The known toxic compounds (those with chlorine atoms in the 2, 3, 7, and 8 positions) were identified, but these were not major components. In general, the degree of chlorination in the PCDD/PCDF product seems to follow the pattern below.



(3-7)

(3-8)

where $x + y \leq 2m$

MONS 018786

Following this pattern, a monochlorobenzene would not generally produce higher than a dichlorodibenzodioxin or dichlorodibenzofuran. Tri- or tetrachlorobenzenes could produce up to hexa- and octa- isomers, respectively (see Table 3-7). Figure 3-4 summarizes the various chlorobenzene reactions discussed above.

Table 3-7

FORMATION OF PCDFs AND PCDDs FROM THE PYROLYSIS OF CHLOROBENZENES AT 620 °C (16)

	PCDFs (ppm)				
Parent Compound	Tetra-	Penta-	Hexa-	Hepta-	Octa-
Trichlorobenzene	2000	5500	2750	250	<25
Tetrachlorobenzene	<10	25	800	2250	1000
	PCDDs (ppm)				
Trichlorobenzene	150	100	<25	<25	<25
Tetrachlorobenzene	<10	25	700	800	150

Toxicity of Chlorobenzene Decomposition Products. Many of the combustion/pyrolysis products of the chlorobenzenes are very highly toxic (Table 3-8). It is generally believed that, on a molecular basis, 2,3,7,8-tetrachlorodibenzodioxin is the most toxic synthetic molecule known to man. Although an identified chlorobenzene PIC, 2,3,7,8-TCDD has not been found except in trace quantities. However, the other PICs, while less toxic than 2,3,7,8-TCDD, are also very toxic.

In general, toxicity seems to be related to chlorine content and position. Chlorinated aromatics with three or fewer chlorine atoms tend to be significantly less toxic than higher chlorinated congeners. Thus, PICs from monochlorobenzene would probably be less toxic than those from tri- or tetrachlorobenzene. However, they are still moderately to highly toxic as discrete compounds. The combined toxic effects could be synergistic and greater, or possibly antagonistic and less. A further problem with these PICs is that, with the exception of vinyl chloride, all are solids or liquids at normal ambient temperatures. Thus, they tend to be found as surficial contaminants with soot in the aftermath of a fire. The soot provides a reservoir for continued exposure unless completely removed.

MONS 018787

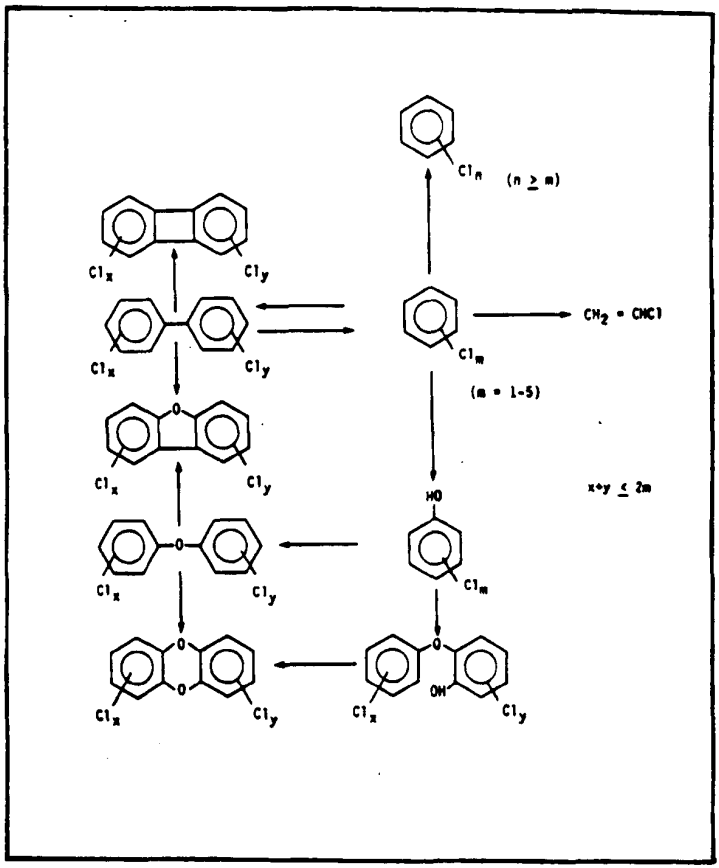


Figure 3-4. Typical Chlorobenzene Thermal Reactions

Table 3-8

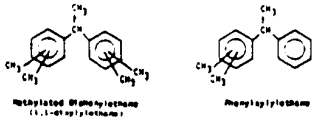
TOXICITIES AND EXPOSURE LIMITS OF CHLOROBENZENE COMBUSTION/PYROLYSIS PRODUCTS (83)

Chlorophenols	LD_{50}, orl-rat		
m-chlorophenol	570 mg/kg		
o-chlorophenol	670 mg/kg		
p-chlorophenol	261 mg/kg		
2,4-dichlorophenol	580 mg/kg		
2,6-dichlorophenol	2940 mg/kg		
2,4,5-trichlorophenol	820 mg/kg		
2,4,6-trichlorophenol	820 mg/kg		
2,3,4,6-tetrachlorophenol	140 mg/kg		
Naphthalenes			
Naphthalene	1780 mg/kg	TLV-TWA	10 ppm
1-chloronaphthalene	1540 mg/kg		
2-chloronaphthalene	2078 mg/kg		
trichloronaphthalene		TLV-TWA	5 mg/m^3
tetrachloronaphthalene		TLV-TWA	2 mg/m^3
pentachloronaphthalene		TLV-TWA	500 ug/m^3
octachloronaphthalene		TLV-TWA	100 ug/m^3
Dioxins			
2,3,7-trichlorodibenzodioxin	29.4 mg/kg (LD_{50}, orl-gpg)		
2,3,7,8-tetrachlorodibenzodioxin	22.5 ug/kg 0.5 ug/kg (LD_{50}, orl-gpg)		
1,2,3,6,7,8-hexachlorodibenzodioxin	1250 ug/kg (LD_{50}, orl-mus)		
1,2,3,4,7,8-hexachlorodibenzodioxin	825 ug/kg (LD_{50}, orl-mus)		
Mixture of 1,2,3,7,8,9- and 1,2,3,6,7,8-hexachlorodibenzodioxins	800 ug/kg		
2,3,7,8-tetrachlorodibenzofuran	5 ug/kg (LD_{50}, orl-gpg)		
Vinyl chloride	500 mg/kg	TLV-TWA	5 ppm

MONS 018789

Methylated Diphenylethane and Phenylxylylethane

General. The chemically similar methylated diphenylethane (1,1-dixylylethane) and phenylxylylethane (see below) are used as components in dielectric fluid mixtures. Edisol II, manufactured by McGraw Edison, is a mixture of the 1,1-bis (3,4-dimethylphenyl) ethane and propyldiphenyl. Phenylxylylethane is found in Dielektrol III (General Electric), Selectrol II (Sangamo), and SAS-295 and SAS-296 (Nisseki Company; mainly the 1-phenyl-1-(3,4-xylyl)- and 1-phenyl-1-(2,4-xylyl)- isomers).



