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POTENTIAL SOURCES OF POLYCHLORINATED DIBENZOTHIOPHENES IN THE PASSAIC RIVER, NEW JERSEY

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ABSTRACT

Recent studies suggested that the presence of elevated levels of 2,4,6,8-tetrachlorodibenzothiophene (2,4,6,8-TCDT) in sediments collected from the lower Passaic River in Newark, New Jersey is due to operations at a former 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) manufacturing facility. This paper reviews the scientific literature to determine if 2,4,6,8-TCDT is commonly found in the aquatic environment and evaluates whether 2,4,6,8-TCDT is associated with the production of 2,4,5-T. Polychlorinated dibenzothiophenes (PCDTs) are generated by chemical processes that are similar to those that result in the formation of polychlorinated dibenzofurans (PCDFs). PCDTs have been found in pulp and paper mill effluents and waste incineration fly ash, and are associated with metal reclamation processes and incineration of PCBs (Peterman et al., 1986; Buser et al., 1991; Rappe, 1992; Sinkkonen et al., 1991, 1992a,b, 1993). Chemical processes similar to those that have resulted in the formation of PCDFs, such as dye, pigment, paint, pesticide, and raw chemical production, are likely significant sources of PCDTs if sulfur-containing organic chemicals are used in the manufacturing process. It has been estimated that there are over 300 PCDD and PCDF sources within the Newark Bay estuary, many of which are likely to have discharged PCDT-containing effluents to the Passaic River (Paustenbach, 1993). Chlorinated thiophenols and other sulfur-containing compounds such as sulfonated benzenes, chlorinated in the 2, 4, and 6 positions, and 2,3,5,2′,3′,5′-hexachlorobiphenyl, present in commercial PCB mixtures (Ballschmitter and Zell, 1980), have precisely the correct configuration of chlorine substitution for 2,4,6,8-TCDT formation. Elevated levels of both 2,4,6,8-TCDT (Pruell et al., 1993) and PCBs (Wenning et al., 1992c) in lower Passaic River sediments suggest that PCDT contamination of these sediments may be related to several sources, most notably, a known PCB contaminated site approximately one mile downstream of the former 2,4,5-T facility. The scientific literature provided no evidence to support the assertion that the presence of 2,4,6,8-TCDT in the environment was related to 2,4,5-T production. The reported presence of 2,4,6,8-TCDT in Passaic River sediments cannot be explained by production practices at the former 2,4,5-T facility.

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INTRODUCTION

Polychlorinated dibenzothiophenes (PCDTs) are sulfur-containing structural analogs of the polychlorinated dibenzofurans (PCDFs) (Buser and Rappe, 1991) (Fig 1). PCDTs are found as mixtures of any number of 135 possible isomers ranging from the mono- to the octachlorinated compounds. Thirty-eight of these are tetrachlorinated dibenzothiophenes (TCDTs). The recent development of high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques for the semi-quantitative analysis of PCDTs (Buser and Rappe, 1991) has stimulated much interest regarding the environmental levels and sources of these compounds, principally because of their structural similarity to PCDDs and PCDFs.

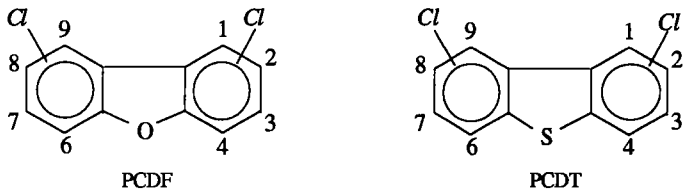


Fig. 1. Polychlorinated dibenzofuran (PCDF) and polychlorinated dibenzothiophene (PCDT) chemical structures (adapted from EPA, 1986)

Several studies have identified PCDTs in pulp and paper mill effluent and various incineration processes (Buser et al., 1991; Sinkkonen et al., 1992a,b). Pulp and paper mills and municipal solid waste incineration are also known sources of PCDFs and polychlorinated dibenzo-p-dioxins (PCDDs) (Rappe et al., 1979; EPA, 1987). Although PCDFs and PCDDs have been studied extensively in water (Meyer et al., 1989; Rappe et al., 1989), soil (Rappe and Kjeller, 1987; Rappe, 1987,1992), air (Smith et al., 1989), sediment (Smith et al., 1990; Rappe, 1992), wildlife (Smith et al., 1990; Rappe et al., 1991), and human tissue (Patterson, 1987), PCDTs have only recently been identified in various environmental media (Cooper, 1993; Pruell et al., 1993).

Interestingly, several recent studies on the lower Passaic River, New Jersey and elsewhere in the Newark Bay estuary have shown that 2,4,6,8-tetrachlorinated dibenzothiophene (2,4,6,8-TCDT) is present in surface sediments (Pruell et al., 1993) and aquatic organisms (Cooper, 1993) at levels that exceed the concentrations of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). For example, Pruell et al. (1993) reported that the mean concentrations of 2,3,7,8-TCDD (656 ng/kg) and 2,3,7,8-TCDF (334 ng/kg) in Passaic River sediments were substantially lower than the concentrations of 2,4,6,8-TCDT (3,680 ng/kg). A similar trend was recently reported in the hepatopancreas of male blue crabs collected from Newark Bay, Raritan Bay, and the Arthur Kill (Cooper, 1993). The levels of total TCDD, TCDF, and TCDT congeners in male blue crabs are shown in Table 1.