Methylated Diphenylethane (1,1-dixylylethane)

Phenylxylylethane

Very little information is available on the physical and chemical properties of these compounds (see Table 3-9).

Table 3-9

PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED DIARYL ALKANES

	Methylated Diphenylethane	Phenylxylylethane
Molecular Weight	238	210
Boiling Point	315 °C	
Flash Point	162 °C	
Specific Gravity	0.97	
Vapor Pressure		0.0008 mm Hg at 25 °C

Thermal Decomposition Products of Dixylylethane and Phenylxylylethane. No information was found on the combustion/pyrolysis products of either of these compounds. The thermal decomposition of chemically similar compounds, diphenylmethane and diphenylethane (bibenzyl), has been studied, however (7).



Diphenylmethane

1,2-Diphenylethane

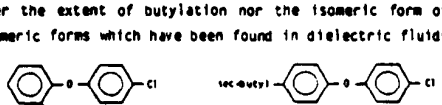
MONS 018790

Pyrolysis of these compounds at 700 °C has yielded benzene, toluene, ethylbenzene, styrene, stilbene, phenanthrene, and fluorene. If dixylylethane and phenylxylylethane follow the same general decomposition mechanisms, then products could include benzene, toluene, xylene, trimethylbenzene, ethylbenzene, ethylxylene, methylated fluorene, methylated phenanthrene, methylated styrene, and so forth. Combustion in the presence of air may produce phenols, cresols, and other oxygen-containing species. It is possible that methylated dioxins or dibenzofurans could be formed. All of this is supposition, however. Without further study, it is impossible to determine with certainty what trace PICs might be formed.

Toxicity of Dixylylethane and Phenylxylylethane Decomposition Products. Since the specific products cannot be identified with certainty, toxicities cannot be determined. None of the possible PICs discussed above is considered to be highly toxic, although several are known or suspected carcinogens. Most are liquids or solids at normal ambient temperatures, and could be expected to deposit on nearby surfaces with soot and other conventional fire by-products.

Butylated Monochlorodiphenylether

General. Butylated monochlorodiphenylether is marketed by Dow Chemical Company under the trade name of Dielectric Fluid C-4 (formerly XFS-4169L). The name specifies neither the extent of butylation nor the isomeric form of the compound. Among the isomeric forms which have been found in dielectric fluids are:



2-sec-butyl-4'-chlorodiphenylether 4-sec-butyl-4'-chlorodiphenylether

The major components of one sample of XFS-4169L were (wt %): 4-chlorodiphenylether (19.6); 2-sec-butyl-4'-chlorodiphenylether (27.2); 4-sec-butyl-4'-chlorodiphenylether (24.0); and small amounts of di- and tri-butylated chlorodiphenylethers (2). Physical and chemical property data were not available on individual isomers.

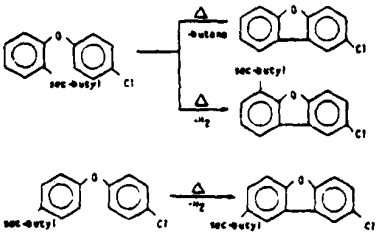
Thermal Decomposition of Butylated Monochlorodiphenylether. There is no information available on the thermal decomposition products of butylated monochlorodiphenylether. However, both the unsubstituted diphenylether and polychlorinated diphenylethers (PCDPEs) have been studied.

MONS 018791

Vapors of diphenylether passed through a glass tube at red heat have been shown to break down into phenol, benzene, and dibenzofuran (46).

At 600 °C, the thermal conversion of PCDPEs into PCDFs is of the same order of magnitude as that from PCBs (17). Lindahl et al. (59) conducted a series of tests with tri- to octachlorodiphenylethers at 600 °C, and concluded that PCDFs form primarily via loss of ortho-H_2 or ortho-HCl with a minor fraction formed by loss of ortho-Cl_2. A few PCDDs were also observed, formed presumably via loss of ortho-Cl_2. The PCDDs formed showed lower chlorination than the PCDPEs. Figure 3-5 shows these reactions.

If butylated monochlorodiphenylethers follow the same mechanisms, the following reactions could result.



(3-9)

(3-10)

(3-11)

Assuming that the chlorine is always in the 4' position, no reaction will occur via Cl_2 loss. This is important as Lindahl et al. (59) observed dioxin formation only via Cl_2 loss. Thus, butylated-4'-chlorodiphenylethers would not be expected to degrade to dioxins.

Also important is the fact that the PCDPE to PCDF reaction is monomolecular. In contrast, the PCB to PCDF reaction is bimolecular, requiring PCB and oxygen molecules, while the chlorobenzene to PCDF reaction is trimolecular, requiring two chlorobenzenes and oxygen. These multimolecular reactions can be significantly less frequent in oxygen-starved or dilute systems. Being monomolecular, neither oxygen content nor PCDPE concentration will affect the rate of PCDPE conversion to PCDF.

MONS 018792

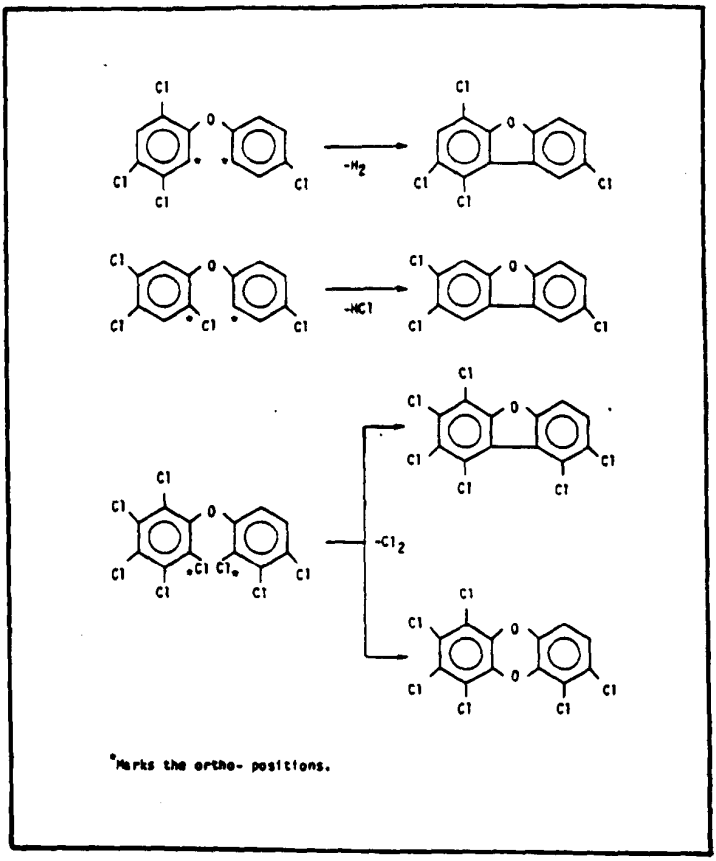


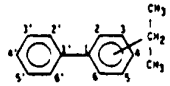
Figure 3-5. Formation of PCDFs/PCDDs from PCDPEs (318)

No other PICs have been identified or suggested for butylated monochlorodiphenylether.