Table 1. Concentrations (ng/kg) of total tetrachlorinated dibenzo-p-dioxins (TCDD), tetrachlorinated dibenzofurans (TCDF), and tetrachlorinated dibenzothiophenes (TCDT) in blue crabs collected from Raritan Bay and Newark Bay

Station	Total TCDD	Total TCDF	Total TCDT
Sandy Hook	50	100	300
Raritan Bay	90	150	490
Wards Point	210	220	1,500
Newark Bay	940	200	14,800

Source: Copper (1993)

Cooper et al. (1993) reported concentrations ranging from 50 to 940 ng/kg for total TCDDs and 490 to 14,800 ng/kg for total TCDTs. Although little is known about the toxicological significance of PCDTs in the environment, recently reported data suggest that the potency of TCDTs to induce aryl hydrocarbon hydroxylase (AHH) is approximately 1/400th that of 2,3,7,8-TCDD (Kopponen et al., 1993). AHH induction has been used as a measure of toxic potency (Safe, 1990). This implies that, in general, a PCDT isomer would need to be present at concentrations 400-fold higher than its corresponding PCDD isomer to elicit a similar toxic response.

While these data suggest that 2,4,6,8-TCDT and possibly other structural analogs may be present in Passaic River sediments and aquatic organisms at higher concentrations than PCDDs and PCDFs, the chemical analyses conducted to date do not provide reliable measures of 2,4,6,8-TCDT concentration. Analyses reported in the literature to date are generally based on the assumption that the mass spectrometer response to 2,4,6,8-TCDT is the same as the response to 2,3,7,8-TCDD. A purified reference standard for 2,4,6,8-TCDT has not generally been used to confirm the results obtained by comparison to the HRGC/HRMS response for 2,3,7,8-TCDD. In addition, it was recently reported that 2,4,6,8-TCDT coelutes with 1,2,8,9-TCDD on the SP-2331 gas chromatography (GC) column (Buser et al., 1991), commonly used for PCDD/PCDF analyses during the 1980s. The coelution of these two compounds occurs only on the SP-2331 column (Buser et al., 1991). By the late 1980s most researchers had replaced this column with the DB-5 column. There is no coelution of 2,4,6,8-TCDT and 1,2,8,9-TCDD on the DB-5 column under the GC operating conditions commonly used for PCDD/PCDF analyses.

Following reports that 1,2,8,9-TCDD was possibly related to a former 2,4,5-T manufacturer on the lower Passaic River (Rappe et al., 1991), Wenning et al. (1992a) reviewed potential sources of 1,2,8,9-TCDD in the aquatic environment. The 1,2,8,9-TCDD isomer has been reported in fly ash and chimney soot, and is a product of PCB and chlorophenol combustion (Wenning et al., 1991). Because of the coelution problem with the SP-2331 column, it is likely that 2,4,6,8-TCDT could have been misidentified as 1,2,8,9-TCDD in work conducted prior to 1990.

Because PCDTs and PCDFs are structurally similar (Sinkkonen et al., 1992a,b), the identification of PCDF sources in the Newark Bay estuary provides the rationale for examining the levels of PCDTs associated with these sources. Numerous sources of PCDFs have been described in the literature including municipal waste incinerators, soot from residential wood burning, and combustion of PCBs and chlorinated benzenes (Wenning et al., 1992a). Of these various PCDF sources, thermal reaction of PCBs and various incineration activities have also been closely associated with the formation of PCDTs (Buser et al., 1991; Buser and Rappe, 1991; Sinkkonen et al., 1991). As such, PCB/sulfur formulations used to impart moisture resistance, flame resistance, insulating, lubricating, and adhesion properties to cloth, paper, and wood (Monsanto Chemical Company, 1971) warrants investigation as potential sources of PCDTs. The use of commercial PCBs in paint formulations (Monsanto Chemical Company, 1971), together with the proximity of paint manufacturers to the former 2,4,5-T facility, also warrants investigation as possible PCDT sources.

The widespread industrialization of the Newark Bay watershed suggests that numerous other PCDT sources may be present. Paustenbach (1993) estimated that over 300 industrial sources may have contributed to the current levels of PCDD/PCDFs in the Passaic River and Newark Bay. Although it has been proposed that 2,4,6,8-TCDT may be a unique chemical marker for discharges from a former 2,4,5-T manufacturing facility (Rappe et al., 1991), the synthesis of 2,4,5-T does not utilize sulfur-containing chemicals (Rappe et al., 1978; EPA, 1980). In this study, we describe the results of a review of the scientific literature to (1) evaluate whether 2,4,6,8-TCDT and other PCDTs could plausibly be generated during the production of 2,4,5-T and (2) determine the extent to which PCDTs,

particularly 2,4,6,8-TCDT, are associated with industrial activities that have historically predominated throughout the Newark Bay estuary.

FORMATION OF POLYCHLORINATED DIBENZOTHIOPHENES

Sinkkonen and Koistinen (1990) reported the formation of five different TCDT isomers by the thermal reaction of 4,5,3′,4′-tetrachlorobiphenyl with 4,5,2′,3′-tetrachlorobiphenyl in the presence of a metal catalyst and elemental sulfur (Sinkkonen and Koistinen, 1990) (Fig. 2). Using a similar approach, but at much higher temperatures (540°C), Buser and Rappe (1991) synthesized several TCDTs by thermal reaction of hexachlorinated biphenyls. The major products along with their respective PCB reactants are shown in Table 2. Comparison of the chlorine substitution patterns of the reactants with that of the products indicates that TCDTs are formed through the loss of ortho-substituted chlorine atoms (Buser and Rappe, 1991).

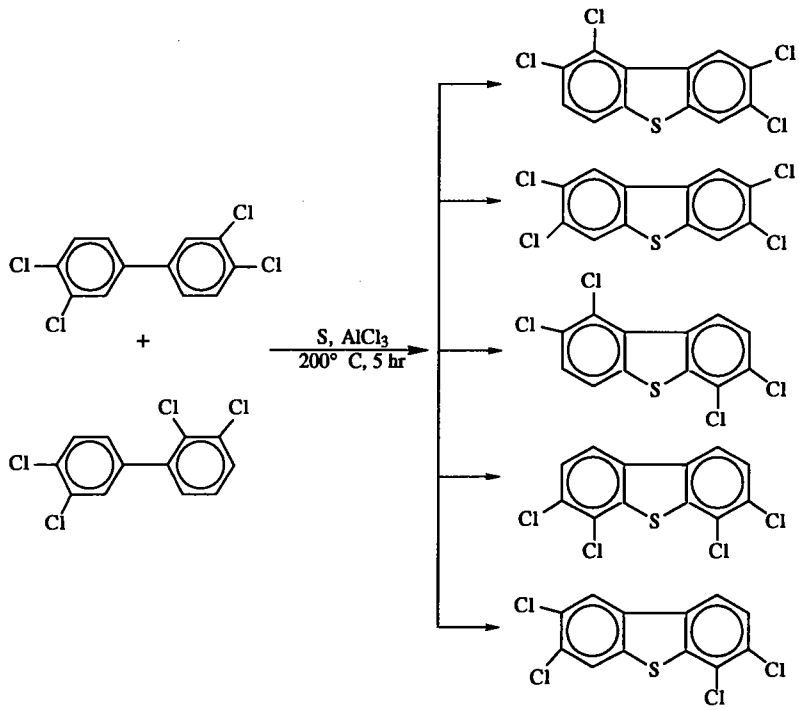


Fig 2. Formation of TCDTs via thermal reaction of 4,5,3',4',-tetrachlorobiphenyl and 4,5,2',3'-tetrachlorobiphenyl with sulfur (adapted from Sinkkonen and Koistinen (1990))

Complex mixtures of PCDTs also have been synthesized by the direct chlorination of dibenzothiophene (Buser and Rappe, 1991). Little is known, however, about the formation of PCDTs under other conditions such as the commercial production of sulfur-containing chemicals whose mechanism of formation, because of structural similarities, may be analogous to the formation of PCDFs. PCDT isomers known to be formed under various conditions are summarized in Table 3.

Research conducted to date suggests that PCDTs may be formed by mechanisms similar to those that result in the formation of PCDFs and PCDDs (Buser, 1992; Sinkkonen et al., 1992a,b). It has been postulated that four criteria

Table 2. Tetrachlorinated dibenzothiophenes (TCDTs) formed by the thermal reaction of hexachlorobiphenyls (HxCB) in the presence of elemental sulfur

HxCB Reacted	Major TCDT Product
2,4,5,2',4',5'-	2,3,7,8-
2,3,5,2',3',5'-	2,4,6,8-
2,3,4,2,'3',4'-	3,4,6,7-
2,4,6,2',4',6'-	1,3,7,9-
2,4,5,2',4',6'-	1,3,7,8-
2,3,4,2',4',5'-	2,3,6,7-
2,3,6,2',3',6'-	1,4,6,9- 1,2,6,9- 1,2,8,9-
2,3,4,5,2',5'-	2,3,4,8-
2,3,5,6,2',5'-	1,2,4,8-

Source: Buser and Rappe (1991)

are ideal for the formation of PCDDs and PCDFs: alkaline conditions, temperatures exceeding 200°C, an oxygen substituted aromatic precursor, and a source of chlorine (EPA, 1980). At sufficiently high temperatures, such as those found in municipal waste incineration, a sufficient source of organic carbon, oxygen, and chlorine may be the only requirements necessary for PCDD/PCDF formation. In non-combustion processes, such as chemical production, the presence of ortho chlorine-substituted phenolics, and to a lessor extent the presence of para-chlorine substituted phenolics, greatly enhances the rate of PCDD/PCDF formation (EPA, 1980).

The structural similarity of PCDTs and PCDFs is the basis for hypothesizing a similar mechanism of formation. Although little data exist on the formation of PCDTs, comparisons of the characteristics of sulfur and oxygen, the benzene carbon-sulfur bond (C_b-S) and carbon-oxygen bond (C_b-O), and of the structures of thiophene and furan suggest a common chemical behavior. Both sulfur and oxygen are Group VI elements and have two outer shell electrons available for covalent bonding (Weaste et al., 1989). In the case of both furan and thiophene, as well as dibenzofuran and dibenzothiophene, the oxygen or sulfur is the center-piece of a 5-member ring where the oxygen or sulfur forms bonds with carbons on either side (Fig. 1). A comparison of the bond dissociation energies (ΔH) for the C_b-S and C_b-O bonds (Cox and Pilcher, 1970), indicate that less energy is required to break the C_b-S bond, and that less energy would be released as a result of C_b-S bond formation as compared to the C_b-O bond.