Toxicity of Butylated Monochlorodiphenylether Decomposition Products. As noted above, there is no definite information on the combustion/pyrolysis products of butylated monochlorodiphenylether. Thus, no toxicity information is available. Assuming that the reactions discussed above are possible, then reaction products could include monochlorodibenzofuran (from the 4-chlorodiphenylether) and butylated (mono-, di-, and tri-) monochlorodibenzofuran. There is no information available on the toxicities of these compounds.

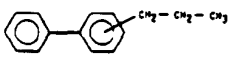
Alkyl Biphenyls

General. Isopropylbiphenyl is manufactured by Westinghouse under the trade name of Wemcol. Wemcol is described by the manufacturer as being predominantly 4-isopropylbiphenyl with considerable amounts of the 3- isomer and traces of more highly substituted biphenyls. However, an independent analysis (107) revealed the following composition (wt %): 3-isopropylbiphenyl (60.3%); 4-isopropylbiphenyl (38.4%); 3,5-diisopropylbiphenyl (0.3%); 3,3'-diisopropylbiphenyl (0.4%); 3,4'-diisopropylbiphenyl (0.2%); and 4,4'-diisopropylbiphenyl (0.1%).



Isopropylbiphenyl

n-propylbiphenyl is mixed with dixylylethane in Edisol II, manufactured by McGraw Edison. Several mono- and dipropyl isomers are possible, but there is no information available on which isomers are found in Edisol II. Table 3-10 presents physical and chemical properties for these compounds.



n-propylbiphenyl

MONS 018794

Table 3-10

PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED ALKYL BIPHENYLS (97)

	Isopropylbiphenyl	n-propylbiphenyl
Molecular Weight	196	196
Boiling Point	270 °C	280 °C
Flash Point	141 °C	>100 °C
Ignition Temperature	435 °C	445 °C
Specific Gravity	1.0	

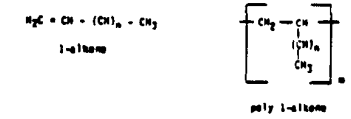
Thermal Decomposition of Isopropylbiphenyl and n-propylbiphenyl. No information was found in the literature on the combustion/pyrolysis products of either of these compounds. Assuming that they degrade by C-C bond fission like other alkyl aromatic compounds, the pyrolysis products could include biphenyl, propylbenzene, propene, and similar compounds. In the presence of air, phenols, alkyl alcohols, unsubstituted and alkyl substituted dibenzofurans, and so forth might be possible. All of this is conjecture, however.

Toxicity of Isopropylbiphenyl and n-propylbiphenyl Decomposition Products. No information is available on the combustion toxicology of these compounds.

PARAFFINIC HYDROCARBONS

Polyalphaolefins

General. A polyalphaolefin (PAO), or poly 1-alkene, is a polymeric chain of alkene monomers with a single double bond in the 1-position.



Among the polyalphaolefins marketed for use as transformer oils are PAO 13CE and PR, manufactured by Uniroyal Chemical and Gulf Oil Chemicals, respectively. PAO 13CE is derived from 1-octene, and has an average molecular weight of 600 (1).

MONS 018795

No mention of the degree of cross-linking was found. Table 3-11 presents the chemical and physical properties of PAO 13CE.

Table 3-11

CHEMICAL AND PHYSICAL CHARACTERISTICS OF PAO 13CE (117)

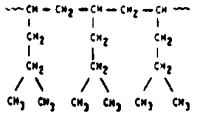
Molecular Weight	600
Flash Point	290 °C
Fire Point	307 °C
Specific Gravity	0.84
Viscosity (Centistokes)	14 at 100 °C

Thermal Decomposition of Polyalphaolefin. Information on the thermal decomposition products of poly (1-octene) is very limited; no specific PICs are named. PAO is reported to undergo practically no thickening or sludge formation when exposed to temperatures of 175 °C for 100 hours (101).

Random chain scission along the backbone chain is the dominant mechanism in the pyrolysis of polyolefins. As the term implies, scission is a random event, and polymer molecules are ffrst broken into large macroradicals. There is a rapid decrease in molecular weight, and almost no monomer is formed in the early stages (39). The expected decomposition products would include a variety of short-, medium-, and long-chain saturated and unsaturated hydrocarbons, mainly olefins, paraffins, and cyclic hydrocarbons (106). In the presence of air, various oxy-species could also be expected.

For instance, pyrolysis (approximately 300 to 350 °C) tests on poly (4-methyl-1-pentene) in vacuum yielded isobutene, propane, isobutane, 4-methyl-1-pentene, isopentane, 2,3-dimethylbutane, n-pentane, propene, and a series of C_{11} to C_{18} branched saturated and unsaturated hydrocarbons (4). In the presence of air, peroxides and hydroperoxides are formed initially, leading to the formation of such products as isobutyraldehyde, acrolein, acetic acid, acetaldehyde, acetone, isobutyric acid, isovaleric acid, isopropanol, ethanol, crotonalydehyde, methanol, isobutanol, propionic acid, oxalic acid, propionaldehyde, butyric acid, butyraldehyde, and n-propanol.

MONS 018796



Poly(4-methyl-1-pentene)

Toxicity of Poly 1-Octene Decomposition Products. No information was available on the combustion toxicology of poly 1-octene. The types of hydrocarbons mentioned above are generally of low to moderate toxicity, but the presence of more highly toxic compounds cannot be ruled out without further testing.

RTEmp

General. RTEmp is a high molecular weight, purified paraffin manufactured by RTE Corporation. It is refined from crude oil and solvent extracted so that there are no aromatic or polyaromatic compounds present.