Table 3. Relative abundance of tetrachlorinated dibenzothiophene (TCDT) isomers in various source categories[a]

HCB/S	%	1254/S	%	DT/Cl	%	MSWI	%	OSI	%	PPM	%
2,3,6,7-	16	2,3,6,7-	40	1,2,6,9-	34	2,3,6,7-	68	2,3,6,7-	71	2,3,7,8-	56
3,4,5,7-	15	1,2,6,9-	26	2,3,7,8-	27	2,3,7,8-	19	2,3,7,8-	29	3,4,6,7-	28
1,2,6,9-	14	2,3,7,8-	19	1,2,8,9-	24	2,4,6,8-	13			UI	16
1,3,7,8-	13	3,4,6,7-	9	2,4,6,8-	13						
2,4,6,8-	12	1,3,7,8-	5	2,3,6,7-	2						
2,3,7,8-	10	2,4,6,8-	1								
1,4,6,9-	8	1,2,8,9-	1								
1,3,7,9-	7										
1,2,8,9-	4										

a. Isomers are ranked according to their relative abundance. HCB/S, thermal reaction of hexachlorobiphenyl with sulfur (Buser et al., 1991); 1254/S, thermal reaction of Aroclor 1254 with sulfur (Buser et al., 1991); DT/Cl,direct chlorination of dibenzothiophene (Buser et al., 1991); MSWI, municipal solid waste incinerator fly ash (Buser and Rappe, 1991); OSI, fly ash from other Swiss incinerators (Buser and Rappe, 1991); PPM, pulp and paper mill effluent; UI, unknown isomer (Sinkkonen et al., 1992b).

The presence of sulfur in the thiophene ring is structurally analogous to the presence of oxygen in the furan ring. As demonstrated by a comparison of bond dissociation constants, the thiophene C-S bond is a weaker bond than the

furan C-O bond. Therefore, the formation of thiophenes, dibenzothiophenes, and PCDTs could occur under less stringent conditions than for furans, dibenzofurans, and PCDFs.

If PCDFs and PCDTs are formed via similar mechanisms, then the existing knowledge of PCDF formation can be used to propose various mechanisms of PCDT formation. For example, the presence of a thiol group and a chlorine in the ortho positions of biphenyl provide ideal conditions for dibenzothiophene formation by nucleophilic substitution of sulfur for chlorine. Following this mechanism, 2,4,6,8-TCDT would be formed by alkaline reaction of 2,3,5-trichloro-2′-thiol-3′,5′-dichlorobiphenyl (Fig. 3). A similar mechanism was proposed for the formation of 2,4,6,8-TCDF (EPA, 1986). Buser and Rappe (1991) have shown that the thermal reaction of 2,3,5,2′,3′,5′-hexachlorobiphenyl in the presence of sulfur yields predominately the 2,4,6,8-TCDT isomer (Fig. 4). This PCB isomer is present in commercial PCB mixtures (Ballschmiter and Zell, 1980).

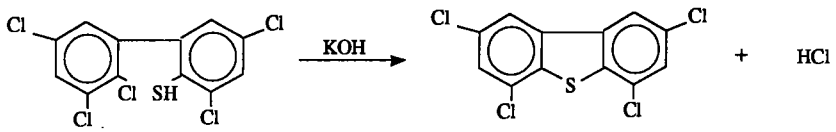


Fig 3. Formation of 2,4,6,8-TCDT by alkaline reaction of 2,3,5-trichloro-2'-thiol-3',5'-dichlorolobiphenyl (adapted from EPA, 1986)

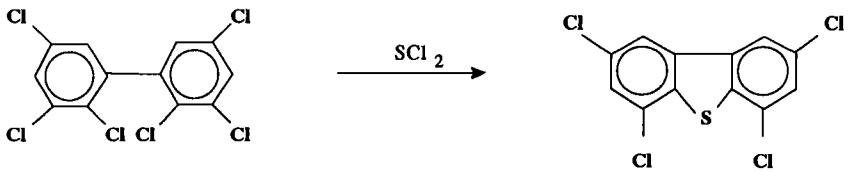


Fig. 4. Formation of 2,4,6,8-TCDT from reaction of 2,3,5,2',3',5'-hexachlorobiphenyl in the presence of sulfur (Buser and Rappe, 1991)

KNOWN SOURCES OF POLYCHLORINATED DIBENZOTHIOPHENES

Known and potential sources of TCDTs are presented in Table 4. The potential chemical process-related and combustion/incineration sources are nearly identical to those that result in the formation of PCDFs, and to some extent PCDDs, and include the chlorine bleaching of wood pulp and the production of pesticides and other chemicals using chlorinated thiophenols as reactants, particularly those with chlorine substitution ortho to the thiol group. A chlorinated thiol or sulfonated benzene with chlorine substituted in the 2, 4, and 6 positions, would provide the ideal symmetry for 2,4,6,8-TCDT formation. The 2,4,6,8-TCDT isomer has specifically been measured following thermal reactions involving PCBs and sulfur (Buser and Rappe, 1991), the direct chlorination of dibenzothiophene, and the incineration of municipal solid wastes (MSW) (Buser and Rappe, 1991; Buser et al., 1991).

Incineration

A major source of 2,4,6,8-TCDT, as well as other TCDTs and PCDTs, in the environment is emissions from MSW and industrial incinerators. For example, Rappe (1992) recently reported the presence of PCDTs in emissions from

iron and steel sintering plants and foundries at approximately the same concentrations as PCDFs (Rappe, 1992). Sinkkonen et al. (1991, 1992b) reportedly found several tetra- and penta-chlorinated dibenzothiophenes in both vapor and particulate stack samples. Neither of these studies provided quantitative estimates of concentration. Soil samples collected from a waste fire pit used to incinerate electrical capacitors containing PCBs (Aroclors® 1242 and 1254) were found to contain 67,000 ng/kg PCDT (Peterman et al., 1986).

Table 4. Known and potential sources of 2,4,6,8-TCDT and other polychlorinated dibenzothiophenes

KNOWN SOURCES
Combustion Sources
Waste incineration
PCB incineration
Miscellaneous Processes
Bleached pulp production
Metal Reclamation
POTENTIAL SOURCES
Combustion Sources
Automobile exhaust
Wood combustion
Oil/gas heating
Chemical Production
PCBs
Trichlorobenzene sulfonates
Miscellaneous Processes
Sewage sludge

Buser et al. (1991) found penta- and tetra-chlorinated dibenzothiophenes in four fly ash samples at concentrations ranging from non-detectable to 30,000 ng/kg; generally, the concentrations of PCDDs and PCDFs were substantially higher in these samples as compared to the concentrations of PCDTs. Interestingly, PCDTs were not detected in the fly ash sample containing the highest concentrations of PCDDs/PCDFs nor the incinerator ash sample with the highest sulfur dioxide concentrations. Moreover, the fly ash with the highest PCDT concentrations was taken from the stack with the lowest temperature and lowest sulfur dioxide concentrations (Buser et al., 1991). In comparison, the concentrations of PCDDs, PCDFs, and PCDTs were relatively low in fly ash from a car shredding facility that used an electric arc furnace with graphite electrodes (Buser et al., 1991). The three most prominent TCDT isomers found in municipal solid waste incineration fly ash are 2,3,6,7-TCDT, 2,3,7,8-TCDT, and 2,4,6,8-TCDT (Table 3). The Buser et al. (1991) study supports the position that chlorinated dibenzothiophene formation requires less severe thermal conditions than is required for PCDF formation. It also suggests that sulfur content may not be a rate limiting factor in the formation of PCDTs.

Pulp and Paper Mill Effluent

Tetrachlorinated dibenzothiophenes have been reported in effluents from pulp and paper mills. Recently, Sinkkonen et al. (1992b) identified two TCDT isomers in Finnish bleached pulp mill effluents, namely 2,3,7,8-TCDT and 3,4,6,7-TCDT as well as an unidentified TCDT isomer. The 2,3,7,8-TCDT isomer was found at the highest concentration, which is analogous to the 2,3,7,8-TCDF isomer that predominates in pulp mill effluents (Sinkkonen et al., 1992b). In an earlier study, however, Sinkkonen and Koistenen (1990) did not detect PCDTs in pulp and paper mill effluent apparently because of a higher detection limit of 500 ng/kg (Sinkkonen and Koistinen, 1990). The 2,4,6,8-TCDT isomer has also been found in the tissue of crabs collected downstream of a Swedish pulp and paper mill (Buser and Rappe, 1991). This suggests that the unidentified TCDT isomer reported by Sinkkonen et al. (1992b) in pulp and paper mill effluents may be the 2,4,6,8-TCDT isomer.

Metal Reclamation

Sinkkonen et al. (1993) recently reported the presence of tetra- and penta-chlorinated dibenzothiophenes in several samples obtained from several high temperature metal reclamation processes. Although the concentrations were in the μg/kg range, specific isomers could not be identified due to the reduced HRGC/HRMS resolution resulting from the simultaneous monitoring of the M^+ and $(M+2)^+$ ions for PCDDs, polychlorinated dibenzothianthrenes, and

polychlorinated diphenyl sulfides. The authors reported that total TeCDTs were found at considerably higher concentrations than PeCDTs.

ENVIRONMENTAL LEVELS OF POLYCHLORINATED DIBENZOTHIOPHENES

The discovery of PCDTs in environmental media is only recent; consequently, research in this area is in its infancy and few environmental data are available. Reported levels of PCDTs found in the environment are presented in Table 5. Only one study has reported on the presence of PCDTs in sediments. Pruell et al. (1993) reported a geometric mean concentration of 3,680 ng/kg (s.d., 1,380) 2,4,6,8-TCDT for six surface sediment samples collected from the lower Passaic River near Newark, New Jersey. The sediments in this reach of the river contain extremely high concentrations of PAHs and petroleum hydrocarbons (Huntley et al., 1993) as well as heavy metals and PCBs (Bonnevie et al., 1993; Wenning et al., 1992c).