RTEmp is also characterized by its lack of halogens and inorganic compounds. The exact composition is difficult to ascertain. According to material supplied by the manufacturers to the Occupational Safety and Health Administration, it is listed as having a boiling point above 427 °C, corresponding to an n-alkane of chain length C_{26}. Table 3-12 presents chemical and physical properties of RTEmp.

Table 3-12

CHEMICAL AND PHYSICAL CHARACTERISTICS OF RTEmp (117, 121)

Boiling Point	427 °C
Flash Point	284 °C
Ignition Temperature	312 °C
Specific Gravity	0.87
Viscosity (Centistokes)	120-140 at 40 °C; 12-14 at 100 °C

Thermal Decomposition of RTEmp. The lack of knowledge of the exact chemical nature of the compound has made it impossible to describe the thermal degradation

products of pyrolysis/combustion. The "fire hazard properties" of RTEmp have been studied under simulation of a "worst case" scenario for a catastrophic transformer failure. The major arcing product reported was hydrogen, with lesser amounts of acetylene, methane, ethylene, and other gaseous hydrocarbons not specifically named (62). All of the above gases are flammable and are believed to contribute to the fireball observed in catastrophic electrical failure tests.

Toxicity of RTEmp Decomposition Products. Since combustion products, and particularly PICs, have not been identified, it is impossible to assess their individual toxicities. However, the toxicities of the gross pyrolysis gases were evaluated using a method developed by Hilado where rats are subjected to inhalation of the actual pyrolysis gases (15). Exact toxicities were not given, but the toxicity of the pyrolysis gases from RTEmp was compared to that of another transformer liquid, a polydimethylsiloxane (Dow Corning 561 silicone transformer liquid). Under the specific test conditions, the toxicity of the RTEmp pyrolysis gases was greater than that of the silicone transformer liquid.

Perchloroethylene

General. Perchloroethylene (tetrachloroethylene; C_2Cl_4) is a nonreactive, nonflammable liquid which has generally been used as a solvent. Table 3-13 lists its chemical and physical properties. It is manufactured as Wecosol™ transformer fluid by Westinghouse, and may be used neat or mixed with mineral oils. Perchloroethylene is also a major component in a relatively new British import, Formel NF (98). This fluid is a mixture of perchloroethylene and three fluorocarbons (112, 112a, and 113).



Perchloroethylene

MONS 018798

Table 3-13

CHEMICAL AND PHYSICAL CHARACTERISTICS OF PERCHLOROETHYLENE

Molecular Weight	165.83
Melting Point	-22.4 °C
Boiling Point	121.2 C at 1 atm
Flash Point	None
Fire Point	None
Vapor Pressure	14 mm Hg at 20 °C
Specific Gravity	1.62

Thermal Decomposition of Perchloroethylene. The amount of data available on the thermal decomposition of perchloroetnylene is quite limited. It is a very stable compound due to high molecular bond dissociation energies and a lack of hydrogen atoms available for abstraction or formation of hydroxy radicals. As a result, few decomposition products would be expected.

Claiborne (21) heated perchloroethylene in varying levels of air in a stainless steel tube to 1000 °C. The principal products were CO_2 and chlorine. A small amount of HCl was found. Phosgene was not detectable either by gas chromatography or mass spectrometry.

Low energy (30 kW-sec input energy for 30 min) arcing experiments generated small quantities of CO, CO_2, chlorine, and HCl (60). No other products were reported.

Decomposition tests on Formel NF-filled transformers produced only traces of chlorine and several chlorofluorocarbons, other than the fluid constituents (98). No HCl or phosgene were detected. The halocarbons were probably produced from the halocarbon components of the fluid mix (see Section 4, Freon 113).

There are reports that perchloroethylene may decompose to phosgene or trichloroacetic acid in the presence of arc welding (25). The tests cited above do not confirm this, but the experimental conditions did not simulate arc welding. It does not appear that these highly toxic compounds are generated under simple pyrolysis or low-energy arcing conditions.

MONS 018799

Toxicity and Exposure Limits of Perchloroethylene Decomposition Products. Table 3-14 lists the toxicities for various known and suspected perchloroethylene decomposition products. The most toxic of the PICs formed are chlorine, phosgene, and trichloroacetic acid, which appear to be clearly more toxic than the parent compound. However, with the exception of chlorine, these PICs seem to be formed in trace quantities, if at all. Furthermore, of the PICs listed, only trichloroacetic acid is likely to be found on surfaces in the aftermath of a fire. The others are gaseous and would readily disperse.

Table 3-14

TOXICITY AND EXPOSURE LIMITS OF PERCHLOROETHYLENE AND DECOMPOSITION PRODUCTS (83)

	inh-hum			inh-rat		orl-rat	unk-man		
	LC_{50}	LC_{LO}	TC_{LO}	LC_{50}	LC_{LO}	LD_{50}	LD_{LO}	TLV-TWA	STEL
Perchloro-ethylene		4000 ppm/ 4H	96 ppm/ 7H					50 ppm	200 ppm
Chlorine		873 ppm/ 30 min		293 ppm/ 1H					
Carbon Dioxide		10%/1 min			65%/ 15 min			0.5%	1.5%
Phosgene (Carbonyl Chloride)	3200 mg/ m^3		25 ppm/ 30 min		50 ppm/ 30 min				
Trichloro-acetic Acid						5000 mg/kg		1 ppm	
Hydrochloric Acid		1300 ppm/ 30 min		3124 ppm/ 1H			81 mg/kg	5 ppm	
Hydrogen Chloride (Gas)		1000 ppm/ 1 min	4701 ppm/ 30 min						

MDNS 018801

Section 4

DIELECTRIC GASES

CHLOROFLUOROCARBONS

General

Freon is DuPont's registered trademark for carbon compounds containing fluorine, and is used only for fluorocarbons that are nonflammable and low in toxicity. Freon 113, used as a dielectric gas, refers to 1,1,2-trichloro-1,2,2-trifluoroethane.



Freon 113

In addition to being used individually as a dielectric gas, chlorofluorocarbon 113 is a component of the Formel NF mixture. This fluid contains two other fluorocarbons, 1,1,2,2-tetrachloro-1,2-difluoroethane (chlorofluorocarbon 112) and 1,1,1,2-tetrachloro-2,2-difluoroethane (chlorofluorocarbon 112a). These two fluorocarbons are not discussed elsewhere in this report, but many of the following comments on Freon 113 decomposition apply to them generally.

Thermal Decomposition of Freon 113

The chlorofluoroalkanes, of which Freon 113 is a member, are thermally stable up to 250 °C (119). At higher temperatures or during arcing, the fluorocarbons can decompose.

Sparking tests on 1,1,1- and 1,1,2-trichlorotrifluoroethane produced the negative ions Cl^-, F^-, Cl_2^-, and CCl_3^- (93). All of these could continue to react with the parent compound. In this test, analyses were not carried forward to identify the final decomposition products.

MONS 018802

Partial combustion of $C_2Cl_3F_3$ at 1000 °C in air produced six trace compounds tentatively identified as CF_4, Cl_2, COF_2, CO, $CClF_3$, and $COCl_2$ (phosgene) (21). In addition, the quartz reaction chamber was noticeably etched, suggesting the possibility of HF formation.

Tests on Formel NF (which contains perchloroethylene as well as the fluorocarbons mentioned above) yielded only Cl_2 and several unidentified halocarbons (98). No phosgene or HCl were detected. Hydrogen chloride would not generally be expected from these compounds because of the lack of hydrogen.

Many fluorocarbon decomposition reactions depend on the presence of at least one hydrogen atom on the molecule. At high temperatures, a hydrogen halide can form, resulting in an unsaturated halocarbon or a halocarbon radical leading to the formation of longer chain molecules and even polymerization. These are fairly common reactions, but would not be expected with Freon 113 or Formel NF.

Toxicity and Exposure Limits of Freon 113 Decomposition Products

Table 4-1 lists the toxicities of the identified Freon 113 decomposition products. Most of these products are more toxic than the parent molecule, and several (phosgene, carbonyl fluoride) are highly toxic. All are generated as vapors, however, and would be expected to disperse with adequate ventilation. Carbonyl fluoride decomposes in the presence of water. Thus, there would be few, if any, highly toxic residues (of the identified PICs) remaining after an incident. There is a potential for highly corrosive and irritating residues of hydrogen chloride and hydrogen fluoride on surfaces, but these present a low toxicity hazard.

SULFUR HEXAFLUORIDE

General

Sulfur hexafluoride (SF_6) can be used alone as a dielectric or in a mixture of gases such as perfluorocarbons. Its physical and chemical properties are listed in Table 4-2.

MONS 018803

Table 4-1

TOXICITY AND EXPOSURE LIMITS OF FREON 113 DECOMPOSITION PRODUCTS (83)

	inh-man			inh-rat		inh-mus		
	LC_{LO}	LC_{50}	TC_{LO}	LC_{LO}	LC_{50}	LD_{LO}	TLV-TWA	STEL
Freon 113				87,000 ppm/ 6 min		25 pph/ 1.5 min	1,000 ppm	1,250 ppm
Carbon Monoxide	4,000 ppm/ 30 min (man)		650 ppm/ 45 min (man)				50 ppm	400 ppm
Phosgene ($COCl_2$)		3,200 mg/m^3	25 ppm/ 30 min	50 ppm/ 30 min			0.1 ppm	
Hydrogen Chloride (Gas)	1,000 ppm/ 1 min				4,701 ppm/ 30 min		5 ppm	
Hydrogen Fluoride			110 ppm/ 1 min	50 ppm/ 30 min			3 ppm	6 ppm
Carbonyl Fluoride (COF_2)					360 ppm/ 1 hr		2 ppm	5 ppm
Tetrafluoro-methane (CF_4)				895,000 ppm/15 min				

MONS 018804

Table 4-2

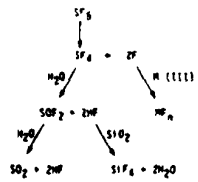
CHEMICAL AND PHYSICAL CHARACTERISTICS OF SULFUR HEXAFLUORIDE (97)

Molecular Weight	146.07
Melting Point	-50.8 °C
Boiling Point	-63.5 °C
Specific Gravity	1.79 (-39 °C) (liquid) 5.11 (20 °C) (vapor)
Vapor Pressure	21 mm Hg @ 20 °C

Thermal Decomposition of Sulfur Hexafluoride

The thermal decomposition of sulfur hexafluoride has been studied under conditions simulating arcing, arc welding, and fires (20, 35, 45, 111). A number of long-lived by-products have been identified.

The principal by-product in most tests was thionyl fluoride (SOF_2). Under sparking at 36 kJ, the typical concentration of SOF_2 deposited into the test cell following 24-hour storage was 1.2% (36). Other identified products (and their concentrations at the conditions above) include sulfuryl fluoride (SO_2F_2 - 0.15%), thionyl tetrafluoride (SOF_4 - 0.22%), silicon tetrafluoride (SiF_4 - 0.03%), and sulfur dioxide (SO_2 - 0.002%). A suggested generalized reaction sequence is (94):



This reaction sequence indicates that sulfur tetrafluoride (SF_4) and hydrogen fluoride (HF) are also decomposition by-products. Both are highly reactive, however, and were not found during analysis.

MONS 018805

Silicon tetrafluoride is not really an SF_6 decomposition by-product. Rather, it is a product of the reaction between HF (a probable decomposition by-product) and silica-containing components of the test cell (or, by inference, the transformer) such as ceramic insulators (36).

The presence of impurities influences the types and quantities of decomposition products formed (35, 111). These impurities can include production impurities in commercial grades of gases, volatilized electrode material, and volatile fractions of other equipment components (e.g., greases). It has been found that the addition of only a few percent of a hydrocarbon impurity can increase SOF_2 production by two orders of magnitude (35). In the presence of hydrocarbons, additional by-products formed can include C_2F_6, CF_4, and $Si(CH_3)_2F_2$ (111).

Finally, as will be noted below, the compounds identified above may not account for all of the toxicity noted in SF_6 decomposition gases (37). It has been suggested that there is a potentially large array of PICs at trace concentrations which have not been identified. For instance, several researchers have hypothesized the production of S_2F_{10}, although it has not been found (36, 37). However, the analyses to date have concentrated on the major PICs; sulfur dioxide at 0.002% (20 ppm) was the lowest PIC concentration.

Toxicity and Exposure Limits of Sulfur Hexafluoride Decomposition Products

Table 4-3 lists toxicity data for sulfur hexafluoride decomposition products. The major products formed during arcing (SOF_2, SO_2F_2, SiF_4, SO_2) are all more toxic than the parent compound, SF_6.

The sparking decomposition products have been found to exhibit strong cytotoxic effects on mammalian cells. The cytotoxicity of the sparking gases was tested using an in vitro cell culture system (Chinese hamster lung cells) (87). The cytotoxicities of the individual decomposition products were tested to identify the most potent cytotoxicant. There were, however, no conclusive results. The sum of the toxicities of the individual products could not account for the toxicity of the sparking gas. The toxicity of a synthetic mixture with a composition similar to that of the identified sparking decomposition products exhibited a toxicity of a lower degree than that of the sparking gas.