Table 5. Environmental levels of PCDTs reported in sediment and shellfish

Location	Environmental Media	Isomer Identified	Concentration[a] (ng/kg)	Reference
Newark Bay Estuary, USA				
Elizabeth	Crabs	TrCDT	140	Buser and Rappe, 1991
Elizabeth	Crabs	2,4,6,8-TCDT	8,300	Buser and Rappe, 1991
Elizabeth	Crabs	Unidentified-TCDT	500	Buser and Rappe, 1991
Elizabeth	Crabs	Unidentified-PeCDT (1)	1,300	Buser and Rappe, 1991
Elizabeth	Crabs	Unidentified-PeCDT (2)	240	Buser and Rappe, 1991
Elizabeth	Lobsters	TrCDT	ND	Buser and Rappe, 1991
Elizabeth	Lobsters	2,4,6,8-TCDT	1,000	Buser and Rappe, 1991
Elizabeth	Lobsters	Unidentified-TCDT	NR	Buser and Rappe, 1991
Elizabeth	Lobsters	Unidentified-PeCDT (1)	60	Buser and Rappe, 1991
Elizabeth	Lobsters	Unidentified-PeCDT (2)	25	Buser and Rappe, 1991
Newark Bay	Crab	Total TCDT	14,800	Cooper, 1993
Newark Bay	Crab	Total PeCDT	350	Cooper, 1993
Newark Bay	Bass	2,4,6,8-TCDT	ND	Rappe et al., 1991
Newark Bay	Lobster	2,4,6,8-TCDT	ND	Rappe et al., 1991
Newark Bay	Crab	2,4,6,8-TCDT	ND	Rappe et al., 1991
Passaic River	Sediment	2,4,6,8-TCDT	3,680	Pruell et al., 1993
Raritan Bay	Crab	Total TCDT	490	Cooper, 1993
Raritan Bay	Crab	Total PeCDT	ND	Cooper, 1993
Sandy Hook	Crab	Total TCDT	300	Cooper, 1993
Sandy Hook	Crab	Total PeCDT	ND	Cooper, 1993
Ward's Point	Crab	Total TCDT	1,500	Cooper, 1993
Ward's Point	Crab	Total PeCDT	60	Cooper, 1993
Missouri, USA	Soil	Total PCDTs	67,000	Peterman et al., 1964
Värö, Sweden[b]	Crab	TrCDT	ND	Buser and Rappe, 1991
Värö, Sweden	Crab	2,4,6,8-TCDT	45	Buser and Rappe, 1991
Värö, Sweden	Crab	Unidentified-TCDT	30	Buser and Rappe, 1991
Värö, Sweden	Crab	Unidentified-PeCDT (1)	40	Buser and Rappe, 1991
Värö, Sweden	Crab	Unidentified-PeCDT (2)	80	Buser and Rappe, 1991

a. Data should be considered as tentative measurements because of lack of pure analytical standard.
b. Measurements identified by authors as tentative values.
c. ND, not detected, NR, not reported.

Cooper (1993) reported measurable concentrations of total TCDT and total PeCDT in hepatopancreas tissue of male blue crabs collected in Newark Bay, the Arthur Kill, and Raritan Bay. The concentration of total TCDT was nearly an order of magnitude greater in Newark Bay crabs than in crabs collected from the other locations. In Newark Bay crabs, the concentration of total TCDT (14,800 ng/kg) was approximately 40-fold higher than the concentration of PeCDT (350 ng/kg) (Cooper, 1993). Similar to Pruell et al. (1993), the authors consider all reported data as tentative identifications since analytical QA/QC methods have not been available to verify these results.

Buser and Rappe (1991) reported the presence of trichlorinated dibenzothiophene (TrCDT), 2,4,6,8-TCDT, and a second TCDT isomer as well as two PeCDT isomers in the crabs collected from the Elizabeth River, located at the confluence of the Arthur Kill and Newark Bay in a region dominated by the Bayway oil refinery complex (Buser and Rappe, 1991). The edible tissues of lobsters collected from the same location contained only the 2,4,6,8-TCDT isomer and two PeCDT isomers at lower concentrations than found in the crabs. The levels in lobsters ranged from 25 to 1,000 ng/kg, nearly three-fold lower than body burdens in blue crabs reported by the authors or by Cooper (1993). The 2,4,6,8-TCDT isomer was also reported in crab samples collected downstream of a pulp and paper mill near Värö, Sweden (Buser and Rappe, 1991).

Rappe et al. (1991) tentatively identified a TCDT isomer, eluting with approximately the same retention time as 1,2,8,9-TCDD, in crab hepatopancreas and meat, lobster hepatopancreas, and striped bass fillet tissue. The crabs were collected at the confluence of the Passaic River and Newark Bay; the lobsters were collected offshore near a former sewage sludge dump site in the New York Bight; and, striped bass were collected from northern and southern sections of Newark Bay (Rappe et al., 1991). Based on its elution pattern and molecular weight, it is likely that this isomer is the 2,4,6,8-TCDT isomer later identified by Pruell and coworkers in crabs from the Passaic River and by Rappe and coworkers in crabs from Värö, Sweden. Assuming that the HRGC/HRMS response for the TCDT isomer is similar to the response for 2,3,7,8-TCDD, a comparison of the spectrographic peak heights indicates that the concentration of TCDT is higher than the concentration of 2,3,7,8-TCDD in crab and lobster hepatopancreas by a factor of approximately 3 and 2, respectively. The concentration of TCDT in hepatopancreas of crab from Newark Bay and lobster from the New York Bight are approximately the same magnitude, whereas the concentration of TCDT in striped bass from the Newark Bay is substantially lower.

DISCUSSION

The information available in the scientific literature indicates that 2,4,6,8-TCDT and other PCDTs are generated by numerous industrial sources during processes similar to those that form PCDFs, but involving sulfur compounds, including pulp and paper production and several incineration processes (Buser et al., 1991; Sinkkonen et al., 1992a,b). The 2,4,6,8-TCDT isomer, in particular, is generated during the combustion of municipal waste (Buser and Rappe, 1991), thermal reaction of PCBs (Buser et al., 1991), direct chlorination of dibenzothiophene (Buser et al., 1991), and has been found in resident aquatic organisms collected immediately downstream of pulp and paper mills (Sinkkonen et al., 1992b). The formation of PCDTs during industrial chemical processes requires both a source of chlorine and a source of sulfur. Further, the selected formation of the 2,4,6,8-TCDT isomer requires a very specific configuration of chlorine substitution of the reactants. 2,4,6,8-TCDT cannot be generated during the manufacture of 2,4,5-T because (1) sulfur is not used in the process and (2) the configuration of chlorine substitution of the 2,4,5-trichlorophenol starting material provides for the predominant generation of 2,3,7,8-substituted tricyclic compounds, not 2,4,6,8-substituted compounds. Such considerations indicate that PCDTs, including 2,4,6,8-TCDT, are unlikely to be generated during the production of non-sulfur-containing chlorinated pesticides such as 2,4-D and 2,4,5-T.