Thus, it is reasonable to assume that there are perhaps several as-yet-unidentified decomposition products which, although present in trace amounts, contribute

MONS 018806

Table 4-3

TOXICITY AND EXPOSURE LIMITS OF SULFUR HEXAFLUORIDE DECOMPOSITION PRODUCTS (83)

	inh-man	inh-rat		orl-rat	inh-mus		
	LC_{LO}	LC_{LO}	LC_{50}	LD_{50}	LC_{LO}	TLV-TWA	STEL
SF_6						1000 ppm	1250 ppm
SOF_2					260 ppm/ 1H	2_3^5 mg (F)/ m^3	
SO_2F_2			3020 ppm/ 1H	100 mg/kg		5 ppm	10 ppm
SiF_4						2_3^5 mg (F)/ m^3	
SO_2	1000 ppm/ 10M	1000 ppm				2 ppm	5 ppm
S_2F_{10}					1780 ppm/ 1H	25 ppb	75 ppb

MONS 018807

significantly to the cytotoxicity of the decomposition gases. One compound that has been suggested is S_2F_{10}, a highly toxic compound with a TLV in the several ppb range.

The identified decomposition products are all gases at normal ambient temperatures, and would present a problem only in the absence of proper ventilation. Hydrogen fluoride may be found on surfaces, but the amount generated does not seem to be significant. The physical state, and thus the persistence and long-term hazard, of the unidentified decomposition products are unknown.

MONS 018808

Section 5

PROPOSED PCB SUBSTITUTES: SOLIDS

INTRODUCTION

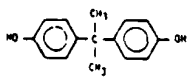
Solid dielectrics can be cast or impregnated into the coils of a transformer, used as films in capacitors, or used as insulation for various parts of transformers, capacitors, or other electrical equipment. There are several types of solid materials which have been considered, including silicone resins, epoxy resins, and a variety of polymers. The two solids to be considered within the context of this review will be epoxy resins and polyvinyl chloride (PVC).

EPOXY RESINS

General

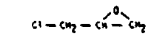
Epoxy resins are those polymers whose monomeric units are linked or cross-linked through an epoxide-hydroxyl dehydration reaction. Cured "epoxy" resins contain few epoxide moieties.

The monomeric units may be simple or complex. The most commonly used resin is based on bisphenol A.



Bisphenol A

This molecule is linked into long chains by a chlorine-containing epoxide compound, epichlorhydrin.



Epichlorhydrin

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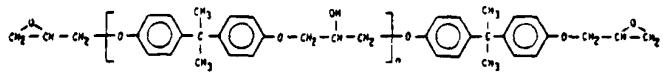
The result is a long chain polyether which terminates with epoxides.



Most commonly, this compound is then "cured" with a cycloaliphatic anhydride or amine as a "hardener" to effect cross-linking (96). The largest producer of resins for use in casting transformer coils used in the United States reports that roughly 80% of their production for transformer coils may be approximated by the above generalities. The remainder use cycloaliphatic compounds in place of bisphenol A. The principal constituent of the material used to impregnate transformer coils is *not* the resin (typically 25% of the mixture) or the hardener (up to 25% of the mixture) but the filler material, a fine siliceous material (usually SiO_2, 50% to 75% of the mixture).

Thermal Decomposition of Epoxy Resins

All epoxy links are etheric, of weaker bond energy than the adjacent carbon-carbon bonds. One might then expect to find the monomer (e.g., bisphenol A) as an initial degradation product. This is not the case. The extensive cross-linking and the presence of the filler, both specifically improve heat resistance and prevent any degradation below temperatures at which the monomers are stable. Pyrolysis of a Novolac epoxy (based on a chain of phenol-methyl moieties rather than bisphenol A) yielded no detectable monomer, but did yield significant amounts of benzene at temperatures above 500 °C (71) (Table 5-1). The major portions of the volatilized fraction of the epoxy is designated Vpyr, an otherwise unidentified material that is volatile at pyrolysis temperatures but liquid at room temperatures. The only data available for the 800 °C material is an average molecular weight of 350.

Lum and Feinstein (63, 64) studied the thermal degradation of Novolac epoxies at relatively low temperatures (0 to 500 °C). Release of significant amounts of benzene, phenol, and cresol was detected in the 300 to 500 °C range.

Table 5-1

VOLATILE PRODUCTS FROM PYROLYSIS OF EPOXY RESIN (66)*

Component†	360 °C	500 °C	800 °C	1200 °C
	(%)			
Hydrogen	--	--	0.8	2.1
CO	4.7	3.1	11.2	25.9
CO_2	16.2	6.0	3.7	1.8
Methane	1.0	0.8	1.6	4.3
Acetylene	0.3	--	--	2.5
Ethylene	--	--	3.0	3.0
Acetone	0.9	2.2	--	--
Propane	--	1.1	--	--
Propylene	6.5	2.3	2.2	--
Ethane	--	--	1.6	--
Cyclopentadienes	--	--	--	0.6
Pentanes	--	0.5	--	--
Benzene	--	1.3	2.8	8.1
Methyl Chloride	5.1	--	--	--
Ethyl Chloride	1.7	--	--	--
Others	--	0.7	--	0.8
Vpyr#	63.6	82.0	73.1	50.9
Volatilized Part of Sample, %	38	75	86	87

*Percentages are based on weight of total volatilized fraction.

†Components in amounts of less than 0.5% are not shown.

#A heavy fraction, volatile at pyrolysis temperature, but not room temperature.

MONS 018811

Oxidative degradation of a complete 800 kVA GEAFOL cast resin transformer was carried out by the Trafo-Union Corporation of the Federal Republic of Germany (5). The experiment consisted of sequentially (not simultaneously) burning a wood fire (1000 °C) under one coil of a transformer, and a propane fire (1200 °C) under the other coil. The filtered combustion gases were fed continuously to a GC/MS apparatus, which accepted a 10-microliter sample each 20 seconds for the duration of the fire. Mass spectra in the range of m/e = 12 to m/e = 650 were recorded each second. The results are shown in Table 5-2. No peaks above m/e > 92 were found. Nowhere are the carbon dioxide concentrations in the smoke reported, so there is no way to exactly convert the peak intensities to absolute concentrations. A further problem with these tests was the failure to separate the wood and propane combustion gases from the resin combustion gases. Consequently, it is impossible to say with certainty which of the product gases are attributable to the epoxy resin.

Table 5-2

PICs FOUND IN FIRE GASES
FROM TWO CAST RESIN TRANSFORMER FIRES (5)

PIC	Wood Fire	Propane Fire
Acetylene	3.6 ppm	3.4 ppm
Aromatic Fragment	0.4 ppm	0.4 ppm
Benzol	1.2 ppm	1.2 ppm
Toluene	1.6 ppm	1.2 ppm

As part of this same series of tests, a sample of resin was burned at 600 °C, and the product gases were analyzed for 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran. Neither was detected down to 50 ppb. No other dioxin or dibenzofuran was analyzed for.

Toxicity and Exposure Limits of Epoxy Resin Decomposition Products

Table 5-3 presents toxicity data for most of the decomposition by-products mentioned above. Few are highly toxic. Several of the by-products, however, are known or suspected carcinogens. These compounds are generally solids or liquids

MONS 018812

Table 5-3

TOXICITY AND EXPOSURE LIMITS OF EPOXY DECOMPOSITION BY-PRODUCTS (83)

	TC_{LO} (inh-man)	LD_{LO} (orl-man)	LC_{LO} (inh-rat)	LC_{50} (inh-rat)	LD_{50} (orl-rat)	LC_{50} (inh-mus)	LC_{50} (inh-mam)	TLV-TWA
Acetone	500 ppm		16,000 ppm/4H					
Acetylene							500,000 ppm/5M	
Benzene	100 ppm			10,000 ppm/7H				
Cresol								5 ppm (skin)
m-cresol					242 mg/kg			
o-cresol					121 mg/kg			
p-cresol					207 mg/kg			
Cyclopenta-diene, 1,3-								75 ppm
Ethylene						95 pph		
Phenol		140 mg/kg		316 mg/m^3				5 ppm

MONS 018813

at normal ambient temperatures, and are a risk via dermal exposure as well as oral or inhalation.

The toxicity of the unidentified Vpyr fraction has not been assessed. Finally, few of the tests conducted to date have been concerned with identifying by-products at trace levels.

POLYVINYL CHLORIDE (PVC)

General

PVC is a synthetic thermoplastic polymer.



It is generally resistant to weathering and moisture, and to most acids, fats, petroleum hydrocarbons, and fungus. It is dimensionally stable with good dielectric properties. The first important use for plasticized PVC was as electrical cable insulation sheathing. The electrical industry is still a major consumer of PVC, with most being used as flexible cable insulation or rigid electrical conduit.

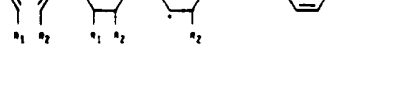
PVC resins are always compounded with a variety of additives. Stabilizers are added to act as scavengers for free radicals produced by heat or light. Metallic salts, oxides, and salts of fatty acids are common stabilizers. Fillers such as calcium or magnesium carbonate can be added to retard the catalytic chain dehydrochlorination effect of released hydrogen chloride. Plasticizers may be added to impart or improve flexibility. Plasticizers may be up to 30% by weight of the compounded plastic. Typical plasticizers include phosphates, dioctylphthalate, and low-molecular-weight propylene glycol polymers. To increase flexibility, vinyl chloride may be copolymerized with vinyl acetate. The vinyl acetate can constitute 3 to 15% of the copolymer. There is no single compound formula used ubiquitously in the electrical industry.

Thermal Decomposition Products of PVC

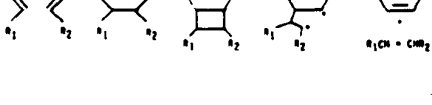
Data on the thermal degradation of PVC are fairly extensive. The major problem with using the data is the variety of PVC formulations available. A given test sample may be stabilized or unstabilized. There are several different stabilizers available. Other additives (plasticizers, fillers, dyes, etc.) can vary in composition as well. The extent to which these additives affect the thermal degradation of the polymer and the extent to which the additives themselves contribute to the final by-product mix are unresolved. Furthermore, most of the published research is not highly specific regarding the formulation or composition of the PVC being tested. Consequently, there is some question regarding the applicability of a particular test result to other PVCs. As a result, the following discussion must be taken as being only generally indicative and not necessarily specific for any particular PVC formulation.

In the absence of oxygen, PVC pyrolyzes by dehydrochlorination (loss of HCl), followed by cyclization of polyene (19, 39, 76). The reaction proceeds via 1,4-elimination of chlorine from cis double bonds, generally from groups at or near chain ends. The principal products formed are benzene and hydrogen chloride (19).

Benzene is believed to form probably by one of the two following mechanisms (76):



(5-1)



(5-2)

MONS 018815

The presence of HCl may catalyze the thermal degradation, but this has been disputed (19, 76).

Benzene is not the only decomposition product. Table 5-4 lists the decomposition yields of several more aromatic compounds at various temperatures from 300 to 800 °C. In addition to these compounds, aliphatic hydrocarbons, β-methylnaphthalene, monochlorobenzene, o-dichlorobenzene, p-dichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,4-trichlorobenzene were also identified in the pyrolysis gases (19).

Table 5-4

DECOMPOSITION YIELDS* OF SOME AROMATICS OBTAINED BY THE PYROLYSIS† OF PVC (GEON-103 EP) AT VARIOUS TEMPERATURES (19)

	Yield, wt %					
Product	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
Benzene	3.50	4.67	5.00	5.23	6.30	9.9%
Toluene	--	0.21	0.67	0.82	1.55	2.10
Ethylbenzene	--	--	0.16	0.18	0.18	0.23
o-Xylene	--	--	0.16	0.18	0.23	0.25
Styrene	--	0.13	0.22	0.37	0.74	1.06
Naphthalene	--	0.47	0.52	0.73	1.50	3.00

*Calculated using gas chromatography with p-dichlorobenzene as an internal standard.

†Samples (powder), 1-3 mg, were pyrolyzed in helium gas; flow rate of helium being 25 ml/min.

Ahling et al. (3) combusted PVC over the range of 570 to 1130 °C. They found from di- to hexachlorinated benzenes, octachlorostyrene, and PCBs. During the combustion experiments, PVC was mixed with wood chips to help sustain combustion.

The combustion of PVC can also yield carbonyl chloride (phosgene) (13). Yields are on the order of 0.06 to 0.15 mg/g (or a concentration of 0.5 to 1.3 ppm from 4 to 7 g decomposed in a 200-l animal exposure chamber). Subjecting the PVC to an electric arc can increase yields of phosgene 10 to 20 times.

MONS 018816

Because of the production of chlorinated benzenes, the formation of PCDDs and PCDFs is a distinct possibility (see Section 3, Chlorobenzenes) (19). The presence of other chlorinated polycyclic aromatics, such as chlorinated naphthalenes, is also feasible. To date, none of these have been identified in PVC pyrolysis gases, but PVC is suspected to be one of the potential sources of the PCDDs and PCDFs found in fly ash and flue gases from municipal and industrial incinerators (19).