The relatively high concentrations of the 2,4,6,8-TCDT isomer as compared to other PCDT isomers in the Passaic River, indicate that incineration is not a likely major source of this compound. The preferential formation of a single isomer is more likely the result of a chemical process involving symmetrical reactants such as 2,3,5,2′,3′,5′-hexachlorobiphenyl (Fig. 4) or 2,4,6-trichlorobenzene sulfonic acid (Fig. 5). Additionally, without the proper

orientation of the chlorines on the rings, it would not be possible to generate 2,4,6,8-TCDT. For example, the production of the pesticide Tetrasul is not likely to result in the formation of 2,4,6,8-TCDT (Fig. 6).

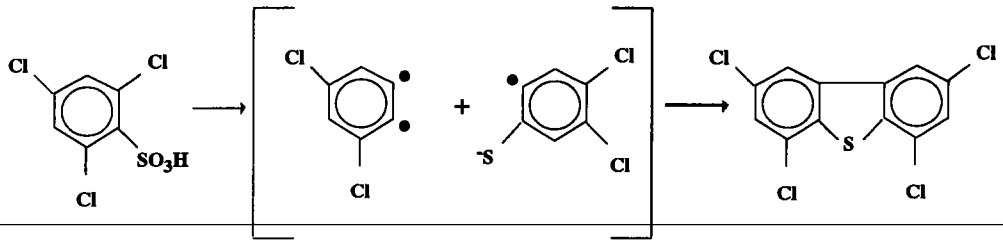
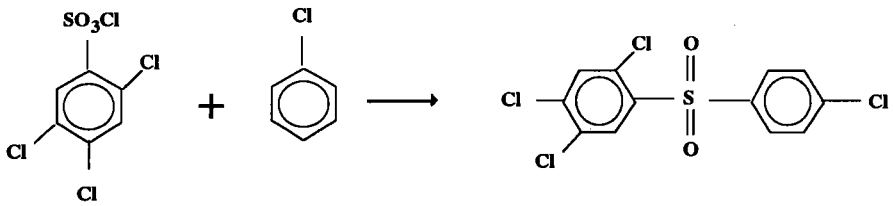
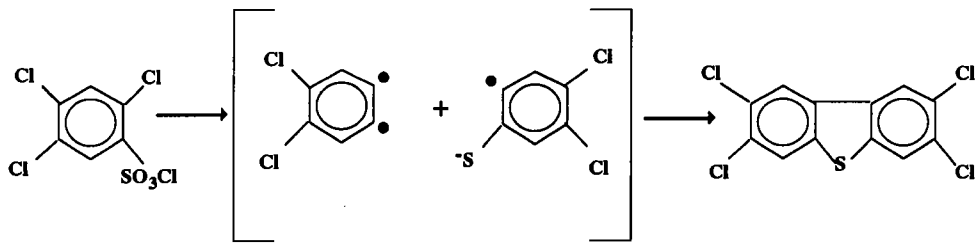


Fig. 5. Possible formation of 2,4,6,8-TCDT from reaction of 2,4,6-trichlorobenzene sulfonic acid

Several other processes have been suggested as possible sources of PCDTs. For example, Buser et al. (1991) suggested that the combustion of automobile tires could result in a significant release of PCDTs (Buser et al., 1991). Oils used in automobile engines are likely to contain high levels of dibenzothiophenes and chlorinated chemicals used as lead scavengers. The thermal reaction of these compounds may generate PCDTs; therefore, their subsequent discharge to surface water and sediments via urban runoff and combined sewer outfalls may be an important source. Although unlikely to contribute significantly to environmental levels, it is also possible that the chlorination of dibenzothiophene, which is abundant in refined petroleum products (Andersson, 1993), could occur in environmental media under some conditions.



a) Tetrasul Production



b) Possible TCDT Formation

Fig. 6. (a) Synthesis of Tetrasul from reaction of 2,4,5-trichlorobenzene sulfonyl chloride and monochlorobenzene, and (b) possible formation of 2,3,7,8-TCDT

The presence of high levels of 2,4,6,8-TCDT in lower Passaic River sediments (Pruell et al., 1993) together with very high levels of petroleum hydrocarbons (Huntley et al., 1993), widely known to contain unchlorinated dibenzothiophenes (Page et al., 1993), suggests that a relationship may exist between the occurrence of these two

chemicals. The reach of the lower Passaic River where the highest concentrations of 2,4,6,8-TCDT (3,680 ng/kg) were reported (Pruell et al., 1993), coincides with the area where the high concentrations of petroleum hydrocarbons (61,000 mg/kg) have been found in previous sediment investigations (Huntley et al., 1993).

Dibenzothiophene is extremely persistent in the environment (MacKenzie and Hunter, 1979). It is abundant in crude petroleum, and has been found at high concentrations in the PAH/petroleum hydrocarbon component of oil spills and in stormwater runoff (MacKenzie and Hunter, 1979). Furthermore, waste oils have been found to contain TCDFs at levels as high as 2,900 ng/kg (Rotard et al., 1987). The presence of dibenzothiophene in petroleum products and the presence of high levels of TCDFs in waste oils suggests the possibility that petroleum hydrocarbon contamination may be a source of chlorinated dibenzothiophenes in lower Passaic River sediments.

Although PCDTs were not widely known to be present in environmental media until three years ago, it appears that the occurrence of these compounds in the aquatic environment is widespread. The data reported by Pruell et al. (1993) and Cooper (1993) suggest that PCDTs may be distributed throughout the Newark Bay estuary because of the hundreds of chemical factories, metal smelters, tanneries, bleacheries, paint manufacturers, and petroleum refineries and storage facilities that operated and discharged to the estuary for more than a century (Cunningham, 1963). Sediments throughout the estuary, particularly those in the lower Passaic River, contain high concentrations of PCBs (Wenning et al., 1992c) and petroleum hydrocarbons (Huntley et al., 1993), both possible sources of the 2,4,6,8-TCDT reported in surface sediment, shellfish, and striped bass. The presence of a PCB-contaminated site (Monsanto Chemical Company, 1991) approximately one mile downstream of the former 2,4,5-T facility, together with the precedented synthesis of 2,4,6,8-TCDT by the thermal reaction of 2,3,5,2′,3′,5′-hexachlorobiphenyl and sulfur (Fig. 4) and the presence of this isomer in commercial PCB formulations (Ballschmiter and Zell, 1980), provide the most plausible explanation for the elevated levels of 2,4,6,8-TCDT in the lower Passaic River.

The relative concentrations and distributions of PCDTs will most certainly vary according to the conditions of their formation; however, the PCDT isomer patterns associated with specific source types should be unique and follow to some extent the general patterns associated with PCDF sources. Sinkkonen et al. (1992b) found that the 2,3,7,8-TCDT isomer predominated in pulp and paper mill effluents which is consistent with the predominance of 2,3,7,8-TCDF in pulp and paper mill effluents. The hexa- and penta-chlorinated dibenzofurans have been shown to predominate in commercial chlorophenols (Rappe et al., 1978), suggesting that, if PCDTs are formed during chlorophenol production, the hexa- and penta-chlorinated dibenzothiophenes would likely dominate. PCDD/PCDF contamination of 2,4,5-T is generally thought to be largely due to the chlorophenol starting materials. Although insignificant compared to the abundance of the hexa and penta isomers, 2,3,7,8-TCDF is the most abundant tetrachlorinated furan in chlorophenols (Rappe et al., 1978), suggesting that 2,3,7,8-TCDT should be detected in environmental media if chlorophenol usage is suspected as a source of PCDTs. The 2,3,7,8-TCDT isomer was not detected in Passaic River sediments (Pruell et al., 1993), which suggests the presence of one or more PCDT sources in the river and elsewhere in the Newark Bay estuary unrelated to 2,4,5-T and chlorophenol production.

CONCLUSIONS

PCDTs have been detected in several processes that are well-known PCDD and PCDF sources (Buser et al., 1991; Sinkkonen et al., 1991, 1992a,b, 1993). The structural similarity of PCDTs and PCDFs suggests that PCDTs and PCDFs are formed via similar mechanisms (Sinkkonen et al., 1992a,b). 2,4,6,8-TCDT and other PCDTs have been shown to be present in fly ash from car shredding facilities and municipal waste incinerators (Buser et al., 1991;

Sinkkonen et al., 1992a,b), in effluent from pulp and paper mills (Sinkkonen et al., 1992a,b), and in metal reclamation processes (Sinkkonen et al., 1993). 2,4,6,8-TCDT has been generated by the thermal reaction of PCBs, by the chlorination of dibenzothiophene, and during municipal waste combustion (Peterman et al., 1986; Buser and Rappe, 1991; Buser et al., 1991).

The relatively high concentrations of 2,4,6,8-TCDT in Passaic River sediments compared to other PCDT isomers strongly argues against sources that manifest random chlorination patterns such as incineration and suggests a chemical process-specific point source. The identification of such a point source must consider whether sulfur is present in the process and whether the configuration of chlorine substitution of the reactants is optimal. 2,4,6,8-TCDT cannot be generated during the manufacture 2,4,5-T because (1) sulfur is not used in the process and (2) the configuration of chlorine substitution of the 2,4,5-trichlorophenol starting material provides for the predominant generation of 2,3,7,8-substituted tricyclic compounds, not 2,4,6,8-substituted compounds. Furthermore, 2,3,7,8-TCDT was not detected in Passaic River sediments (Pruell et al., 1993). Chlorinated thiophenols and other sulfur-containing compounds such as sulfonated benzenes, chlorinated in the 2, 4, and 6 positions, and 2,3,5,2′,3′,5′-hexachlorobiphenyl (Buser and Rappe, 1991) have precisely the correct configuration of chlorine substitution for 2,4,6,8-TCDT formation. The identification of users and generators of these types of compounds will be essential in evaluating potential sources of 2,4,6,8-TCDT in the Passaic River. At the present, the relationship between PCBs and 2,4,6,8-TCDT appears to be the most plausible, given the known presence of 2,3,5,2′,3′,5′-hexachlorbiphenyl in commercial PCB mixtures (Ballschmiter and Zell, 1980), the presence of PCBs in Passaic River sediments (Wenning et al., 1992c), and the proximity of a PCB-contaminated site to the river (Monsanto Chemical Company, 1991).

The presence of 2,4,6,8-TCDT in shellfish from Newark Bay, the New York Bight, and Sweden indicates that this compound is probably widespread in industrialized areas of the world. Future research in this area will undoubtably focus on evaluating and confirming new potential sources.

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