Toxicity and Exposure Limits of PVC Thermal Degradation Products

Table 5-5 lists the toxicities for the identified PVC degradation products. Speculative by-products, such as PCDDs, PCDFs, PCNs, etc., are not included, although the circumstantial evidence for their production is good. Their toxicities are discussed elsewhere in this review.

The identified PVC by-products are of variable toxicity, but generally fall into the moderate to high toxicity range. In addition, several are known or suspected carcinogens. Most of these compounds are solids or liquids at normal ambient temperatures, and could be found in soot or on surfaces after a fire. Phosgene, a gas, is the notable exception.

MONS 018817

Table 5-5

TOXICITIES AND EXPOSURE LIMITS OF PVC THERMAL DEGRADATION BY-PRODUCTS (83)

	LC_{50} (inh-hum)	TC_{LO} (inh-hum)	TD_{LO} (orl-hum)	LC_{LO} (inh-rat)	LC_{50} (inh-rat)	LD_{50} (orl-rat)	LD_{LO} (orl-rat)	TLV-TWA
Phosgene	3200 mg/m^3	25 ppm/ 30M		50 ppm/ 30M				100 ppb
Benzene		100 ppm			10,000 ppm/7H			10 ppm
Toluene		200 ppm		4000 ppm/ 4H				100 ppm
Ethylbenzene		100 ppm/ 8H		4000 ppm/ 4H				100 ppm
o-Xylene				6125 ppm/ 12H				
Styrene		600 ppm		5000 ppm/ 8H				50 ppm
Naphthalene						1780 mg/kg		10 ppm
Methylnaphthalene							5000 mg/kg	
Monochlorobenzene						2910 mg/kg		75 ppm
o-Dichlorobenzene				821 ppm/ 7H		500 mg/kg		
p-Dichlorobenzene			300 mg/kg			500 mg/kg		75 ppm
1,2,4-Trichloro-benzene						756 mg/kg		

MONS 018818

Section 6

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MONS 018827

Appendix A

GLOSSARY AND ABBREVIATIONS

Gpg	Guinea pig
Hum	Human
Inl	Inhalation
LC_{LO}	Lethal concentration low
LC_{50}	Lethal concentration fifty
LD_{LO}	Lethal dose low
LD_{50}	Lethal dose fifty
Lethal Concentration Fifty	A calculated concentration of a substance in air, exposure to which for a specified time (H - hours, M - minutes) is expected to cause the death of 50% of a defined animal population
Lethal Concentration Low	The lowest concentration of a substance in air which has been reported to have caused death in humans or animals
Lethal Dose Fifty	A calculated dose of a substance which is expected to cause the death of 50% of a defined animal population
Lethal Dose Low	The lowest dose of a substance reported to have caused death in humans or animals
Mus	Mouse
Orl	Oral
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PCN	Polychlorinated naphthalenes
PIC	Product of incomplete combustion
pph	Parts per hundred
ppm	Parts per million
STEL	Short-term exposure limit; maximum allowable exposure concentrations for 15-minute exposure

MONS 018828

TCDD	Tetrachlorodibenzo-p-dioxin
TCDF	Tetrachlorodibenzofuran
TC_{LO}	Toxic concentration low
TD_{LO}	Toxic dose low
TD_{50}	Toxic dose fifty
Threshold Limit Value	The ACGIH-recommended concentration of a substance to which most workers can be exposed without adverse affect; may be expressed as time-weighted average (TWA), short-term exposure limit (STEL), or ceiling value (CL)
TLV	Threshold limit value
Toxic Concentration Low	The lowest concentration of a substance in air to which humans or animals have been exposed for any given period of time that has produced any toxic effect
Toxic Dose Fifty	A calculated dose of a substance reported to cause toxic effects in 50% of a defined population
Toxic Dose Low	The lowest dose of a substance reported to produce any toxic effect in humans or animals
TWA	Time-weighted average; average allowable exposure over an 8-hour workday or 40-hour work week

Appendix B

GENERIC AND TRADE NAMES

Benzylneocaprate	FARADOL 100 (Asea)
Butylated monochlorodiphenylether	DIELECTRIC FLUID C-4 (Dow), XFS-4169L (Dow)
DC 200 (Dow)	Polydimethylsiloxane
DC 561 (Dow)	Polydimethylsiloxane
Di-2-ethylhexyl phthalate	Component of DIELECTROL II (General Electric) and SELECTROL I (Sangamo)
DIELECTRIC FLUID C-4 (Dow)	Butylated monochlorodiphenylether
DIELECTROL II (General Electric)	Di-2-ethylhexyl phthalate
DIELECTROL III (General Electric)	Dixylylethane
Dixylylethane	DIELECTROL III (General Electric), SELECTROL II (Sangamo), SAS 295 Nisseki), SAS 296 (Nisseki)
EDISOL II (McGraw Edison)	Mixture of methylated diphenylethane and propyldiphenyl
Epoxy	GEAFOL (Trafo-Union)
F 101 (SWS Silicone)	Polydimethylsiloxane
F 190 (SWS Silicone)	Polydimethylsiloxane
FARADOL 100 (Asea)	Benzylneocaprate
FORMEL NF (ISC Chemicals)	Mixture of perchloroethylene and freons
Freon	Component of FORMEL NF (ISC Chemicals)
GEAFOL (Trafo-Union)	Epoxy
Isopropylbiphenyl	WEMCOL (Westinghouse)
L 305 (Union Carbide)	Polydimethylsiloxane
Methylated diphenylethane	Component of EDISOL II (McGraw Edison)
PAO 13CE (Uniroyal)	Poly 1-octene

MONS 018830

Appendix B (continued)

Perchloroethylene	WECOSOL (Westinghouse), component of FORMEL NF (ISC Chemicals)
Poly 1-octene	PAO 13CE (Uniroyal), PR (Gulf Oil)
Polydimethylsiloxane	DC 200 and DC 561 (Dow Corning), F 101 and F 190 (SWS Silicone), L 305 (Union Carbide), SF 97 (General Electric)
PR (Gulf Oil)	Poly 1-octene
Propylbiphenyl	Component of EDISOL II (McGraw Edison)
SAS 295 (Nisseki)	Dixylylethane
SAS 296 (Nisseki)	Dixylylethane
SELECTROL I (Sangamo)	Mixture of di-2-ethylhexyl phthalate and trichlorobenzene
SELECTROL II (Sangamo)	Dixylylethane
SF 97 (General Electric)	Polydimethylsiloxane
Trichlorobenzene	Component of DIELECTROL II (General Electric), SELECTROL I (Sangamo)
WECOSOL (Westinghouse)	Perchloroethylene
WEMCOL (Westinghouse)	Isopropylbiphenyl
XFS-4169L (Dow)	Butylated monochlorodiphenylether

MONS 018831